Determination of boron and fluoride sources in groundwater: Batch dissolution of carbonate rocks in water

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High natural fluoride (up to 6.1 mg/l) and boron (up to 2.1 mg/l) concentrations in groundwater are recorded in western Estonia, where a carbonaceous Silurian–Ordovician aquifer system is the main source of drinking water. The aim of this study is to examine the dissolution of boron and fluoride from different carbonate rocks using batch dissolution tests. The total boron and fluorine concentration within carbonate rocks varies between 100–1000 and 5–150 mg/kg, respectively. Generally, boron and fluoride concentrations increase as the amount of terrigenous material in the rock increases. Laboratory leaching experiments showed that the amount of leached boron and fluoride was proportional to the content of these elements in the rock samples. Further, boron and fluoride concentrations in leachates were positively correlated with the amount of terrigenous material in rocks. Both boron and fluoride concentrations in leachates continually rose over 49 days of leaching. Long-term water-rock interaction is responsible for the high boron and fluoride contents in groundwater of western Estonia.

Keywords: boron, fluoride, carbonate rock, water-rock interaction, batch dissolution

INTRODUCTION

Low concentrations of fluoride (F^-) in drinking water have a beneficial effect on dental health by reducing the incidence of caries, and long-term exposure to excessive fluoride is known to give rise to dental and skeletal fluorosis (Billings *et al.*, 2004; WHO, 2008). Experiments with animals have shown that excessive concentrations of boron (B) in drinking water lead to malfunctioning of the reproductive system e.g., reduced fertility and sterility, low fetal weights. Incidences of metabolic disorders and acute neurological effects have also been observed (Price *et al.*, 1996; WHO, 2008). The studies regarding effects of boron exposure in humans are few, but the minimal data available report short-term irritant effects of the upper respiratory tract (Garabrant *et al.*, 1985; Wegman *et al.*, 1994). Additionally, a study by Chang *et al.* (2006) reported a positive relationship between industrial B exposure and reproductive health. Because of their impact upon human health, the occurrence of F^- and B in groundwater is an important aspect of hydrochemistry, and therefore has been studied widely. However, few studies focus on water-rock interaction as a source of F^- and B in groundwater (Özgür, 2001; Saxena and Ahmed, 2001; Chae *et al.*, 2006; Xu *et al.*, 2006; Abdelgawad *et al.*, 2009).

F occurs in water primarily as the negatively charged F^- ion. It is mainly released into groundwater through weathering and leaching of F-containing minerals in rocks. F is abundant in various rock forming minerals, e.g., fluorite, apatite, micas, amphiboles, and certain clay minerals. Because of similar ionic radii, F^- can replace the hydroxyl ion (OH^-) in many minerals. Fluorite (CaF_2) has been generally considered as a dominant source of groundwater F^- , however, its solubility in fresh water is low (Hem, 1985; Kundu *et al.*, 2001; Saxena and Ahmed, 2003; Sujatha, 2003; Rafique *et al.*, 2008; Naseem *et al.*, 2010; Reddy *et al.*, 2010). It is also suggested that high F^- concentrations in groundwater may result from dissolution of biotite and apatite, which can contain significant amounts of F at the OH^- sites of their octahedral sheet (Hem, 1985; Rafique *et al.*, 2008; Desbarats, 2009; Reddy *et al.*, 2010). High F concentrations are also associated with volcanic activity. Thus, elevated concentrations of F^- are often found in geothermal waters (Kundu *et al.*, 2001; Desbarats, 2009). Fresh volcanic ash may be rich in F^- , and ash interbedded with other sediments can contribute to high F^- concentrations in groundwater in such areas (Hem, 1985).

It has been observed that elevated B concentrations in groundwater are often associated with high F^- concentrations (Queste *et al.*, 2001; Earle and Krogh, 2006; Desbarats, 2009). Similarly to F^- , B is released into the groundwater mainly through the weathering of rocks, seawater intrusion into aquifers, and volcanic activity

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Fig. 1. Location (a) and geological map (b), and a north-south geological cross-section (c) of the area. The line indicates the position of the cross section.

(Hem, 1985; Gemici and Tarcan, 2002; Pennisi *et al.*, 2006). In aqueous solutions, B is mostly present as the borate anion— $\text{B}(\text{OH})_4^-$ —and undissociated boric acid— $\text{B}(\text{OH})_3$ —(Mather and Porteous, 2001; Gonfiantini and Pennisi, 2006; Pennisi *et al.*, 2006). The distribution of these species depends on the pH of the aqueous environment. At pH of ~ 7 , most B is present in the form of $\text{B}(\text{OH})_3$. The borate ion fraction gradually increases with increasing pH (Gemici and Tarcan, 2002; Gonfiantini and Pennisi, 2006).

According to the European Union drinking water directive (Council Directive 98/83/EC, 1998), the permissible limits for F^- and B are 1.5 mg/l and 1 mg/l, respectively. Excessive concentrations of these elements are frequently encountered in western Estonia, where a carbonate Silurian–Ordovician aquifer system is the most prominent drinking water source (Karro *et al.*, 2006, 2009; Karro and Uppin, 2013). The natural concentrations of B and F^- in western Estonian groundwater reach up to 2.1 and 6.1 mg/l, respectively. Health problems related to drinking water in Estonia are mainly caused by the high levels of F^- and B in groundwater (Indermitte *et al.*, 2009; Indermitte, 2010). Despite the health concerns of elevated F^- and B concentrations in drinking water, the geochemistry of those elements in groundwater has not been studied thoroughly in Estonia. Thus, laboratory experiments on batch dissolution of carbonate rocks were performed in this study.

One factor controlling the groundwater chemistry is the lithological composition of water-bearing rocks. The presence of F and B bearing minerals in the host rock and their interaction with water are considered to be the main causes for F^- and B enrichment in groundwater. This study aims to determine the geological sources of F^- and B and to assess their dissolution processes, focusing on the interaction of water and different carbonate rocks. The results of this study could aid in the development of groundwater wells that meet water quality requirements with regard to F^- and B.

STUDY AREA

Estonia, the northernmost of the Baltic countries, is situated in the north-east of Europe. It lies on the east coast of the Baltic Sea and has an area of 45,227 km². Geologically, Estonia is located in the north-western part of the East-European Platform. The sedimentary beds of the East-European Platform lie on the southern slope of the Baltic Shield, and decline southward at about 3–4 m/km. The Estonian Paleoproterozoic basement is overlain by Neoproterozoic (Ediacaran) and Paleozoic (Cambrian, Ordovician, Silurian and Devonian) sedimentary rocks, covered by Quaternary deposits (Fig. 1) (Raukas and Teedumäe, 1997).

Both the Ordovician and Silurian sequences in Estonia consist mainly of shallow water carbonates—limestone,

dolomite, and marlstone with clayey interlayers. An exception is the basal part of the Ordovician sequence, which contains terrigenous sediments—silty and clayey sandstones and graptolite argillites. Several clay-rich altered volcanic ash beds—K-bentonites—are also recorded in the Silurian and Ordovician stratigraphic record (Hints *et al.*, 2008; Kiipli *et al.*, 2008; Somelar *et al.*, 2010).

Hydrogeologically, Estonian sedimentary rocks form a typical artesian basin, wherein five aquifer systems (Middle–Devonian, Middle–Lower–Devonian, Silurian–Ordovician, Ordovician–Cambrian, and Cambrian–Vendian) are isolated from each other by impervious beds. Quaternary deposits, consisting predominantly of glacial till and glacio-lacustrine sandy loam, form the uppermost aquifer system, which is used as a domestic drinking water source (Perens and Vallner, 1997).

Ordovician and Silurian carbonate rocks form the Silurian–Ordovician aquifer system (hereafter S–O aquifer system), which is an important, and in places the only, source of drinking water in central and western Estonia and on islands of the West-Estonian archipelago. The upper 30 m of the S–O aquifer system is extremely cavernous, with numerous cracks and fissures. The water in the fissure systems and karst cavities of the carbonate bedrock is fast-flowing. Silurian and Ordovician carbonate rocks have fragmentary 1–2 m thick water-conducting zones with parallel lamination and an abundance of fissures, where groundwater flows in a lateral direction. These zones are separated from each other by 5–10 m thick layers in which groundwater flows predominantly in vertical fissures. The caverns and fissures decrease in deeper part of the S–O aquifer system and the aquifer system transforms into an aquitard (Perens and Vallner, 1997).

The S–O aquifer system has an $\text{HCO}_3\text{--Ca--Mg}$ and $\text{HCO}_3\text{--Mg--Ca}$ water type with total dissolved solids (TDS) mainly below 0.6 g/l in the upper 30–50 m portion. In coastal areas and greater depths the concentration of Cl^- and Na^+ in the groundwater increases and an $\text{HCO}_3\text{--Cl--Na--Mg--Ca}$ water type with TDS between 0.3–1.5 g/l is widespread (Perens *et al.*, 2001).

MATERIALS AND METHODS

Simple batch dissolution experiments were carried out on 20 different carbonate rock (limestone, dolomite, clayey limestone, clayey dolomite, and marlstone) samples selected from 91 rock samples previously analyzed by Uppin and Karro (2012). The chemical composition of carbonate rocks was analyzed at ACME Analytical Laboratories Ltd., Vancouver, Canada in 2008–2010, where SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , Na_2O , K_2O , TiO_2 , P_2O_5 , MnO , Cr_2O_3 , Ba, Sr, Cu, Ni, Co, B, and F concentrations were measured. Rock samples were crushed and

pulverized to a 200-mesh-size and dried at 105°C prior to analysis. The chemical composition of the rocks was determined using standard Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) techniques. F concentrations were analyzed by specific ion electrode.

The mineral composition (quartz, calcite, dolomite, apatite, K-feldspar, albite, illite/illite–smectite, kaolinite, chlorite, pyrite, and biotite) of the rock samples were determined via using the Rietveld X-ray powder diffractometry (XRD) technique at Department of Geology, University of Tartu. Ground and homogenized unoriented powder samples were measured on a Bruker D8 diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation over the range $2\text{--}70^\circ 2\theta$, with a scan step of $0.02^\circ 2\theta$ and a count time of 2 s per step. Quantitative mineral composition was determined by full-profile Rietveld analysis using SIROQUANTTM software system (Taylor, 1991; Ward *et al.*, 2001). The full profile XRD pattern Rietveld method considers the integrated intensities of the particular diffractogram peaks and compares natural and artificial mixtures along the whole length of the diffractogram, thus providing significantly more information for mineral quantification (Ward *et al.*, 2001).

Leaching tests of carbonate rocks were carried out in tightly capped conical polyethylene flasks (500 ml), where 30 g powdered rock samples (mesh size $<1\ \mu\text{m}$) were treated with 300 ml distilled water. Batch dissolution tests were performed at room temperature (20°C) using a shaker table (GFL 3005) at a constant shaking rate of 150 rpm. The leachates were filtered using $45\ \mu\text{m}$ resin and refrigerated until analysis. After 48 hours, all the 20 leachate samples were analyzed for F^- and B; of these, 7 samples were also analyzed for main cations (Ca^{2+} , Mg^{2+} , K^+ , and Na^+) and anions (Cl^- , SO_4^{2-} , and HCO_3^-). B concentrations in leachates were determined colorimetrically (Nicolet Evolution 300) using Azomethine-H method (Watson, 1998). F^- , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , and SO_4^{2-} concentrations were analyzed using an ion-chromatograph (Dionex ICS-1000) at Department of Geology, University of Tartu. The accuracy and precision of analyses were tested by running duplicate analyses on selected samples. In addition, the HCO_3^- concentrations of the solutions were determined potentiometrically in the Tartu laboratory of Estonian Environmental Research Centre.

Long-term leaching experiments were continued with the 7 samples from the initial leaching test for 49 days. Leachate samples were taken after 7, 14, and 49 days. The batches were designed to maintain a constant water-rock ratio of 10:1. Sufficient amounts of rock powder and distilled water were used to enable repeated samplings of small solution aliquots (6 ml) without significantly changing the water-rock ratio. pH values were obtained using a pH meter (Mettler Toledo SG8-ASK) in all experiments

at specific time intervals.

The saturation indices (SI) of fluorite (CaF_2) and calcite (CaCO_3) in groundwater samples were calculated using the computer program PHREEQC (Parkhurst and Appelo, 1999).

RESULTS AND DISCUSSION

The S–O aquifer system in Estonia consists of different carbonate rocks, mainly limestones, dolomites, and marlstones with more clayey interlayers, including clay-rich altered volcanic ash beds—K-bentonites (Nestor and Einasto, 1997; Hints *et al.*, 2008; Kiipli *et al.*, 2008; Somelar *et al.*, 2010). Leaching of the host rocks is considered to be the major natural source of F^- and B in groundwater; therefore, chemical composition of aquifer forming rocks has been examined. B and F concentrations in Estonian limestones and dolomites vary between 5–20 mg/kg and 100–500 mg/kg, and can reach up to 150 mg/kg and 1000 mg/kg in marlstones, respectively. Furthermore, K-bentonites are rich in B (50–1000 mg/kg) and F (400–4500 mg/kg). Generally, an increase in clay content is followed by an increase in the B and F concentrations in carbonate rocks (Uppin and Karro, 2012). This can be seen in Fig. 2. In addition, Fig. 2 presents the strong positive correlation between B and F concentrations in carbonate rocks. B and F concentrations of the rock samples used in the batch dissolution tests are shown in Table 1.

Several studies have suggested that F-containing minerals like fluorite, micas (biotite), apatite, amphiboles, and clay minerals could be possible sources of F^- in groundwater (Hem, 1985; Kundu *et al.*, 2001; Saxena and Ahmed, 2003; Sujatha, 2003; Rafique *et al.*, 2008; Desbarats, 2009; Naseem *et al.*, 2010; Reddy *et al.*, 2010). B is associated with clay minerals, but may also occur as an accessory constituent of tourmaline, biotite, and amphiboles (Hem, 1985; Gemici and Tarcen, 2002; Gonfiantini and Pennisi, 2006; Pennisi *et al.*, 2006). Based on the XRD analyses (Table 2), the main constituents of the carbonate rock samples used in the leaching tests are determined to be calcite and dolomite (up to 99%, depending on the rock type) with the addition of quartz (0.7–31.1%), K-feldspar (0.5–6.9%), and illitic clay minerals (0.8–32.5%). Additionally, small amounts of apatite (up to 1.2%), albite (up to 1.9%), chlorite (up to 8.3%), and pyrite (up to 1.2%) can be found in some rock samples. Biotite was not detected in the studied carbonate rocks; concentrations of up to 4.2% of the whole rock occur only in K-bentonite samples (Hints *et al.*, 2008). Among the studied carbonate rocks, the proportion of illitic clay minerals (11.7–32.5%) is highest in the marlstones (Table 2). Estonian carbonate rocks containing apatite tend to be rich in F (Uppin and Karro, 2012). However, apatite is

Fig. 2. Bivariate plot of F and B contents in the different carbonate rocks that form Silurian–Ordovician aquifer system (data from Uppin and Karro, 2012).

probably not a significant source of F^- in the groundwater because of its low solubility (Desbarats, 2009). In this study, the apatite content of rock samples was low (below 1.2%) and no correlation between apatite and F^- concentration in the leachates was detected.

A previous study focusing on the chemical composition of aquifer forming carbonate rocks (Uppin and Karro, 2012) showed that lower $\text{CaO}/\text{Al}_2\text{O}_3$ ratios, representative of terrigenous material, were accompanied by elevated B and F concentrations in carbonate rocks. Furthermore, higher B and F concentrations in rocks were related to lower $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios, common to clayey material (mainly illitic clay minerals) in carbonate rocks in Estonia. Overall, elevated B and F concentrations in carbonate rocks were clearly concentrated in the terrigenous fraction of the rock and were bound to clay mineral phases. The terrigenous material in the Silurian and Ordovician carbonate rocks consists mainly of clay and silt fractions with sand occurring only occasionally.

The dissolution rate of chemical elements, including B and F, into groundwater depends on numerous factors such as the chemical and mineralogical composition of aquifer forming rocks, the groundwater chemistry, pH, and the temperature of the environment, and the time available for water-rock interaction, etc. All these factors should be considered when interpreting the formation of groundwater chemistry. In order to estimate and compare the contribution of the different rock types to the natural sources of B and F, the influence of other environmental factors (e.g., differences in groundwater chemistry) should be minimized. Simple laboratory batch dissolution tests enable the creation of uniform conditions

Table 1. The concentrations of B and F in aquifer forming carbonate rocks and in leachates after 2, 7, 14, and 49 days of batch dissolution tests

		Rock samples (mg/kg)		Leachates (mg/l)							
				2 days		7 days		14 days		49 days	
		B	F	B	F ⁻	B	F ⁻	B	F ⁻	B	F ⁻
1	Limestone	11	260	0.10	0.43						
2	Limestone	4	176	0.05	0.10						
3	Dolomite	8	374	0.08	0.16	0.12	0.20	0.13	0.17	0.19	0.21
4	Dolomite	7	220	0.05	0.08	0.10	0.10	0.08	0.09	0.15	0.09
5	Dolomite	9	495	0.14	0.16						
6	Dolomite	12	363	0.05	0.38						
7	Dolomite	36	350	0.15	0.17						
8	Clayey limestone	40	683	0.19	0.52	0.27	0.57	0.27	0.57	0.28	0.60
9	Clayey limestone	37	500	0.21	0.38	0.26	0.43	0.23	0.42	0.29	0.45
10	Clayey limestone	9	396	0.07	0.34	0.07	0.44	0.09	0.48	0.13	0.51
11	Clayey limestone	15	341	0.16	0.18	0.13	0.20	0.17	0.21	0.42	0.24
12	Clayey limestone	10	440	0.05	0.35						
13	Clayey limestone	15	341	0.05	0.22						
14	Clayey limestone	9	410	0.04	0.11	0.03	0.15	0.06	0.19	0.09	0.26
15	Clayey dolomite	21	660	0.16	0.27						
16	Clayey dolomite	17	550	0.06	0.38						
17	Clayey dolomite	3	187	0.05	0.26						
18	Marlstone	43	430	0.50	0.60						
19	Marlstone	68	525	0.71	0.45						
20	Marlstone	140	1029	1.40	0.85						

Table 2. Whole-rock semi-quantative mineral composition of the Silurian and Ordovician carbonate rocks (wt.%). I-S, illite-smectite

		Calcite	Dolomite	Quartz	K-feldspar	Albite	Illite/I-S	Chlorite	Apatite	Pyrite
1	Limestone	85.1	5.4	2.7	1.3	1.3	3.5			0.8
2	Limestone	99.3	0.1	0.7						
3	Dolomite	37.9	54.2	2.6	2.4		1.3	1.2		0.4
4	Dolomite		90.8	3.5	3.4	0.8	0.8			0.7
5	Dolomite		96.8	1.1	0.5		0.9			
6	Dolomite		91.6	3.6	3.0	0.5	0.9			
7	Dolomite		90.0	3.0	1.4		3.7	1.3		
8	Clayey limestone	59.2	19.4	9.2	4.3		5.3	2.3		
9	Clayey limestone	86.5	2.3	4.3	1.7		3.3		0.8	1.2
10	Clayey limestone	81	3.9	4.5	3.7		4.0	1.5		1.4
11	Clayey limestone	80.4	6.5	6.0	2.7		1.9		1.2	0.8
12	Clayey limestone	53.7	26.5	11.4	4.0	0.9	1.5			
13	Clayey limestone	84.9	4.0	2.1	2.3	1.0	2.6		1.2	0.8
14	Clayey limestone	48.3	41.1	5.9	3.1		1.3			0.2
15	Clayey dolomite	1.2	83.8	5.6	2.4	1.1	3.3	2.1		
16	Clayey dolomite	29.3	51.6	3.8	2.2	1.9	7.5	2.2		1.2
17	Clayey dolomite		85.9	6.6	1.9	1.2	2.7			
18	Marlstone	68.9	5.8	8.1	2.1		11.7	1.9	1.1	
19	Marlstone	38.7	8.6	31.1	4.0		15.0	1.8		0.9
20	Marlstone	17	14.4	18.6	6.9	1.2	32.5	8.3		1.0

for leaching experiments. In this study, 20 crushed carbonate rock samples were leached in distilled water for two days. The long-term test continued with seven rock samples. The results of the test, focusing on B and F⁻ concentrations in leachates, are summarized in Table 1.

After two days of leaching, B concentrations varied between 0.04–1.40 mg/l, and the F⁻ concentration ranged between 0.10–0.85 mg/l in the leachates. The highest amounts of B and F⁻ were leached out from the marlstone samples. A basic assumption is that the concentrations of

Fig. 3. F^- and B concentrations in leachates plotted against the amount of terrigenous compounds and illite/illite-smectite contents in carbonate rocks.

B and F^- in the leachates depend on the abundance of these elements in rocks. However, this is only a first approximation. The results after two days of the experiment showed that the leachate B and F^- concentrations were positively correlated with the amount of the terrigenous material as well as illitic clay minerals in the rock samples (Fig. 3). According to several studies (Saxena and Ahmed, 2003; Sujatha, 2003; Gonfiantini and Pennisi, 2006; Pennisi *et al.*, 2006; Rafique *et al.*, 2008; Naseem *et al.*, 2010), significant amounts of B and F in rocks are considered to be related to clay minerals. Ion-exchange and adsorption are the most typical processes through which B and F are bound to clay minerals. A thorough study by Du *et al.* (2011) describes the adsorption mechanisms of F^- on kaolinite, montmorillonite, chlorite, and illite. In this study, leachate concentrations of B ($r = 0.91$)

and F^- ($r = 0.81$) show a good correlation with K_2O concentration in the carbonate rocks. Considering the mineralogical composition of the carbonate rocks (Table 2), it can be assumed that B and F originate from the same minerals, most likely illitic clay minerals. Thus, B and F in groundwater are mainly leached out from clayey material, such as clayey limestones, clayey dolomites, marlstones, and domerites. Consequently, it can be presumed that the long-term leaching of clayey carbonate rocks provides the elevated F^- and B concentrations in the groundwater of western Estonia.

During the 49 days of the leaching test, B and F^- concentrations in the solutions continually exhibited an increasing trend (Fig. 4); however, remarkable amounts of B and F were leached out during the first week of the test. The same trend was observed during batch dissolu-

Fig. 4. Variations of B and F^- concentrations in leachates during the water-rock interaction test. Sample numbers are as shown in Tables 1 and 2.

tion experiments of granite samples in water (Chae *et al.*, 2006; Abdelgawad *et al.*, 2009), where the leached F^- contents increased rapidly at the beginning of the test with only a slight increase in its concentration thereafter. Batch dissolution experiments by Chae *et al.* (2006) showed that F^- concentrations approached a maximum value of about 10 mg/l during the first week of leaching and then decreased to the level of 8 mg/l. Calculated saturation indices showed that the solution approached a saturated or supersaturated state with respect to fluorite after less than 200 h, while calcite saturation was not reached within this time. Therefore, Chae *et al.* (2006) suggested that fluorite precipitation occurred in the latter part of the experiments, which controlled the F^- concentration in the solution. However, the results of the batch dissolution tests of the current study (Fig. 4) as well as the study by Abdelgawad *et al.* (2009) demonstrate a continuous increasing trend in dissolved F^- and B concentrations. This may indicate that the saturation state of the solution with respect to fluorite was not achieved during the 49-day dissolution tests.

The increase in B and F^- concentrations with reaction time indicates the importance of the residence time of the groundwater in aquifer forming rocks. Generally, the amount of dissolved chemical substances in groundwater increases with depth because of slower water exchange and longer residence times in the aquifer. Deviations from this general tendency in abstracted groundwater can be explained by differences in the constructions of wells,

their open intervals, and in the type and structure of the opened rocks. It has been shown that the elevated F^- and B contents in Estonian groundwater are related to deeper wells with short screens opening clayey carbonate rocks (Karro and Uppin, 2013). The long open interval of the drilled well enables the mixing of waters with different chemical compositions, which results in groundwater dilution and lower F^- and B concentrations. Further, high F^- and B concentrations are often associated with alkaline waters rich in Na^+ and Cl^- ions, as shown in several regional studies (Queste *et al.*, 2001; Gemici and Tarcan, 2002; Saxena and Ahmed, 2003; Sujatha, 2003; Chae *et al.*, 2007; Rafique *et al.*, 2008; Desbarats, 2009) as well as in the case of the Estonian Silurian–Ordovician aquifer system (Karro and Uppin, 2013). Groundwater in Silurian and Ordovician carbonate rocks is predominantly of an HCO_3^- –Ca–Mg chemical type with a high Ca^{2+} concentration and low amounts of F^- and B. High F^- and B concentrations are associated mainly with alkaline groundwaters rich in Na^+ and Cl^- ions, represented by $Cl^-HCO_3^-$ –Na and $HCO_3^-Cl^-$ –Na types of waters. The pH values of groundwater in S–O aquifer system range between 6.76–8.48, and higher values are common to groundwater in West-Estonia (Karro and Rosentau, 2005; Karro and Uppin, 2013). Besides, the average clay content of the Silurian and Ordovician sequences tends to increase from north to south and south-west in Estonia (Nestor and Einasto, 1997). Thus, in the western part of the country, the carbonate rocks are generally represented

Table 3. The concentrations of main anions, cations (mg/l), and pH in leachates used as input data for the calculations of saturation indices

		2 days								49 days							
		Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	pH	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	pH
3	Dolomite	13.2	3.1	59.8	10.6	6.6	7.5	8.9	8.92	18.0	8.6	168.0	12.1	6.2	18.6	28.6	7.91
4	Dolomite	17.9	48.2	96.4	9.8	5.8	24.5	23.9	8.77	19.8	136.2	192.0	11.2	6.2	47.0	43.7	8.04
8	Clayey limestone	4.8	4.9	137.0	7.8	15.2	16.2	79.2	8.31	8.5	15.2	279.0	7.2	14.8	20.6	65.3	7.34
9	Clayey limestone	5.0	46.9	70.8	4.3	8.8	4.6	25.1	8.53	4.5	64.4	83.0	3.0	7.1	9.2	40.6	7.95
10	Clayey limestone	5.7	21.3	80.8	1.9	4.2	5.5	25.0	7.96	9.4	70.3	102.0	3.8	6.5	7.9	58.5	7.62
11	Clayey limestone	3.6	7.6	86.6	2.0	5.4	3.7	16.1	8.45	4.4	20.4	160.0	1.2	4.8	9.7	50.1	7.56
14	Clayey limestone	3.7	4.8	63.4	1.8	3.0	3.2	11.8	8.87	3.7	4.0	107.0	1.8	1.6	6.4	29.6	8.06

by clayey limestones and marlstones. Due to the increase in the clay content of the aquifer forming rocks, prolonged groundwater residence time and water-rock interactions, Ca²⁺ is replaced by Na⁺ through ion-exchange processes, and the pH value of groundwater slightly increases. This leads to the formation of alkaline groundwater of an HCO₃-Cl-Na or Cl-HCO₃-Na chemical type, which favors the leaching of F⁻ and B into the groundwater.

The batch dissolution tests of the current study showed that pH values of the leachates increased rapidly up to 8.9 during the first days of the experiments due to the consumption of hydrogen ions during the dissolution of carbonate minerals and then decreased gradually to <8.0 by the end of the test. Analogous behavior of pH values was observed in case of a granite dissolution study by Chae *et al.* (2006), where the solution pH reached 9.5 at the beginning of the experiment and decreased slightly over the next 500 h, and then stabilized at ~8.0. Several hydrochemical studies suggest that the pH value of groundwater is positively correlated with B and F⁻ (Queste *et al.*, 2001; Gemici and Tarcan, 2002; Chae *et al.*, 2007; Rafique *et al.*, 2008; Desbarats, 2009; Karro and Uppin, 2013). This implies that an alkaline environment preferably favors the release of F⁻ and B into the water. Thus, the high pH value at the beginning of the batch dissolution test could be one of the factors that contribute the leaching most of the F⁻ and B during the first two days.

F⁻ ions released into the groundwater are considered to be controlled by the degree of saturation of fluorite and calcite, and the concentration of Ca²⁺, HCO₃⁻, and Na⁺ ions in groundwater, among other natural geochemical processes (Saxena and Ahmed, 2003; Rafique *et al.*, 2008; Mamatha and Rao, 2010). Therefore, the saturation indices (SI) of fluorite and calcite have been calculated using PHREEQC (Parkhurst and Appelo, 1999). Equation (1) is used to calculate the saturation state of water with respect to solid mineral phases:

$$SI_x = \log \left[\frac{IAP}{K_x} \right] \quad (1)$$

Fig. 5. Calcite saturation index versus fluorite saturation index for leachate samples after 2 and 49 days of the leaching experiments. Sample numbers are as shown in Tables 1 and 2.

where SI is the saturation index of mineral x, IAP is the ion activity product, and K_x is the equilibrium solubility product of mineral x. A positive saturation index indicates that the solution is supersaturated with mineral x and the mineral should precipitate out from the solution. A negative value indicates that the solution is undersaturated with respect to mineral x. Thus, the observed mineral, if present, should be dissolved. The following equations explain the saturation of groundwater with respect to calcite and fluorite (Sreedevi *et al.*, 2006):

$$K1 = \frac{[\text{Ca}^{2+}][\text{HCO}_3^-]}{[\text{H}^+]} \quad (3)$$

$$K_2 = [\text{Ca}^{2+}][\text{F}^-]^2 \quad (5)$$

where K_1 and K_2 are the equilibrium solubility products of calcite and fluorite dissolved in water, respectively. Due to the relatively low solubility of fluorite, the occurrence of aqueous F^- is predominantly controlled by the availability of free Ca^{2+} ions in the water. From Eq. (5), it is apparent that a decrease in Ca^{2+} may be followed by an increase in F^- . From Eqs. (3) and (5), the following relation is derived:

$$\frac{[\text{HCO}_3^-]}{[\text{H}^+][\text{F}^-]^2} = \frac{K_1}{K_2}. \quad (6)$$

From Eq. (3), if pH is constant, an increase in Ca^{2+} is accompanied by a decrease in HCO_3^- . Therefore, an increase in HCO_3^- should be followed by enrichment of F^- in solution.

Saturation indices of calcite and fluorite from selected samples were calculated after 2 days and 49 days of shaking. The input data of the geochemical model included the concentrations of main anions and cations in the leachates, pH values (Table 3), and temperature (20°C). Considering the errors in field measurements and SI computation, approximate boundaries for equilibrium zones ($-0.5 < \text{SI} < 0.5$) were defined by Carillo-Rivera *et al.* (2002) and Mamatha and Rao (2010). All samples were near equilibrium with respect to calcite and undersaturated with respect to fluorite (Fig. 5). The fluorite SI slightly increases with reaction time and did not reach equilibrium even after 49 days. Further, the results by Karro and Uppin (2013) showed that the groundwater in S–O aquifer system is undersaturated or in equilibrium with respect to fluorite. Samples approaching equilibrium with respect to fluorite typically have F^- concentrations higher than 2 mg/l. This is markedly higher than those analyzed from the leachates (up to 0.6 mg/l) during the laboratory tests (Table 1). However, in both cases—laboratory leachates and natural groundwater—samples with higher F^- values are saturated with respect to calcite. Thus, F^- concentrations in groundwater can increase as a result of the precipitation of calcite, which removes Ca^{2+} from solution, allowing more fluorite to be dissolved.

CONCLUSIONS

B and F^- concentrations (up to 2.1 mg/l and 6.1 mg/l, respectively) are common in groundwater in western Estonia, where the main drinking water resource is a

carbonaceous Silurian–Ordovician aquifer system. Leaching of the clayey carbonate rocks that form the aquifer is the probable natural source of B and F^- in alkaline HCO_3^- –Cl–Na or Cl– HCO_3^- –Na types of groundwater in this area. Batch dissolution tests were performed in order to understand the origin of B and F^- rich groundwater in western Estonia and to determine if high F^- and B levels in water could be attributed to certain rock types. B and F contents in Estonian limestones and dolomites vary between 5–20 mg/kg and 100–500 mg/kg, and reach up to 150 mg/kg and 1000 mg/kg in marlstones, respectively. Twenty rock samples were crushed to powder and leached in distilled water for 2 days. The test continued with seven rock samples, and leachate samples were taken on the 7, 14, and 49 day of the test. After 49 days of leaching, B and F^- concentrations in solutions showed increasing trend; however, a significant amount of B and F were leached out during the first week of the test. The saturation state of the solution with respect to fluorite was not achieved during the long-term dissolution tests. B and F^- concentrations in the leachates are clearly correlated with terrigenous material and further with the illite/illite–smectite fraction in rock samples, which indicates that the most likely sources of B and F^- in water are ion-exchange and adsorption processes associated with clay minerals. Furthermore, F^- ions released into the groundwater are controlled by the degree of saturation of fluorite and calcite. F-rich water is saturated with respect to calcite—precipitation of CaCO_3 removes Ca^{2+} from solution allowing more fluorite to be dissolved. The results of this study show that the local geology (rock types) must be considered when developing new water supply wells. The opening of clayey rocks by well screens should be avoided to ensure a safe drinking water supply with appropriate B and F^- concentrations.

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