



# Chemical and isotopic evidence to clarify the salinity of the bedrock groundwater at Finnish mining site

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## ABSTRACT

*Study region:* Lithium mine in Ostrobothnia, Western Finland.

*Study focus:* Clear anomalous electrical conductivity horizons and high salinity (Cl, Na, Ca) of groundwater were identified in several exploration boreholes. As these could not be explained thoroughly with geological variations, further studies on the origin of the anomalies were suggested. It was speculated that the abrupt rise in electrical conductivity shows a horizon of waters of different ages, the lower being either old brine, or having ancient marine origin. To understand the processes controlling the hydrochemistry and the evolution of the salinity of the groundwater, the hydrogeochemistry and isotopic composition ( $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ,  $87\text{Sr}/86\text{Sr}$ ,  $3\text{H}$ ,  $14\text{C}$ ,  $\delta^{13}\text{C}$ ) was analysed in 13 boreholes, two lakes, a test pit and a stream.

*New Hydrological insights for the region:* The isotope and geochemistry results indicate long residence times (up to 10,000 years BP), but no strong water-rock interaction and a typical Litorina  $\text{SO}_4$  layer is missing. The mismatching results could be explained by 1) the fact that even a small amount of ancient brine or ancient sea water mixing with fresh groundwater would affect water geochemistry, while the isotopic composition would stay immutable, or 2) the salinity originates from pre-Litorina  $\text{SO}_4$ -poor brackish groundwater due to an earlier uplift from the Baltic Sea. Therefore, the groundwaters of the site are interpreted as a mixture of modern meteoric and fresh  $\text{HCO}_3$  water, brackish pre-Litorina subglacial groundwater, and glacial melt water.

## 1. Introduction

The Geological Survey of Finland studied the bedrock groundwater balances at Syväjärvi mine site in winter 2016–2017 in Western Finland (Pasanen and Pullinen, 2017). Based on the study clear anomalous electrical conductivity horizons of groundwater could be identified in several boreholes. The site is owned by a lithium mining company which aims to open an open pit mine at the site in near future. The high salinity needs to be considered when designing the water management solution for the mine dewatering of the open pit and discharging the excess water to the environment. Elevated salinity has been found to play an important role in the degradation of freshwater ecosystems, such as the decline of aquatic macroinvertebrate communities and the decrease of photosynthetic rate of aquatic plants (Horrigan et al., 2005; Zimmerman-Timm, 2007). Salinity has also been found to affect the dissolution of other elements (Davies and Hall, 2007). Therefore, discharging the saline dewatering water into the surface water systems without treatment could result in substantial changes to the water quality and be hazardous for the downstream aquatic ecosystems. Elevated salinity poses also challenges to mine water management (pipeline corrosion and water treatment) (Iakovleva et al., 2015; Stets et al., 2018; Li et al.,

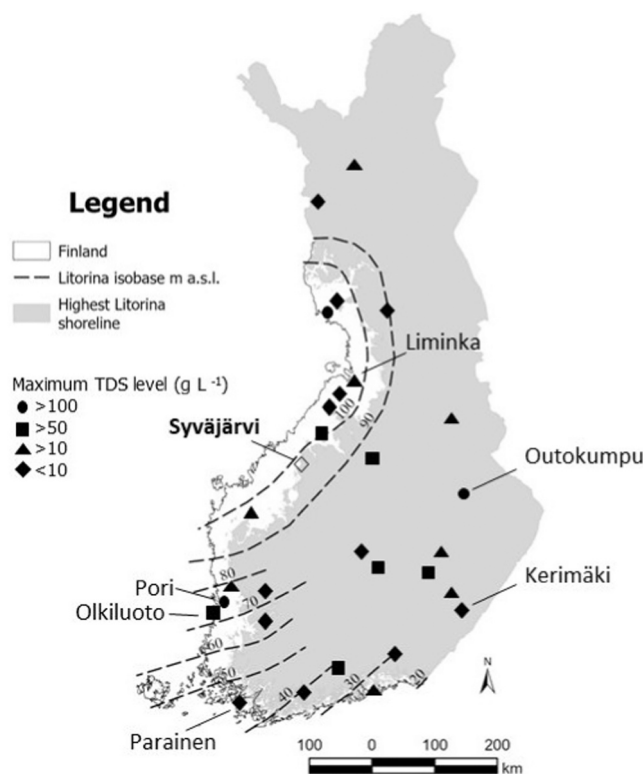
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2022) as well as the ability to recycle water back to the process. In fact, there are many mines in Finland (e.g. Kotalahti mine, Kemi mine, Kittilä mine) facing difficulties with saline groundwater as they have proceeded deeper in the bedrock (Miettinen et al., 2015; Larkins et al., 2018; Turunen et al., 2020; Hyvärinen, 2021), because the salinity was not anticipated when planning of the water management of the mine. This has complicated the water management and treatment of the mine waters, as the water management strategies were not originally planned for saline waters and there is not enough capacity built to separate different types of dewatering waters. Furthermore, due to its high-water solubility and non-biodegradability, removal of chloride from wastewater is expensive and quite challenging. Chloride removal is usually accomplished thorough oxidation, chemical precipitation, membrane separation or using different adsorbents such as an ion exchange (e.g. Iakovleva et al., 2015; Li et al., 2020, Zhang et al., 2021, Li et al., 2022).

Groundwater is usually a mixture of water from different origins and of different age. Brackish (total dissolved solids, TDS <10 g/l, Cl 0,55–5,5 g/l) and saline groundwater (TDS >10 g/l, Cl 5,5–55 g/l) to hypersaline brines (TDS >100 g/l) are common in crystalline basements worldwide. Saline waters can be found almost everywhere in the Fennoscandian Shield, especially in depths of 1–2 kilometres below the ground or more (e.g. Nurmi et al., 1988, Blomqvist, 1999, Vieno, 2000, Frape et al., 2003, Kietäväinen, 2017), but high salinities have been detected in shallow bedrock wells, as well (cf. Hyyppä, 1984). Despite multiple studies on salinity, the subject is still under debate and there are several hypotheses of the origins of saline bedrock waters. According to several studies (e.g. Frape and Fritz, 1987, Bottomley, 1994, Pitkänen et al., 1999, Luukkonen et al., 1999) the deepest groundwaters and brines are old (>10,000 years, or even Precambrian) and their distinctive salinity and isotopic composition is suggested to originate from prolonged water-rock interaction, without connection to the local, meteoric circulation of groundwater. The geological processes which could lead to increased salinity and distinctive isotopic composition are e.g. weathering of silicates (hydrolysis) (Edmunds et al., 1987; Grimaud et al., 1990), formation of zeolites (Stober and Bucher, 2004), or dissolution and leakage of fluid inclusions (Nordstrom et al., 1989). Another hypothesis for the groundwater salinity is seawater and/or cryogenic origin (through freezing) (Herut et al., 1990; Bottomley et al., 1999; Starinsky and Katz, 2003) and infiltration of residual brines into the bedrock during the Pleistocene glacial periods, or evaporation (Bottomley et al., 1994; Louvat et al., 1999, Gascoyne, 2004; Bottomley and Clark, 2004). The development of a continental ice sheet requires about 20,000 years (Barry et al., 1975). The long cold period will also create a thick permafrost layer on bedrock which prevents infiltration of fresh water into the bedrock. Together with freezing, this tends to concentrate salts in the underlying groundwater layers (Nurmi et al., 1988).

In the Fennoscandian Shield, the shallow saline groundwater horizons are likely to be related to climatic and shoreline changes of

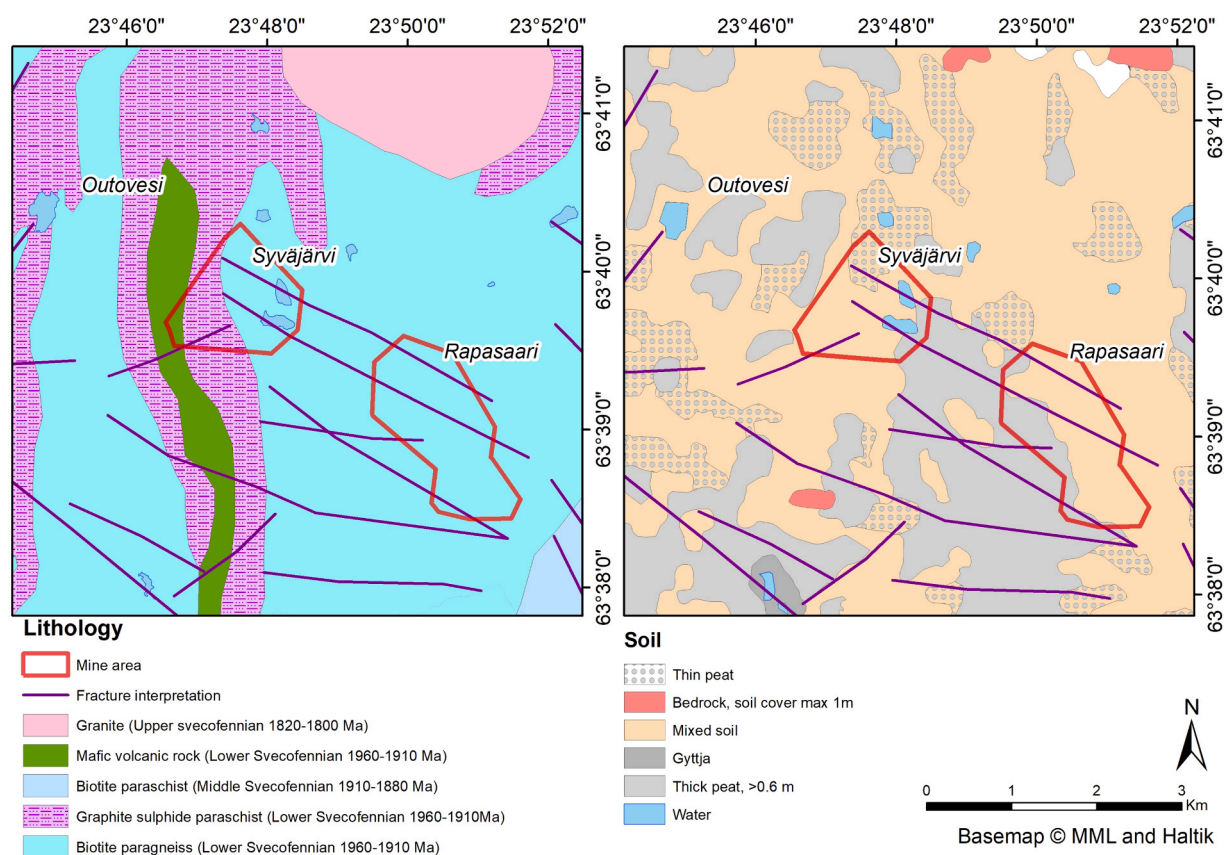


**Fig. 1.** The grey area and the isobases represents the highest Litorina shoreline (Map GTK, 2013). The study site of this study (Syväjärvi) is marked with open diamond, whereas the reference sites of Liminka, Pori, Olkiluoto, Outokumpu, Parainen, and Kerimäki (from Hyyppä, 1986, Nurmi et al., 1988 and Pitkänen et al., 1999) used throughout this paper have been named and marked with black symbols based on their TDS levels. The deep (>300 m below the ground) bedrock groundwater study sites with elevated levels of total dissolved solids (TDS) in Finland (map modified from Kietäväinen, 2017).

the Baltic Sea after the deglaciation phase about 10,000 years ago or even to preglacial times (e.g. Fritz and Frape, 1982, Clark, 1997, Kloppmann et al., 2002, Posiva, 2009). The continental ice sheet created an isostatic subsidence on the Earth's crust which also affected the pore volume and permeability of the fractures in bedrock. After the ice sheet melted the crust started to rebound and the permeability and the pore volume of the bedrock to increase. Large areas were covered with sea water which infiltrated into the bedrock. As the crust continued to rebound, the submerged areas emerged from the sea and the saline waters percolated deeper into the bedrock, while upper parts were filled with fresh meteoric water (Nurmi et al., 1988). Most of the shallow saline wells have been observed below the highest Litorina shoreline which varies between 21 to 100 m a.s.l (above modern sea level, the shaded areas in Fig. 1), being highest (88–100 m a.s.l.) in the Ostrobothnia region on the western coast of Finland (Glückert, 1989). It has been speculated that below this level postglacial clay deposits have trapped the seawater into underlying bedrock structures, and these groundwaters have usually distinct, sulphate ( $\text{SO}_4$ ) horizon indicating the influence of the sea water (Lahermo and Lampén, 1987; Nurmi et al., 1988; Pitkänen et al., 1996). The depth of these saline groundwater horizons varies greatly between one to several hundreds of metres below the ground and the thickness of the horizon between 20 to 60 m (cf. Hyypä, 1984). Meteoric waters are dominant in 50–200 m of depth in coastal areas of Finland and Sweden, whereas inland the same layer will descend to depths of several hundreds of metres (Nurmi et al., 1988; Pitkänen et al., 2002). Saline wells are found also above the highest Litorina shoreline and further inland the origin of the salinity in wells is not related to Baltic Sea stages, but to water-rock interaction and shield brines (e.g. Nurmi et al., 1988, Laaksoharju et al., 2008).

As the EC anomalies of the Syväjärvi site could not be explained thoroughly with geological variations, further studies on the origin of the anomalies were suggested (Pasanen and Pullinen, 2017). It was speculated that the abrupt rise in electrical conductivity shows a horizon of waters of different ages, the lower being either old brine, or having ancient marine origin. In both cases the lower layer should have a very slow hydrologic cycle compared to the upper waters, mixing maybe prevented by the density differences and the lack of hydraulic connections. Another hypothesis was that the elevated concentrations resulted from solid compounds leaching from the fractures.

Various methods can be used to study the origin of saline groundwater. For example, certain ion-ion ratios such as Br/Cl are specific for certain marine components of the bedrock fracture groundwater (e.g. Litorina and Baltic seawater). On the other hand, water develops different isotopic fingerprints in different environments and therefore it can be used to identify the hydrological system



**Fig. 2.** Location of the Syväjärvi study site, the Rapasaari background site and Outovesi, the third mining development site. Lithology and soil of the region. The lithology of the area belongs to the Pohjanmaa Schist Belt, which comprises of the Palaeoproterozoic (1,79 Ga) supracrustal rocks. Purple lines represent the fractures interpreted based on the ERT data by Pasanen and Lerssi (2018).

(surface water-groundwater interaction, hydraulic connections between boreholes, evaporation, silicate hydrolysis etc). In order for the mine to be able to be prepared for the water management challenges posed by saline groundwater, the origin, amount, and extent of saline water must be determined. To understand the processes controlling the hydrochemistry and the evolution of the salinity of the groundwater, the major and trace element geochemistry and isotopic composition ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) of water were investigated. In addition, groundwater age characterisation ( $^3\text{H}$  and  $^{14}\text{C}$ -DIC,  $\delta^{13}\text{C}$ -DIC) was subcontracted from Hydroisotop GmbH for the samples of the last sampling campaign.

## 2. Study site

### 2.1. Geological setting

The study was conducted at the lithium mining development site in Ostrobothnia region in Western Finland (Fig. 1) The Syväjärvi site belongs geologically to the Pohjanmaa Schist Belt, which is surrounded by the Central Finland Granitoid Complex in the east and Vaasa granitoid complex in the west (Vaasjoki et al., 2005; Ahtola et al., 2015, Fig. 2). The Pohjanmaa belt comprises of the Western Finland Palaeoproterozoic (1,79 Ga) supracrustal rocks. The most common rock types within the Pohjanmaa belt are mica schists and mica gneisses, which are intercalated with metavolcanic rocks. Spodumene pegmatites ( $\text{LiAlSi}_2\text{O}_6$ ) crosscut the Svecofennian (1.95–1.88 Ga) metavolcanic and metasedimentary rocks at the northern edge of the belt (Alviola et al., 2001; Ahtola et al., 2015). The Syväjärvi lithium (Li) deposit are part of the Kaustinen Li pegmatite province (Alviola, 2001; Martikainen, 2012). The typical rocks are mica schists and intermediate volcanic rocks with associated agglomeratic layers, spodumene pegmatites, muscovite pegmatites and some more sulphide rich schists (black schists). The mica schists are mostly greywackes and may sometimes contain staurolite. The main minerals in spodumene pegmatite are albite, quartz, K-feldspar, spodumene and muscovite. The Syväjärvi Li deposit comprises of several lithium pegmatite dykes which have a varying strike from SW-NE to SE-NW, sometimes N-S. The dyke swarm is about 500 m long, 1 to 22 m thick and dips  $30\text{--}40^\circ$  towards west (Ahtola et al., 2010).

The Syväjärvi site is situated 85 m a.s.l. and the nearest coast, the Botnia Bay, is located 39 km from the site. The study site has gone through several glaciations and deglaciations, of which the latest one, Weichselian, ended about 10,000 years ago. The surroundings of the site rose from the Baltic Sea about 5000 to 7000 years ago and the highest Litorina shoreline is located 88–100 m a.s.l. in the area (Glückert, 1989). However, the interpolation of the shoreline has been difficult in the region due to the low amount of reference sites available for the modelling. Furthermore, since the region is rather flat and covered with peatlands, even a small change in altitude will move the line hundreds of metres inland or towards Baltic Sea shore (Åberg, 2013).

The soil of the study site consists of mixed soil layers, mainly sandy till and heavily drained peatlands. The sediments underlying the peat deposits of the site have not been studied in detail, but at close by site, where the deposits have been studied in more detail (e.g. Koivusaarenneva approx. 35 km from the site), there are at least a till layer from the Saalian-Stage glaciation and an organic-bearing silt and sand layer from the Eemian-stage interglacial underlying the younger, Weichselian- and Holocene-stage deposits. In Northern and Western Finland, including the Ostrobothnia region, there are more pre-Weichselian sediment occurrences found than elsewhere in Finland. These sediment layers consist mainly of sand and silt and have been sufficiently thick to resist glacial erosion to some extent (Lunkka et al., 2016; Iisalo, 1992). The relief of the site is rather flat, but there are small ribbed and hummocky moraine hills sparsely scattered around the site (Lunkka et al., 2016; Ahtola et al., 2010; GTK, 2015). There are also some glacial lineations (drumlins, flutings) close by (GTK, 2015). The thickness of the sedimentary deposit varies between 3,6 to 15,7 m (Keliber, 2015).

### 2.2. Hydrogeology

The surroundings of the study site are heavily ditched (Fig. 2), and the runoff flows towards the small lakes of Heinäjärvi and Syväjärvi. Lake Heinäjärvi discharges into Lake Syväjärvi, which discharges further into Ruohojärvenoja stream. The water quality in both lakes is poor, characterised with elevated nutrient concentrations (Ramboll 2017), but low metal concentrations. Lake Syväjärvi is acidic and its buffering capacity is poor. Heinäjärvi lake is close to neutral and its buffering capacity varies between poor and good. In both lakes and the stream, the electrical conductivity is low.

There is a limited amount of data on shallow groundwater (levels, flow paths etc) due to low amount of observation wells, short observation times (2018–2019) and lack of proper groundwater modelling of the site (Envineer, 2020). Groundwater recharges mainly on small till deposits and peatlands, and the areas are discontinuous, scattered and there are no classified groundwater areas (aquifers) at the site. The closest classified aquifers are located 6 and 8 km from the site (Ahtola et al., 2010). The groundwater levels in shallow groundwater wells stay rather constant throughout the year and seem to flow towards the ditches and lakes (Envineer, 2020). The groundwater observation wells are located mainly outside and further from the boreholes studied in this study (Fig. 4), which prevents the comparison between shallow and bedrock groundwater aquifers.

According to the slug and pumping tests conducted in previous study (Pasanen and Pullinen, 2017), the bedrock of the site has typical hydraulic conductivity values for crystalline bedrock (cf. Bouwer, 1978), varying between  $K = 6,8 \times 10^{-8}$  m/s to  $K = 4,7 \times 10^{-6}$  m/s in studied boreholes.

### 2.3. The mining and water management plans

The mining company plans to also open two other lithium mines, Rapasaari, and Outovesi in close vicinity of the Syväjärvi site (Fig. 2). The ore processing for all three mines will be carried out at the Rapasaari mine site approx. 2 km away from the Syväjärvi site.



The Syväjärvi and Heinäjärvi lakes will be drained to construct the open pit at the site. Diversion ditches and channels will be constructed around the mine site to avoid contamination of natural clean waters and to minimise the mine water volumes. The mine waters (dewatering water of the open pit and drainage from the waste rock sites) will be collected in settling ponds at the Syväjärvi site and discharged to Ruohojärvenoja stream via treatment wetlands. The same wetland will be used for clean waters. The Ruohojärvenoja stream will discharge to Ullavanjoki River further downstream. (Envineer, 2020).

### 3. Materials and methods

#### 3.1. Field studies and preparations for sampling

The outline of the workflow has been presented in Fig. 3. The exploration boreholes were used for the groundwater studies (Fig. 4). The dip of the studied boreholes varies between 40° and 89°, and the depth between 33 and 259 m below ground. Most of the boreholes are orientated towards east (azimuth being 90°). The boreholes do not have casing, which enables studying the bedrock and groundwater in fractures.

The geological data, such as lithology and Rock Quality Designation (RQD), of the drill cores as well as the geological maps and geophysical data were used to interpret the possible fractures zones and faulting of the bedrock, which could aid in locating the hydraulic connections between the boreholes as well as the hydraulically active zones due to fracturing or discontinuities of geological units. RQD can be used to assess fissures, fractures, and discontinuities of a rock mass (Shingal and Gupta, 1999). RQD is expressed as a percentage and as the faulting or fracturing of the bedrock increases the RQD decreases. Therefore, low RQD could possibly also mean an increasing of the relative permeability of the bedrock (Poteri, 2009) and was used in this study to aid in locating the most conductive fractures zone along the borehole for water sampling. The data was received from the mining company, through literature review (e.g. bedrock maps) and from the on-going geophysical investigations at the site (unpublished data).

The first round of field studies was conducted in April 2017 and the last in October 2021. The field studies were started with electrical conductivity (EC) logging to locate all boreholes with anomalous EC. The lightweight logging system consisted of CDT-sensors (Aqua Troll 200; InSitu, 2017). The sensor was lowered into the borehole with a low, constant velocity of 1–2 m/s to avoid mixing of water. The EC logging was repeated in 2017, 2018, 2020 and 2021, as some of the boreholes were extended and some new

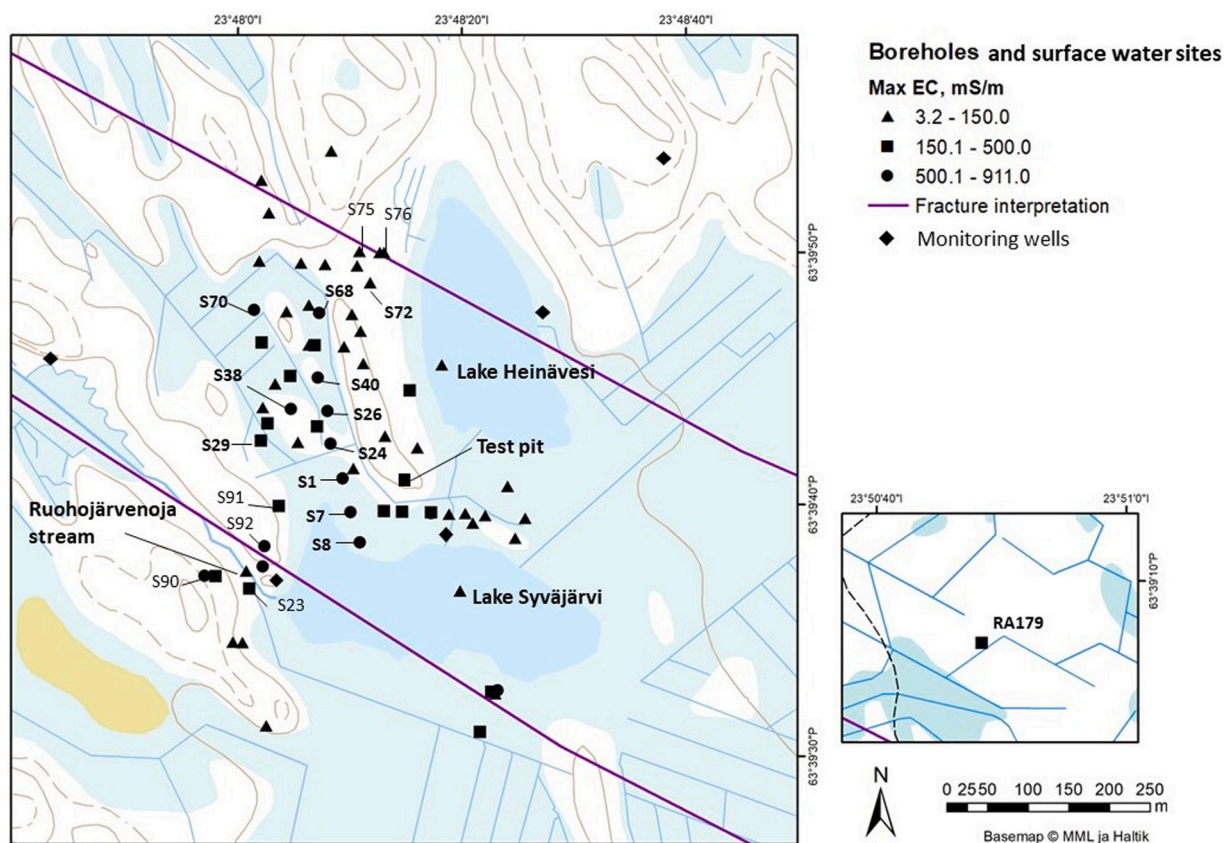
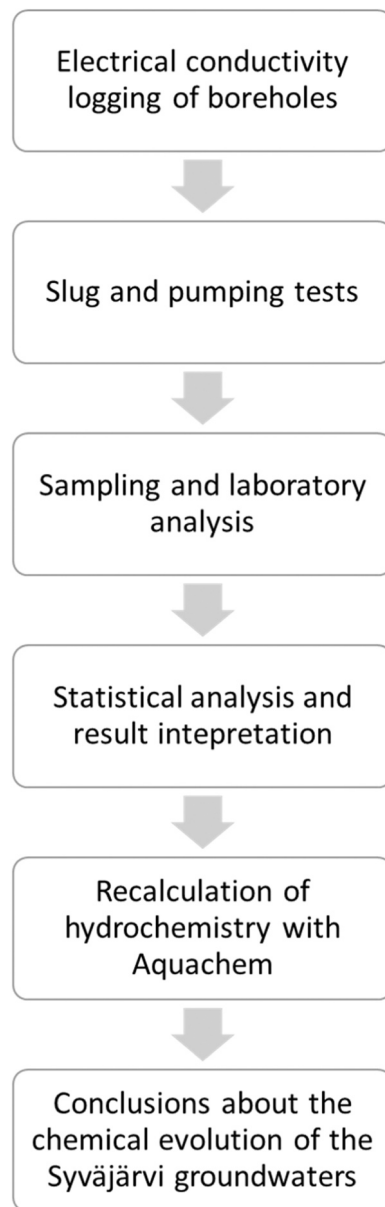


Fig. 4. The variation of the EC-values in studied boreholes and surface waters. Purple lines represent the fractures interpreted based on the ERT data by Pasanen and Lerssi (2018). The characters of the labelled boreholes are described in more details in this paper. The sampling sites are marked in bold letters, other sites were monitored only for EC.



**Fig. 3.** Outline of practical aspects of the study.

boreholes were drilled after the studies of [Pasanen and Pullinen \(2017\)](#). All together 64 boreholes were logged during this study.

The hydraulic conductivity of the bedrock was determined by slug-testing. Slug-tests conducted on open drillhole yield an estimate of an average hydraulic conductivity for each drillhole and the resulting responses cannot be targeted on specific depths. Rather, the responses are a result of the contributions from the most hydraulically active fractures and fissures that intersect the drillhole. Therefore, the open drillhole slug-tests yield an indication of the average hydraulic conductivity of the fractures intersecting the drillhole. The slug-tests were conducted on 10 boreholes in 2020.

The pumping test was performed to verify the slug testing results and to study the hydraulic connections between the drillholes. Response on the water level in the monitored drillholes during a pumping test is indicative of the hydraulic conductivity of the fracture zones providing the linkage. The pumping test was conducted on borehole S38 in 2020, while 10 surrounding boreholes were monitored for water level and EC throughout the pumping. Additionally, the results of slugs and pumping tests of [Pasanen and Pullinen \(2017\)](#) were utilised for interpretation for hydraulic conductivities and connections in bedrock.

Table 1

The hydrochemistry (soluble concentrations), stable isotope compositions and physico-chemical parameters of the samples. The sampling techniques are Mod. Bailer = modified bailer and PBP = pumping with packers. The concentrations in bold were below the detection limit, the detection limit was used to calculate TDS and mass balances. The concentrations in italic are recalculated with Aquachem, due to analysis error which resulted in mass balance error. Reference waters are from Pitkänen et al. (1999).

Sampling point	Depth	Technique	Date	Sr	Ca	K	Mg	Na	Br	Cl	SO4	Alkalinity	TDS	EC	pH	ORP	O-18	H-2	d-excess
<b>Boreholes</b>	m			ug/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mmol/l	mg/l	uS/cm		mV			
<b>S1</b>	25	Tube	Jun-18	691	68	3,5	12	85,3	0,9	220	6,5	0,97	517	990	7,5	-49	-12,8	-92,7	10
	94	Tube	Jun-18	4960	729	6,6	81	512	11	2600	4,3	0,6	2620	7690	7,5	-60	-13,3	-98,5	7,5
	100	Mod. Bailer	Apr-17	5220	479	5,3	56	391	6,4	1800	2,2	0,75	2839	5160	7,6	-94	-13	-96,4	7,6
<b>S24</b>	39	PBP	Nov-17	84	12	4,2	4	26	<b>0,05</b>	7	6,9	0,95	177	200	7,4	-81	-12,9	-92,8	10,6
	73	PBP	Oct-21	920	104	6,2	18	143	<b>0,5</b>	444	10,7	1,3	916	1620	7,6	-80	-12,8	-93	9,6
	80	PBP	Jul-21	5930	675	11	102	566	8,8	2328	1,4	0,7	3795	6750	7,6	-185	-12,6	-92,6	8,3
<b>S26</b>	89	Mod. Bailer	Apr-17	4080	369	7,3	38	240	4,4	1100	2,6	0,77	1853	3700	7,3	-103	-13,6	-99,6	9,3
	136	Tube	Nov-17	3330	461	10	68	387	6,4	1600	3,9	0,65	2620	3500	7,8	n/a	-13,1	-97,2	7,2
	51	Tube	Jun-18	113	20	2,6	4	15	0,2	34	11	0,42	138	260	7	-58	-12,6	-90,1	10,9
<b>S29</b>	102	PBP	Jun-18	3620	650	9,9	81	596	11	3100	4,4	0,49	4458	5840	7,6	-50	-12,8	-96,1	5,9
	117	Tube	Jun-18	4980	496	7,9	62	448	7,5	1900	7,1	0	2928	5840	7,1	n/a	-12,7	-94,3	7,5
	123	PBP	Oct-21	5590	765	7,6	64	701	0,5	2734	0,7	1,4	4260	7900	7,6	-19	-13,1	-96,3	8,3
<b>S38</b>	158	Tube	Nov-17	2040	289	10	38	263	3,9	1000	7,8	0,21	1640	7100	7	n/a	-11,9	-86,8	8,1
	14	PBP	Oct-21	108	13	4,1	5	54	<b>0,5</b>	14	16,1	1,58	301	420	8,2	3,3	-12,8	-94,5	7,7
	14	PBP	Jul-21	181	23	4,9	7	51	0,2	38	7,9	1,25	295	380	8	-189	-12,9	-95,9	7,5
<b>S40</b>	19	Tube	Jun-18	1780	198	6,2	20	210	2,8	650	4,1	0,93	1208	2410	7,9	157	-12,9	-93,5	9,3
	45	Tube	Nov-17	331	60,6	8,9	10	86	0,79	190	7,8	0,8	462	850	7,2	n/a	-12,2	-88,5	9,4
	82	Tube	Jun-18	5340	533	10	56	488	7,8	1900	4,3	0,48	3066	5980	7,6	106	-12,9	-95,2	8
<b>S45</b>	92	Mod. Bailer	Apr-17	314	29	3,3	6	81	0,3	93	14	1,34	391	620	6,7	92	n/a	n/a	n/a
	124	PBP	Oct-21	4950	663	7,9	66	634	<b>0,5</b>	2409	0,7	1,03	3869	7260	7,6	-19	-13,3	-96,5	9,7
	125	PBP	Jul-21	4750	567	10	71	546	5,1	2014	0,05	0,75	3311	6160	7,7	-128	-13,3	-95,4	10,8
<b>S68</b>	146	Tube	Jun-18	4340	649	9	72	568	9,3	2300	4,2	0,57	3688	7410	7,5	72	-12,5	-92,9	7,4
	155	Tube	Nov-17	2710	391	11	43	392	5,8	1400	3,9	0,48	2310	4660	7,9	40	-12,3	-90,5	8,2
	157	PBP	Nov-17	3120	432	10	47	429	6,5	1600	3,3	0,49	2593	4790	7,9	109	-12,4	-91,5	7,5
<b>S70</b>	103	Mod. Bailer	Apr-17	82	12	2,7	4	12	<b>0,05</b>	4,8	12	0,55	116	180	7,4	-59	-12,6	-91,1	9,9
	18	Tube	Jun-18	64	9	2	2	6,8	0,1	7,9	16	0,25	75	120	7,6	n/a	-13,1	-94,6	10
	134	PBP	Jul-21	5880	744	11	11	517	4	2133	1,4	0,34	3470	7800	7,9	-92	-11,7	-86,7	6,7
<b>S72</b>	59	Mod. Bailer	Apr-17	7080	479	4,8	48	377	6,6	1600	1,8	0,63	2603	5060	7,7	-64	-12,8	-90,1	7,2
	86	Tube	Jun-18	239	26	1,5	2	95	<b>0,5</b>	110	5	1,18	387	640	8,5	41	-12,9	-93,2	9,8
	139	PBP	Jul-21	165	19	1,3	2	71	0,2	55	13	1,65	364	420	8,7	-151	-13	-93,8	10,1
<b>S8</b>	202	Tube	Jun-18	5870	659	4,9	11	485	7,8	1900	5	0,18	3102	6190	7,1	38	-12,2	-90,1	7,1
	57	Tube	Jun-18	54	6,9	2,7	2	31	<b>0,05</b>	3	25	0,7	156	210	8,2	n/a	-13,3	-94,7	10,3
	134	PBP	Jul-21	54	6,2	1,9	1	47	<b>0,05</b>	2,8	18	1,56	269	220	8,9	-132	-13,2	-95	10,5
<b>Background 2 km</b>	69	Mod. Bailer	Apr-17	7530	500	8	46	409	7,2	1700	4,8	2,36	2973	5400	7,6	-77	-12,8	-95,5	7,2
	RA179	PBP	Oct-21	1080	180	5,5	27	207	<b>0,5</b>	618	0,1	1,56	1240	2400	7,5	n/a	-12,7	-92,1	9,8
<b>Surface water</b>																			
<b>Stream</b>	0,5	B	Jul-21	37	7,1	0,9	2	4,4	<b>0,05</b>	2,6	3,1	0,05	27	52	5,9	79	-11,9	-87,4	2,8
	1	B	Jun-18	15	2,5	0,7	1	2,3	<b>0,05</b>	1,9	2,8	0,08	21	32	7	241	-11,5	-87,9	3,7
	1	B	Jun-18	13	2,4	0,7	1	2,2	<b>0,05</b>	2	2,8	0,09	22	31	6,6	184	-11,4	-87,8	3,3
<b>Syväjärvi Lake</b>	1	B	Jul-21	15	2,9	0,3	1	1,9	<b>0,05</b>	1,4	2,7	0,06	17	26	5,7	132	-7,88	-69,2	-1,3
	1	B	Oct-21	17	3,1	0,5	1	1,4	<b>0,5</b>	1,9	4,2	0	12	31	4,4	n/a	-11,9	-87,4	7,8
	1	B	Jun-18	11	2,2	0,6	1	1,5	<b>0,05</b>	0,7	2,7	0,08	19	26	7,8	496	-9,39	-77,6	-2,5
<b>Heinäjärvi Lake</b>	1	B	Jul-21	13	2,6	0,7	1	1,8	<b>0,05</b>	0,8	3,5	0,08	22	34	7,9	27	-7,79	-67,1	-4,8
	3	B	Jun-18	139	22	6,1	4	35	0,3	70	20	0,46	214	390	7,6	39	-10,8	-86,6	0
	2	B	Jul-21	90	17	5,6	3	21	0,2	34	13	0,89	196	470	8,3	47	-8,76	-71,4	-6,2
<b>Test pit</b>	1	B	Oct-21	94	16	5,7	3	18	0,5	35	15	0,39	142	170	7	n/a	-8,24	-72,3	-6,4
<b>Reference waters</b>																			
<b>Litorina Sea</b>				2680	151	134	448	3674	22,2	6500	890	n/a	n/a	n/a	7,6		-4,7	-37,8	-0,2
<b>Glacial Melt water</b>				1	0,13	0,15	0,1	0,15	0001	0,7	0,05	n/a	n/a	n/a	5,8		-22	-166	10

### 3.2. Sampling

The boreholes with EC anomalies (above 420  $\mu\text{S}/\text{cm}$ , the average level in till covered areas in Finland, Hyyppä, 1984) were prioritised for water sampling based on the EC loggings and previous groundwater studies by Pasanen and Pullinen (2017). Some of the boreholes were chosen due to their anomalous EC values and the others having lower EC values were chosen as reference points. One borehole (RA179) located in Rapasaari site approx. 2 km from the study site was chosen for a background sample.

Altogether 35 groundwater samples and 9 surface water samples in 13 boreholes, two lakes, one stream and a test pit were taken in November 2017, June 2018, October 2018, July 2021 and October 2021 (Table 1 and Fig. 4). Different water sampling techniques were used: modified 4 m bailer sampler in 2017, tube sampling (Nurmi and Kukkonen, 1986) in 2018 and pumping with expandable packers in 2021. The surface water samples were collected directly to the bottle.

The modified bailer method and tube sampling require lowering the sampler with low speed to avoid mixing of different water horizons. The bailer and tube sampling methods allow collecting samples only along the borehole profile, but not from surrounding bedrock fractures. Therefore, the water sampling was continued with isolating suitable bedrock fractures with expandable packers from the rest of the borehole and pumping until the volume of the tube and the isolated zone between the packers was replaced. The selection of the suitable fracture zones and sampling depths was based on the RQD and drill core data received from the mining company as well as the EC loggings carried out in this study.

Numerous aliquots of water were collected from each sample point to facilitate multiple analyses. Table 1 indicates which sample points, techniques and analysis were carried out during each event. One 50 ml and one 100 ml bottle of unfiltered, unpreserved water was collected for analysis of stable isotopes ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) and major anions ( $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ), respectively, from all sampling sites during all campaigns. Two one-liter bottles of unfiltered, unpreserved water were collected for the tritium and radiocarbon analysis in October 2021. To stabilise the inorganic carbon at  $\text{pH} > 12$  NaOH was added in the samples for the radiocarbon ( $^{13}\text{C}$  and  $^{14}\text{C}$ ) analysis by the Hydroisotop GmbH laboratory before the analysis. To identify the possible solids leached from the bedrock fractures another 100 ml was filtered for anion analysis in the first sampling campaign in 2017 (Turunen et al., 2017). In addition to water analysis, the solids were vacuum filtered from water and analysed for total concentrations through dissolution with hot nitric acid (7 M  $\text{HNO}_3$ ). A 100 ml sample aliquot for analysis of dissolved cations was field filtered and acidified using 0.5 ml  $\text{HNO}_3$ , while a second acidified, but unfiltered 100 ml aliquot was used for analysis of total cations. Field blanks were collected for each analysis during each sampling campaign. The sample pre-treatment (e.g. sample filtration and preservation) was conducted immediately upon sample collection.

### 3.3. Analytical methods

Major and trace elements, pH, redox, EC, dissolved oxygen concentration and alkalinity were determined from the samples, together with the stable isotopic composition of water ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ). The analysis represents the substances which might affect the salinity as well as the treatment needs and possibilities for the future mine. The samples from the last campaign in October 2021 were analysed also for Sr isotopes and age determination ( $^3\text{H}$  and  $^{14}\text{C}$ -DIC,  $\delta^{13}\text{C}$ -DIC).

The geochemical analyses were done as subcontractor work in Labtium laboratory in Espoo and in Metropolilab laboratory in Helsinki. The samples from the last campaign in October 2021 were analysed also in the laboratory of University of Helsinki, to compare the results of different laboratories. The major cations were measured by ICP-OES following ISO standard method SFS-EN ISO 11885, while tracer elements were analysed by ICP-MS following ISO standard method SFS-EN ISO 17294-2. Anions were analysed by ion chromatography techniques following ISO standard method SFS-EN ISO 10304.

Stable and Sr isotopic analyses and corresponding sample preparation were conducted at the Research Laboratory of Geological Survey of Finland in Espoo, Finland. All sample preparation steps utilised deionized Milli-Q water (resistivity of  $\geq 18.2 \text{ M}\Omega \text{ cm}$ ). Acid washed Teflon vials were used during digestions and column separation. All acids were either single or double-distilled (sub-boiling), depending on the initial acid purity class. Water samples were analysed for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  using Cavity Ring Down Spectroscopy (CRDS) following the principles of Brand et al. (2009). Before the analysis, the samples were filtered to  $<0.45 \mu\text{m}$  in the laboratory. The isotope ratios are reported using standard  $\delta$  notation relative to Vienna Standard Mean Ocean Water (VSMOW). Repeatability ( $2\sigma$ ) was  $<0.2\%$  for  $\delta^{18}\text{O}$  and  $<0.10\%$  for  $\delta^2\text{H}$ , respectively.

The strontium (Sr) isotopes were collected only on the last field campaign in October 2021, including five groundwater and two surface water samples. Depending on the Sr-concentration of each sample, a sufficient amount of Sr was evaporated and diluted (1 ml 3.2 N  $\text{HNO}_3$ ) for analysis. Strontium specific ion exchange resin (TrisKem Sr Resin, 50–100  $\mu\text{m}$ ) was used to purify Sr. The isotope ratio was measured using MC-ICPMS in dynamic mode (50  $\mu\text{l}$  meinhart nebuliser, a DSN and a Multi-Collector Inductively Coupled Plasma Mass Spectrometer (Nu Instruments TM) at low mass resolution ( $\Delta m/m = 400$ ). Each session of Sr analyses by MC-ICPMS was bracketed with standard reference material NBS-987. The average value for the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of NBS-987 from MC-ICPMS was  $0.710264 \pm 0.000063$  ( $2\text{sd}$ ,  $n = 14$ ).

The Hydroisotop GmbH laboratory did the age characterisation ( $^3\text{H}$  and  $^{14}\text{C}$ -DIC,  $\delta^{13}\text{C}$ -DIC) for the samples of October 2021. Tritium was analysed using fluid scintillation spectroscopy LSC after electrolytical enrichment and analysed in tritium units (TU) with double standard deviation ( $1\text{TU} = 0.119 \text{ Bq/L}$ ). The tritium result is related to date of measurement and there is no half-life correction.  $^{13}\text{C}$  was analysed using isotope-ratio mass spectrometry (IRMS) and measured in relation to VPDB-standard ( $1\sigma = \pm 0.3\%$ ).  $^{14}\text{C}$  was analysed using accelerator mass spectrometry (AMS) and measured in  $\text{pmC}$  with double standard deviation ( $100 \text{ pmC} = 0.226 \text{ Bq/g carbon}$ ).

The alkalinity of the water samples was measured on site using a HACH titrator (sulphuric acid titration). The physical properties



(pH, Eh, EC, DO, T) of water samples were measured using either a Mettler Toledo instrument or YSI Professional Plus multi-parameter probe at the time of sample collection.

## 4. Results

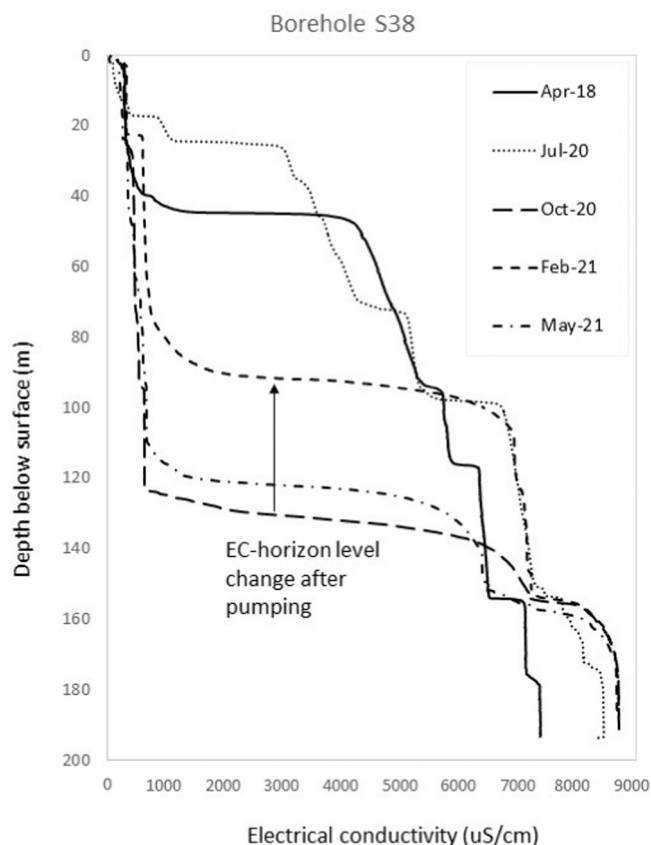
### 4.1. Electrical conductivity (EC) and total dissolved solids (TDS)

There are fluctuations in concentrations and EC between sampling campaigns, most likely due to different sampling techniques (tube, bailer, pumping), and varying sampling depths of each campaign. The EC varied between 100 and 9110  $\mu\text{S}/\text{cm}$  in groundwater (Fig. 4). In comparison, the EC values of the surface waters varied between 26 and 460  $\mu\text{S}/\text{cm}$ , being highest in the test pit. It is worth to mention, that there is a difference between the maximum EC-values measured with a CTD-logger while screening the whole borehole length and when measured with a multiparameter device within sampling. The EC-values presented in Table 1 were measured from the samples in the field, whereas the EC-values presented in Figs. 4, 5 and 9 were measured with a CTD logger while logging the EC horizons.

In most of the boreholes the changes in EC are abrupt, but there are a few boreholes where the change is more gradual with several EC horizons (e.g S38, Fig. 5). The anomalous EC horizon seems to be concentrated in the boreholes lined up in the middle of the study site going from the boreholes located near Syväjärvi Lake towards the boreholes located in the Northwest corner of the site (Fig. 4). Outside this line the EC levels decrease significantly. Based on the TDS values (74–4457 mg/l, Table 1), none of the groundwaters can be classified as saline (TDS > 10 g/l) or brine (TDS > 100 g/l), at most as brackish (TDS 1–10 g/l).

### 4.2. Hydraulic connections

Similarly to groundwater observation wells (Envineer, 2020), the groundwater levels seem to be rather constant also in boreholes and ascending towards the lakes. The hydraulic conductivities of the bedrock based on the slug and pumping tests carried out in 2020 within this study were consistent with the results of Pasanen and Pullinen (2017), the K values ranging from  $K = 6,0 \times 10^{-8}$  m/s to  $K = 9,0 \times 10^{-7}$  m/s in studied boreholes. According to the pumping test, there is a hydraulic connection between some boreholes. For



**Fig. 5.** EC-loggings of S38 borehole in 2018, 2020 and 2021. The pumping test was carried out in October 2020, the red line presenting the situation before the pumping in October 2020 and yellow line in February 2021.

instance, while borehole S38 was pumped, the anomalous EC horizon in borehole S24 sank from 80 m of depth to 140 m of depth. However, the water table decreased only by 20 cm in same borehole S24. Similarly, in borehole S40 the EC horizon sank from 120 m to 138 m of depth and the EC value rose from 3000 uS/cm to 5600 uS/cm, while the water table sank only by 20 cm. On the other hand, in borehole S31 the water table dropped by 1.3 m, but the EC profile stayed relatively the same. In several other boreholes in the vicinity of S38 no significant changes in water table nor EC were detected. The EC horizon in borehole S24 had recovered in five months whereas the recovery of the EC horizon in boreholes S40 and S38 took eight months (Fig. 5).

#### 4.3. Hydrogeochemistry of water

During sampling campaigns performed in July 2021 and October 2021, notable balance errors (up to 40%) were observed. It was speculated that the error could derive from the dilution practises made in the lab for the most saline samples to enable analysis with ion-chromatography, resulting in too low Cl concentrations. Therefore, the samples of the October 2021 campaign were reanalysed in the University of Helsinki in addition to the commercial laboratory used before. In the reanalysis the balance errors were below  $\pm 5\%$ , and therefore these new results from the October 2021 campaign are included in the interpretation. Unfortunately, there were no water samples left from the July 2021 sampling campaign for reanalysis. The samples from July 2021 campaign of which balance error exceeded  $\pm 15\%$  were therefore recalculated with AquaChem 2014.2 (Waterloo Hydrogeologic) to adjust the Cl concentrations, total dissolved solids (TDS) and the missing alkalinity ( $\text{HCO}_3^-$ ) to adjust the balance error. The recalculated values are marked in italic in Table 1. Also, since the alkalinity was measured only in the field while sampling, and not again in the laboratory, it is likely that some of the balance error mentioned above derives from the possible reactions between the time of sampling and transportation to the laboratory, which could have also affected the alkalinity of the samples before analysis.

Due to low hydraulic conductivity of the fracture zones a high-pressure bladder pump (Geotech) with low capacity was used for sampling in last two sampling campaigns in 2021. This extended the transport times from the borehole to the ground and led the samples to be longer time in direct contact with air (cyclic pumping rate). In result, diffusion with atmospheric gases might have affected the oxygen and  $\text{CO}_2$  sensitive parameters, such as alkalinity, redox, Mn, stable isotopes and radiocarbon. Furthermore, the sampling methods changed between the sampling campaigns from bailer and tube sampling throughout the whole length of the borehole to pumping within isolated sections. With packers the zone of sampling is more spatially restricted and aimed to sample the water in fractures than without packers, and it is likely that other sampling methods represent the water quality within longer stretches of borehole than with packers and therefore are more diluted in terms of salinity.

Chloride (Cl) concentrations ( $n = 45$ ) vary between 2,8 and 3100 mg/l in groundwaters and between 0,65 and 70 mg/l in surface waters (Table 1). The highest concentration in surface water was detected in the test pit, which might have connection to boreholes via fracture network. Positive, statistically significant ( $p < 0.01$ ) Spearman rank correlation coefficient was detected between Cl, Sr, Br, Na, Ca, Mg and Li, but not with depth, nor  $\text{SO}_4$ . Elevated  $\text{SO}_4$  concentrations (up to 25 mg/l) were found mainly in boreholes with fresh groundwater and in the test pit.

The water quality data of the study area plotted on the Piper trilinear diagram is shown in Fig. 6. According to all sampling campaigns, groundwater can be roughly divided between two water types, the brackish groundwater being Ca-Na-Cl water type and the rest mainly Na-Ca- $\text{HCO}_3$  water type, which indicates surface water or meteoric water influence in these wells. The background groundwater sample was Ca-Na-Cl water type. The proportion of magnesium increased in surface waters, water type being mainly Ca-Na-Mg- $\text{HCO}_3$ . None of the water samples seem to resemble the reference waters of Litorina Sea, Baltic Sea, Subglacial or Glacial melt water from Pitkänen et al. (1999).

All water samples were mainly close to neutral (pH 5,9–8,87) and the lowest pH values were detected in Syväjärvi Lake and its discharging stream. Slightly reducing conditions prevailed in most of the boreholes, but some had also oxidising conditions (Table 1). All boreholes had low oxygen concentrations (0,28–7,38 mg/l). Alkalinity (as  $\text{HCO}_3^-$ ) varied between 0,21–2,36 mmol/l in groundwaters and between 0–1,2 mmol/l in surface waters. Uncertainty of the alkalinity measurement by titration method is estimated to be

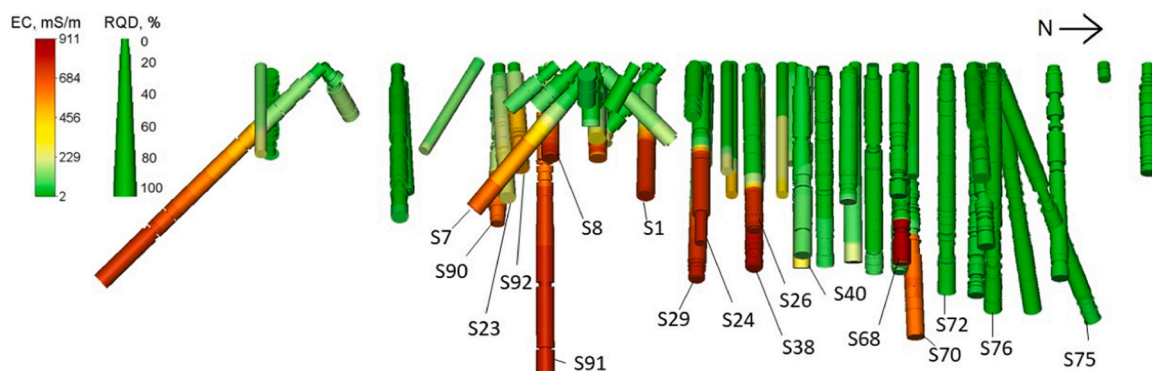


Fig. 9. The vertical cross-section of the boreholes, the vertical variation of EC and RQD values along the boreholes, RQD marked as thickness of the width, thinner being more fractured. The orebody declines toward north-west (to the right in figure.).

≤15%.

The concentration of sulphur in solids analysed in 2017 (See Appendix 1, modified from Turunen et al., 2017) is low in comparison to e.g. Cu, Co, Zn, and As, which indicates the presence of clay minerals. Since the dissolved concentrations of sulphidic metals and As in water are low compared to the concentrations in solids, these have been dissolved from the fractures, inter and intra-granular pore space of the rock matrix or from fluid inclusions enclosed in minerals.

#### 4.4. Isotope composition and age characterisation

The isotopic composition of water samples is presented against local and global meteoric water lines in Figs. 7 and 8 (LMWL; Kortelainen, 2007, GMWL; Craig, 1961). The LMWL is derived from precipitation data collected from a set of local sites around Finland. The isotopic composition of groundwater and precipitation in Finland usually plots on this line and waters plotting off the LMWL can indicate intrusion of surface water into groundwater or a source of shield brine. When water evaporates its isotopic composition gets heavier giving more positive isotopic  $\delta$ -values. The evaporated water such as lake water locates below the LMWL, whereas shallow groundwater and precipitation plot usually on the LMWL. The d-excess value indicates the origin and the rate of evaporation and can be calculated from the  $\delta^{18}\text{O}$  ja  $\delta^2\text{H}$ -values. The d-excess values of less evaporated water are approx.  $10 \pm 1\text{‰}$ , whereas for evaporated water the value is clearly below  $10\text{‰}$  or might also be negative.

Within the groundwater samples the  $\delta^2\text{H}$  varied from  $-86,7\text{‰}$  to  $-99,6\text{‰}$  (VSMOW) and in surface water samples from  $-67,1\text{‰}$  to  $-87,9\text{‰}$  (VSMOW).  $\delta^{18}\text{O}$  varied in groundwater from  $-11,68\text{‰}$  to  $-13,28\text{‰}$  (VSMOW) and in surface waters from  $-7,79\text{‰}$  to  $-11,9\text{‰}$  (VSMOW). In all sampling campaigns, the stable isotopic composition of the waters plots mainly on the local meteoritic water line (LMWL), or below it, surface waters indicating naturally higher values due to evaporative loss. D-excess value varied in surface waters between  $-6,4$  and  $7,8$  and in groundwaters between  $5,9$  and  $10,9$  (Table 1).

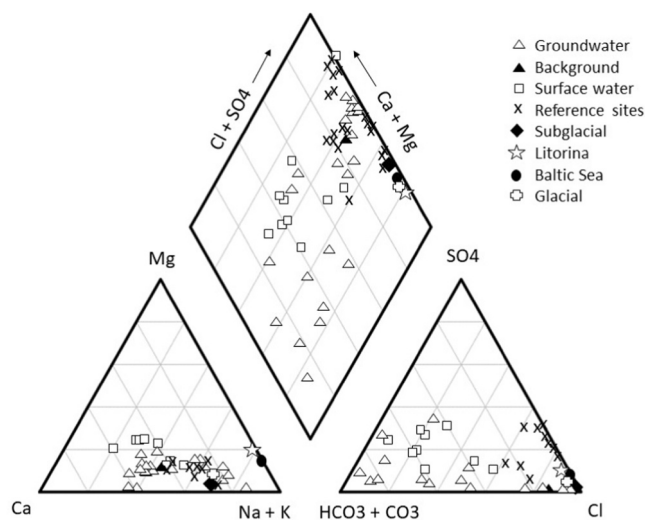
Sr isotopes were determined only in October 2021 campaign. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios varied between 0720 and 0731, being highest in surface waters and lowest in boreholes S38 (lower sample) and S26 (Table 2).

As it was speculated that the elevated salinity of the groundwater originates either from brines or ancient sea water, therefore indicating higher residence times, tritium was used to indicate recent water contribution to the groundwater system, and radiogenic carbon as an exact dating tool for the residence times. The age characterisation results ( $^{14}\text{C}$ -DIC,  $\delta^{13}\text{C}$ -DIC) are presented in Table 2. The tritium content of borehole S26 and background were under the detection limit. Otherwise, tritium ranged between very low  $0.7 \pm 0.7$  and moderate  $3.0 \pm 0.7$  TU in boreholes S38 and S24 to very high  $7.5 \pm 0.8$  TU in Syväjärvi Lake. The  $^{14}\text{C}$ -DIC content of the samples ranged between  $14.2 \pm 0.2$  and  $48.3 \pm 0.3$  pmC and  $\delta^{13}\text{C}$ -DIC between  $26.5$  to  $17.9\text{‰}_{\text{VPDB}}$ .

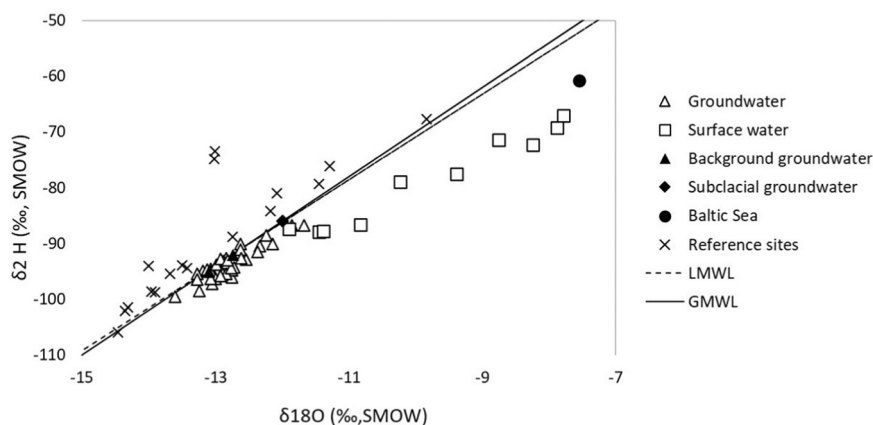
## 5. Discussion

### 5.1. Connection between electrical conductivity and bedrock fractures

As in several previous studies worldwide (e.g. Hyypä, 1984, Lahermo and Lampén, 1987) the change in Syväjärvi anomalous EC horizon is abrupt (Fig. 9). The boreholes outside of the anomalous line in the middle of the site are oftentimes shallower, and it is likely that these boreholes do not meet with the saline groundwater horizon. Some of the boreholes were extended after the first sampling campaigns of 2017 and 2018 and in consequence the level of the EC increased, and the depth of the anomalous horizon changed (e.g. in



**Fig. 6.** Major ion composition from different borehole, background and surface waters of the site, plotted on the piper diagram with Finnish reference sites (from Nurmi et al., 1988 and Hyypä, 1986), Litorina, subglacial, glacial and Baltic Sea reference waters (from Pitkänen et al., 1999).

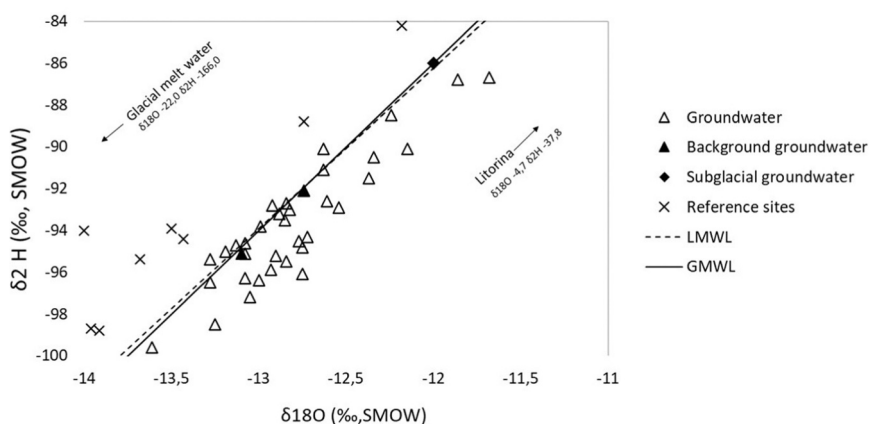


**Fig. 7.** The stable isotope composition of borehole groundwater, surface waters in Syväjärvi site and reference sites or waters plotted with the local Finnish and global meteoric water line (LMWL Kortelainen, 2007 and reference values for Baltic Sea and Subglacial groundwater Pitkänen et al., 1999, other references sites Nurmi et al., 1988 and Hyypä, 1986).

**Table 2**

The  $^{87}\text{Sr}/^{86}\text{Sr}$ , tritium, and radiocarbon results of the October 2021 samples and reference waters of Litorina and Baltic Sea from Pitkänen et al. (1999).

	Depth	$^{87}\text{Sr}/^{86}\text{Sr}$	Tritium (3 H)	$\delta^{13}\text{C-DIC}$	14 C-TIC
<i>Boreholes</i>			TU	‰ VPDB	pmC
S38	14	0725	$0.7 \pm 0.6$	-17,9	$45.7 \pm 0.3$
S38	124	0720	$0.7 \pm 0.7$	-26,5	$24.2 \pm 0.2$
S24	73	0721	$3.0 \pm 0.7$	-21,9	$48.3 \pm 0.3$
S26	123	0720	<0.6	-22,4	$14.2 \pm 0.2$
<i>Surface waters</i>					
Syväjärvi Lake	1	0731	$7.5 \pm 0.8$	n/a	n/a
Test pit	1	0728	n/a	n/a	n/a
<i>Background 2 km</i>					
RA 179	0	0723	<0.6	-19,7	$19.2 \pm 0.3$
<i>Reference waters</i>					
Litorina		0709	n/a	-1	43,00
Baltic Sea		0709	n/a	-1,68	115,8



**Fig. 8.** A closer look for the stable isotope composition of borehole and background groundwater in Syväjärvi site and reference sites or waters plotted with the local Finnish and global meteoric water line (LMWL Kortelainen, 2007 and reference values for Subglacial groundwater Pitkänen et al., 1999, other references sites Nurmi et al., 1988, and Hyypä, 1986).

S38, Fig. 5). It is likely that the boreholes now extending deeper reach the bedrock fractures with the saline groundwater letting it enter the borehole. The depth of the EC horizon starts in shallower depths (approx. 40 m) in boreholes located closer to the Lake Syväjärvi than in the North-western part (approx. 120 m), whereas the water level in all boreholes stays rather constant, dipping only slightly

towards north as the topography ascends. Furthermore, the EC is clearly elevated (e.g. 1500 uS/cm in borehole S-8) also in the top layers of the boreholes close to Lake Syväjärvi, whereas in the northern part the EC tends to be around background levels (e.g. 240 uS/cm in borehole S-70) in the top layer, despite the elevated EC values in the bottom. The decline of the EC horizon is concurrent with the decline of the ore formation towards north (Fig. 9) and it is likely that, as healthier, more intact bedrock, the ore formation constrains the saline groundwater in certain depths.

Despite the low RQD values of the drill logs indicating fracturing in several boreholes, the permeability of many fractures was too low to enable sampling with isolating a zone between two packers in some of the boreholes. This could derive from the fact that RQD does not include information of the discontinuity of the aperture, and on the other hand a hydraulically active fracture may not necessarily be associated with a highly fractured rock which is a typical property of fractured crystalline bedrock (Sen, 1996; Kittilä et al. 2018). In the boreholes where isolating the most fractured zones did not yield enough water, only one packer was used to isolate the upper freshwater part of the borehole from the bottom, allowing sampling from the anomalous horizon only.

As observed in pumping tests, there is hydraulic connection between the different boreholes and the observed EC horizons, but it is not very prominent. There is no clear connection between the high EC and RQD data except in borehole S24, where the upper surface of high EC horizon (72 m hole length) is located in the vicinity of the fractured bedrock zone (63.75–68.30 m hole length), just below it. This is the only borehole from which a possible path of high EC water migration can be identified based on the drilling log. In other boreholes where high EC has been detected, no clear migration route can be interpreted. For instance, despite the elevated EC in boreholes S1, S7 and S8, the borehole log seems to be rather intact (Fig. 9), whereas, in boreholes S75 and S76 the bedrock is rather fractured, but the EC levels are low. Furthermore, based on the results of geophysical measurements (electromagnetic VLF-R) done by Pasanen and Lerssi (2018), the fracture zones observed (Fig. 4) do not fall in the same places as the fractured zones detected based on the RQD data (Fig. 9). Several of the boreholes (S23, S81, S85, S91, and S92) pierce the possibly interpreted southern fracture zone deeper down (considering the decline of the boreholes mainly towards south-east), but only few of those boreholes have high EC (S91 and S92). The fracture zone interpreted in the northern part of the study site possibly runs through boreholes S75 and S76 (Fig. 4), where no water of high EC has been detected. As said previously, the permeability of many fractures was observed to be lower than expected based on the RQD value and in many places sampling depth needed to be changed and/or the pumping rate and time needed to be adjusted. This derives from the fact, that due to low or non-existent primary (matrix) porosity crystalline igneous and metamorphic rocks such as those in the study site can be considered as virtually impervious (Olofsson, 1994; Healy and Cook, 2002). The permeability, hydraulic connections and flow pathways comprise typically connected, discrete fractures and other discontinuities, of which hydraulic connectivity can vary considerably even over relatively short distances. The flow and transport are typically highly anisotropic, which means that they are largely determined by the distribution of interconnected fractures and their strike and not so much on the direction of hydraulic gradients (Day-Lewis et al., 2017). Moreover, in the glaciogenic areas, such as the study site, the weathered zone to enable infiltration into the bedrock has been eroded or is very thin and the recharge conditions have changed also due to the glaciogenic rebound of the crust (e.g. Zhang and Sanderson, 1995; Shingal and Gupta, 1999; Aydin, 2001; Banks et al., 1992; Eronen, 1994). Usually, the fresh groundwater layer occurs down to 50–200 m of depth below the highest Litorina shoreline and is usually found in shallower depths near coast than inland (Lahermo and Lampén, 1987). However, the thickness and depth of the freshwater layer depend largely on local topography, the thickness and composition of the overburden, and the structure and hydraulic conditions within the bedrock. For instance, in the reference site of Parainen (Fig. 1), small coastal island, the freshwater layer continues down to 490 m of depth which indicates effective infiltration along subvertical fracture zones (Nurmi et al., 1988). In contrast, at the Syväjärvi site the freshwater layer extends only down to 40–120 m of depth. Similar shallow depths are met also in Olkiluoto site (Fig. 1, Pitkänen et al., 1999). In both, Syväjärvi and Olkiluoto site, the depths, concentrations, and EC levels also fluctuate a lot within a relatively small area, indicating that the different water types exist localised and might be restricted to less conductive or dead-end fractures. Therefore, it is likely, that though the brackish water was able to infiltrate into the bedrock due to increasing hydraulic gradient during the deglaciation, the formerly open fractures and permeable zones have again lost their hydraulic active features for the freshwater to infiltrate deeper into the bedrock.

Water of high EC probably flows in the cracks, but its flow area as well as flow velocities can be considered small except for the fracture zone observed in borehole S24. Based on these observations, as well as on the basis of the large depth level fluctuations of the EC horizons, it is considered unlikely that the high electrical conductivity water is associated with the fracture zones. However, the places where fractures were observed were mainly in areas without any boreholes, and therefore the results will not rule out the possibility that the brackish groundwaters could not exist also there. Furthermore, the boreholes are rather shallow (exceeding max. 250 m of depth) and the salinity might increase further down. Most likely the fresh surface water infiltrating at the surface has gradually displaced brackish and saline groundwater in the bedrock at shallower depths due to land uplift and changing hydraulic gradients.

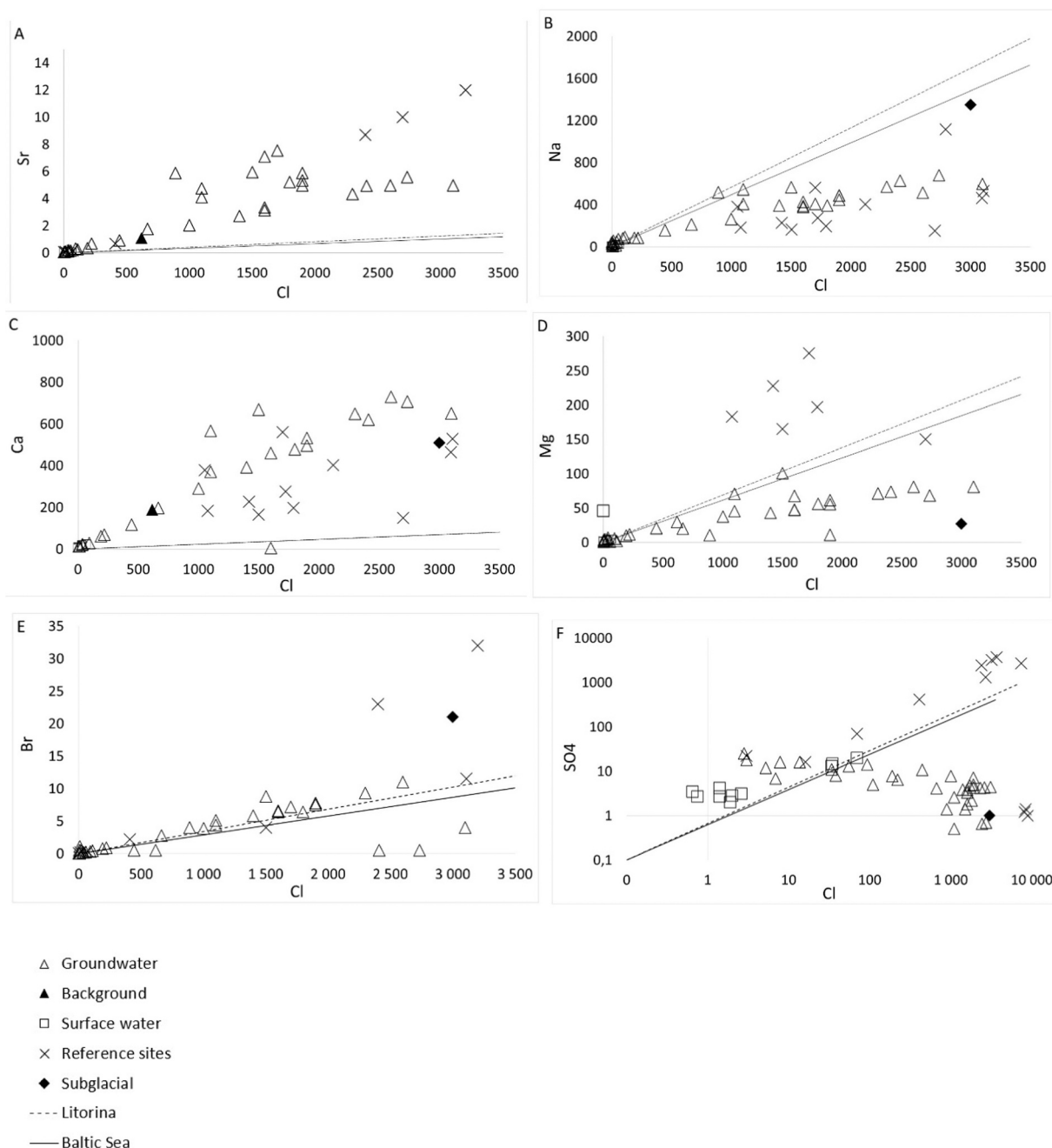
## 5.2. Hydrogeochemical evolution

In Northern Europe groundwaters with marine origin tend to be located around the coastal areas of the Baltic Sea (e.g. Lindewald, 1985; Lahermo and Kankainen, 1986; Nordstrom, 1986) and most of the saline wells have been observed below the highest Litorina shoreline (Hyypä, 1984; Lahermo and Lampén, 1987; Nurmi, 1988; Pitkänen et al., 1999; Smellie et al., 2014; Kietäväinen, 2017), the former Baltic Sea stage which preceded the present Baltic Sea stage about 7500–2500 years ago. Most of these boreholes extent deeper (e.g. 2.5 km in Outokumpu, Kietäväinen, 2017) within the bedrock and their chemical and isotopic characteristics are beyond the characteristic of the Syväjärvi site (e.g. TDS > 41,000 mg/l in Liminka, Nurmi et al., 1988).

As seen in Table 1, the reason for the high EC of the deep groundwater in boreholes across the anomalous line is the elevated anion



(Cl, Br) and cation (Na, Ca, Mg, K and Sr) concentrations. Concentrations of cations and anions in the mentioned boreholes were abnormally high suggesting first the contamination of old brines or ancient sea water. One of the hypothesis for the origin of the salinity was that the elevated concentrations resulted from solid compounds leaching from the fractures. In fact, the solid geochemistry from the sampling campaign of 2017 (Turunen et al., 2017) indicates the presence of sulphidic metals and metalloids (e.g. Cu, Zn, As) which cannot be related to sea water influence but to ore geology and/or mineral dissolution in fractures. However, the bedrock in Syväjärvi site does not contain minerals with Cl and Br as major or trace elements and their concentrations cannot therefore be influenced by mineral dissolution. On the other hand, due to the same reason, and the fact that both are chemically conservative



**Fig. 10.** The ratios of (a) Sr/Cl, (b) Na/Cl, (c) Ca/Cl, (d) Mg/Cl, (e) Br/Cl, and SO<sub>4</sub>/Cl of the Syväjärvi study site, and reference sites (from Hyypä, 1986, Nurmi et al., 1988 and Pitkänen et al., 1999) in relation to Litorina and Baltic Sea reference values (from Pitkänen et al., 1999). The surface waters are plotted on the diagrams but plot on the minimum corner of the X and Y axis due to very low concentrations. The concentrations of SO<sub>4</sub> are in logarithmic scale.

elements, they can be used as a tracer for the origin of the salinity in this study. When plotting the Br/Cl ratio with reference values of Litorina and Glacial melt water end members (Fig. 10e), the results of this study plot nicely along the mixing line. In contrast, the concentrations of Ca and Sr are strongly enriched and Na, Mg and SO<sub>4</sub> concentrations depleted relative to sea water (Fig. 10a, b, c, d, f), which indicates a significant saline source other than pure sea water. The ratios are similar to those found in brackish groundwaters of the Olkiluoto site (Pitkänen et al., 1999). The depletion of Mg in comparison to sea water (both Litorina and modern Baltic Sea in Fig. 10d) could indicate incorporation of Mg into the secondary minerals such as chlorite and other hydroxyl silicate (Edmunds et al., 1987; Fritz and Frape, 1982) or to montmorillonite (Hounslow 1995). Groundwaters of the Syväjärvi site are enriched in Ca compared to sea water (Fig. 10c). This reflects a source for Ca within the bedrock as Ca is assumed to precipitate as calcite in fractures. Sr follows similar trend as Ca, which is expected since they belong to the same alkali earth group. However, the trend is not as linear with Sr than with Ca. This could derive from the abundance of Sr-bearing pegmatites, k-feldspar and muscovite in some boreholes (Ahtola et al., 2015).

Many of the above-mentioned reference sites below the highest Litorina shoreline have distinct “Litorina layer” with elevated SO<sub>4</sub> concentrations, which is missing from the Syväjärvi site. The mismatching signature for SO<sub>4</sub> could be explained by sulphate reduction. The SO<sub>4</sub>/Cl mass ratio can be used to indicate sulphate reduction (Morris and Riley, 1966; Griffioen et al., 2013). Ratios which are lower than sea water ratios (0,14) could indicate sulphate reduction, whereas the ratios above 0,14 would indicate sulphate addition e.g. due to anthropogenic activities (fertilisers etc) or pyrite oxidation. The samples with highest salinity have SO<sub>4</sub>/Cl mass ratios below that of sea water, which could in fact indicate sulphate reduction. However, the sulphate concentrations of this study (max. 25 mg/l, Table 1) are significantly below the reference concentrations of the Litorina Sea (890 mg/l, e.g. Pitkänen et al., 2004; Gimeno et al., 2008). Pitkänen et al. (2004) estimated, that the sulphate reduction of the Litorina seawater would have decreased the initial sulphate concentrations only by 7–10%. When comparing the results with the results of other studies along the Fennoscandian shield (e.g. Pitkänen et al., 1999, 2004 and Gimeno et al., 2008), the SO<sub>4</sub> concentrations of groundwaters having Litorina origin have been around 500 mg/l. Furthermore, the highest sulphate concentrations of this study were detected in boreholes with lower salinity, including Cl, which also excludes the marine origin for sulphate. Other explanation for the missing sulphate could be mixing with pre-Litorina SO<sub>4</sub>-poor brackish groundwater and/or by an earlier uplift from the Baltic Sea above the Litorina stage shoreline, as due to higher salinity of sea water than of groundwater, it should have been able to infiltrate into the bedrock by density turnover (Pitkänen et al., 1994, 1996 and 1999). The Syväjärvi site is located on the edge of the highest Litorina stage shoreline (GTK, Åberg, 2013, 2013), and therefore earlier uplift could explain the missing SO<sub>4</sub>. In fact, in Olkiluoto site similar layer of bedrock groundwater without SO<sub>4</sub> have been interpreted to originate from mixing of glacial melt water with pre-Litorina, brackish subglacial groundwater, which could be also the background for the brackish groundwaters in Syväjärvi site.

### 5.3. Isotopic evolution of water

Besides salinity, deep groundwaters and specifically the shield brines, often have distinct H and O isotopic composition plotting above the global meteoric water line (GMWL, Craig, 1961, Frape et al., 2003), like in the reference site of Outokumpu in Eastern Finland (Kietäväinen, 2017). Since the stable isotopic composition in all of the studied boreholes plot mainly on the local meteoric water line (LMWL), or below it, there is no clear evidence of hydrothermal, magmatic or metamorphic origin for the groundwater i.e. water-rock interaction has not strongly affected the salinity. In fact, based on the stable isotopes the groundwater resembles present precipitation and local groundwater composition. There are small variations in isotopic composition of groundwater between sampling events, but the variation is too narrow to be influenced by the seasonal variations and it seems that there is not strong hydraulic connection to surface waters at the site. The isotopic composition indicating meteoric origin could be explained by the fact that even a small amount of ancient brine or saline groundwater mixing with fresh modern groundwater layer would greatly affect the water geochemistry, while the isotopic composition would stay immutable. Furthermore, the pumping and slug tests indicate low hydraulic conductivity of the bedrock, which prevents the upper fresh groundwater horizon mixing with the brackish groundwater horizon deeper down.

In comparison to references of Litorina and Baltic Sea isotope composition, the Syväjärvi isotope composition is closer to the reference of subglacial groundwater and very close to the background isotope composition of the region (Figs. 7 and 8). On the other hand, the isotopic composition at some of the reference sites (e.g. Kerimäki, Olkiluoto and Parainen) is not very different from the Syväjärvi site (Figs. 7 and 8). The isotopic composition of the glacial melt water would have lower O isotopic values than modern precipitation (<sup>18</sup>O –22‰ and –13,43‰, respectively) (Kietäväinen et al., 2013), which is not the case at the Syväjärvi site. According to the modelling of Pitkänen et al. (1999), the isotopic composition of the subglacial water is about <sup>18</sup>O –10‰ and the mix of the glacial melt water and subglacial water would range between <sup>18</sup>O –13 — –16‰. When considering the modelled concentrations of Cl (1500–2000 mg/l) and SO<sub>4</sub> (<1 mg/l) of the mixture it seems that the brackish groundwater of the Syväjärvi site could in fact be a mixture of glacial melt water and subglacial water. Since the groundwater samples of the Syväjärvi site have linear behaviour regarding especially Ca, Na and Mg (Fig. 10), it seems that their concentrations are in fact controlled mainly by mixing.

There is a difference in <sup>87</sup>Sr/<sup>86</sup>Sr ratios between deeper, more saline groundwater samples and fresher groundwater and surface waters. The <sup>87</sup>Sr/<sup>86</sup>Sr ratios get lighter as the salinity and depth increases. The isotope ratios are clearly heavier than the ratios of the Sea water (~0709) (Åberg and Wickman, 1987; Löfvendahl et al., 1990; Peterman et al., 1999; Negrel et al., 2005) which suggests a radiogenic Sr source. Furthermore, the trend between Cl and Sr content diverges from the sea water dilution line, which would also reflect Sr enrichment related to water-rock interaction instead of sea water origin (Frape et al., 1984; Bottomley et al., 1994). The abundance of pegmatites, k-feldspar and muscovite in local bedrock (Ahtola et al., 2015) could explain the heavier isotope ratios in groundwater due to their tendency to have high Rb/Sr ratios. According to Martikainen (2012), the Rb content of the Syväjärvi deposit

is on average 437 mg/kg and Sr 27 mg/kg. This would also support the subglacial groundwater as the origin for the brackish groundwater of the site.

As expected, the Syväjärvi lake sample had very high tritium content, indicating young age and short residence time. The sample from 72 m of depth in borehole S24 contains a moderate amount of tritium, indicating a considerable proportion (up to 40%) of young water component (estimated residence time of >42 years). In borehole S38, both samples contained very low amounts of tritium and therefore young water component. The sample from borehole S26 and background (RA179) did not contain any detectable amount of tritium, therefore the young water content is estimated to be minor. The radiocarbon results indicate considerable ages for groundwaters at the site. The estimated ages range from 2000 to 4000 years for boreholes S24 and S38 (upper part), 6000 to 8000 years for boreholes S38 (deeper part) and background (RA179), and 8000 to 10,000 years for borehole S26. As the samples from borehole S24 and S38 contained tritium, it is assumed that the younger  $^{14}\text{C}$ -DIC age results from mixing with young water component and there might be a hydraulic connection to the surface, or the mismatching residence time results from mixing of the water body while sampling. The estimated  $^{14}\text{C}$ -DIC ages of the brackish groundwater samples are concurrent with the assumption that the salinity would derive from prior to Litorina stage of the Baltic Sea up to 10,000 years ago. This is also supported by the modelled carbon isotope signature ( $\delta^{13}\text{C} \approx -17 \text{ — } -22\text{‰}$ ) of the mixture of glacial melt and subglacial waters by Pitkänen et al. (1999).

The  $\delta^{13}\text{C}$ -DIC isotope data can be used to infer the sources and evolution of dissolved inorganic carbon in the investigated groundwater (Clark, 1997). In crystalline bedrock, groundwaters have generally similar  $\delta^{13}\text{C}$  as that in soil  $\text{CO}_2$  (about 23‰, Aravena and Wassenaar, 1993). The partly enriched values of  $\delta^{13}\text{C}$ -DIC and considerable DIC-uptake by dissolution (DIC up to 3.5 mmol/L) in boreholes background and S38 (upper part) indicate exchange with inorganic carbon of the overburden and/or the bedrock. In contrast, very low  $\delta^{13}\text{C}$ -DIC values of the other boreholes (S38 deeper part, S24 and S26), show only some secondary effects related e. g. to rock-water interactions, or carbon isotope exchange. This would support also the other results (e.g. Ca and Sr enrichment in comparison to the sea water) indicating that the origin for the salinity cannot be sea water, but more likely water rock interaction.

#### 5.4. Conceptual model for groundwater evolution at the Syväjärvi site

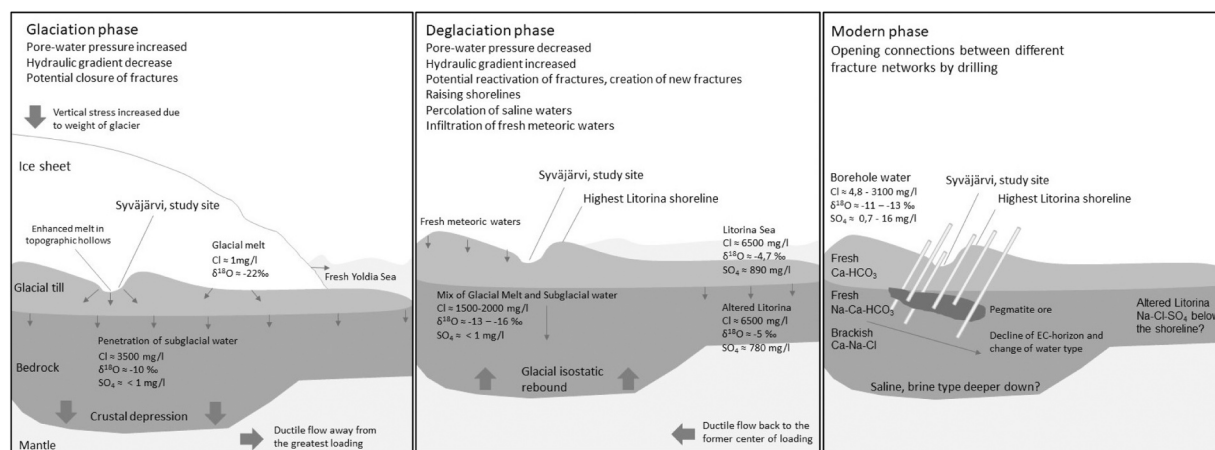
The schematic in Fig. 11 presents the bedrock groundwater evolution of Syväjärvi study site from the last glaciation until present day. The evolutionary path is based on the finding of this study and the comparison made with several other studies (the reference sites presented throughout this paper and in Fig. 1). The changes in climate play a significant role in the paleohydrogeological evolution of the Syväjärvi site which has gone through several glaciations and interglacials during the Quaternary period. As presented in earlier sections, the uppermost groundwater within the bedrock represents the modern, dilute  $\text{HCO}_3$  type meteoric groundwater, which occurs down to 40–120 m of depth. Below the fresh groundwater layer there is a brackish Ca-Na-Cl type groundwater. Unlike in many other sites within the coastal areas of the Baltic Sea a typical Litorina  $\text{SO}_4$  rich layer is missing at the Syväjärvi site and the main endmembers of the brackish groundwaters identified within this study are the subglacial water and glacial melt water. The salinity of the Syväjärvi groundwater is also lower than in reference sites of this paper (Fig. 1). The results of this study did not support the hypothesis that water-rock interaction and shield brines would have greatly affected the evolution of groundwaters of the site and it is therefore left out from this model. However, as the boreholes are rather shallow and brines are usually met in depths of 1–2 km or more (Nurmi et al., 1988), their existence deeper down and cannot be ruled out.

During the glaciation phase the vertical pressure increased, and hydraulic head decreased in bedrock due to weight of the glacier (Fig. 11). The glacial melt water was able to infiltrate the bedrock especially in topographic hollows and mix with the brackish subglacial groundwater due to high head pressure of the ice load (e.g. Pitkänen et al., 1999, Hutri 2007). As the glacier started to retrieve the pore-water pressure decreased and hydraulic head increased due to glacial rebound. As the land uplifted and shorelines retrieved inland the hydraulic head field changed again and the saline groundwaters percolated deeper, letting the modern fresh meteoric water to infiltrate despite the density turnover between these two distinct water types. As the typical  $\text{SO}_4$  Litorina layer is missing, it is likely that Syväjärvi is located above the highest Litorina shoreline, as the saline sea water should have been able to intrude and mix with fresher groundwater.

## 6. Conclusions

As in several previous studies worldwide (e.g. Hyyppä, 1984, Lahermo and Lampén, 1987) the change in Syväjärvi anomalous EC horizon and salinity is abrupt, anomalous EC varying between 40 to 120 m of depth depending on the borehole. As the salinity of the background sample located 2 km from the site was also elevated, it seems that the brackish groundwater does not exist as pockets only on the study site but as a continuous formation in a wider region, most likely all the way to the coast of the Baltic Sea.

The Syväjärvi brackish groundwaters are a mixture of two to three end-member water compositions. The original hypothesis was that the brackish groundwater has an origin of ancient sea water and/or brine. However, since only a few of the groundwater samples lie above the FMWL line and isotopic ratios are mainly congruent with the local groundwater, there is no indication of strong water-rock interaction in higher temperatures nor considerably longer mean residence time and therefore brine cannot be the main reason for the salinity. Furthermore, the maximum  $\text{SO}_4$  concentrations were too low for sea water and found solely in boreholes with modern fresh water, and/or nearby black shist occurrences, which rules out also the Litorina end member. On the other hand, the Syväjärvi brackish groundwaters have similar characteristics (Cl,  $^{18}\text{O}$ , lack of  $\text{SO}_4$ ) than the groundwater classified as a mixture of glacial melt waters and pre-Litorina subglacial groundwaters detected in the Olkiluoto site (Pitkänen et al., 1999 and 2004). It is likely that after the retreat of the icesheet, the diluted glacial melt water infiltrated and mixed with the brackish subglacial groundwater resulting in the current groundwater concentrations of the Syväjärvi site. As mentioned in the introduction, the interpolation of the highest



**Fig. 11.** Schematic of the bedrock groundwater evolution of Syväjärvi study site from Glaciation phase until present day. The figure is not to scale and is illustrated based on the conclusions made within this study. The reference concentrations of Glacial melt, subglacial, altered Litorina and Litorina waters are from Pitkänen et al., 1999. (Figured altered from Pitkänen et al., 1999 and Hutri 2007)

Litorina shoreline in the region has been difficult, and the accuracy of the modelling might deviate even hundreds of metres either inland or towards the sea (Åberg, 2013). Therefore, the boreholes and the saline horizons may also lie above the Litorina shoreline. The earlier up-lift of the Syväjärvi site from the Litorina Sea is supported also by the age determination results indicating residence times of up to 8000–1000 years BP.

As said, the boreholes of the site are shallow, and there is clear indication (e.g. stable water isotopes, tritium and hydraulic testing) of modern water input in brackish groundwaters. It is very likely that the salinity of the groundwaters will increase and isotope composition will change with depth, as mixing with modern meteoric waters decreases. Further studies on groundwater could be conducted when the mining company opens the mine and excavates the open pit which enables studying the groundwater layers deeper in the bedrock. This could enable finding the “true” end member compositions of brackish pre-Litorina groundwater and/or brine.

The salinity affects the water quality and treatment possibilities of the future mine. Although a natural characteristic of the local groundwater, high salinity should be removed before discharging the water to the environment to avoid has not been published before or currently being considered for publication elsewhere. Some of the results of the study have been published as customer reports (both public and confidential), to which the manuscript refers where applicable. The submitted publication is approved void any adverse impact on ecology, but possibly also for reuse purposes of water. The mining company received their environmental permit for the operation in the beginning of the 2022. In the permit the permitting authority had set a limit for sulphate in discharge, but not for chloride. The missing limit for Cl was based on the fact that  $\text{SO}_4$  and Cl tend to correlate in groundwaters originating from Litorina stage. According to the results of this study, the salinity of the groundwaters of the Syväjärvi site seem not to originate from the Litorina stage and as the Cl and  $\text{SO}_4$  do not to correlate, the  $\text{SO}_4$  concentrations cannot indicate occurrence of Cl. However, due to high concentrations in groundwater, the environmental permit requires the mining company to also monitor the Cl concentrations in waters, and if elevated, the limit might be set also for Cl in future.

#### CRediT authorship contribution statement

**Lukkarinen Vaula:** Writing – review & editing, Writing – original draft, Visualisation, Software, Methodology, Investigation. **Turunen Kaisa:** Writing – review & editing, Writing – original draft, Visualisation, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Korkka-Niemi Kirsti:** Validation, Supervision, Data curation.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests and geochemistry results indicate long residence times (up to 10,000 years BP), but no strong financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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## Appendix 1. The geochemistry of the solids in water in 2017 sampling campaign (Modified from Turunen et al., 2017)

Borehole		S40	S38	S24	S1	S7	S8
Fe	mg/kg	57,300	100,000	57,700	51,100	63,100	78,100
Al	mg/kg	17,900	39,100	21,500	31,900	34,000	32,500
Ca	mg/kg	14,700	16,100	19,200	34,700	30,700	37,500
Mg	mg/kg	7230	18,600	11,100	21,500	19,900	21,000
K	mg/kg	5530	12,200	5450	5790	8540	11,000
Na	mg/kg	2060	2300	1740	3970	4220	5850
Ti	mg/kg	1230	738	2900	2250	1090	2860
P	mg/kg	1070	1810	1490	1600	1440	1630
Mn	mg/kg	706	1170	581	1320	1300	1070
Li	mg/kg	297	130	90	437	615	252
Cr	mg/kg	114	154	122	138	152	135
Sr	mg/kg	46	122	126	159	188	238
V	mg/kg	92	120	93	141	138	137
Be	mg/kg	7,8	3,4	5,2	147	12	5,3
U	mg/kg	4,1	9,0	9,1	32	14	10
B	mg/kg	< 5	8,3	6,5	9,4	9,3	15
Th	mg/kg	3,1	18	7,9	3,4	3,5	3,6
Se	mg/kg	1,2	2,8	2,9	1,7	1,5	1,6
Bi	mg/kg	0,3	0,9	0,3	1,5	1,6	0,5
Tl	mg/kg	0,4	0,5	0,3	0,2	0,4	0,4
S	mg/kg	2180	1640	806	587	1950	900
Zn	mg/kg	463	1420	145	217	335	594
Cu	mg/kg	140	251	189	390	862	403
Ba	mg/kg	130	460	138	202	298	364
Ag	mg/kg	8,6	9,0	10	13	471	2,6
As	mg/kg	96	44	45	37	48	83
Co	mg/kg	13	23	14	16	23	15
Ni	mg/kg	60	91	65	53	71	70
Pb	mg/kg	8,3	29	13	64	17	8,0
Rb	mg/kg	35	64	31	23	44	47
Mo	mg/kg	11	3,8	8,5	2,8	1,4	66
Cd	mg/kg	0,7	0,4	0,2	1,2	1,0	0,3
Sb	mg/kg	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

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