



Research papers

Hydrogeochemical characterisation of the groundwater in the crystalline basement of Forsmark, the selected area for the geological nuclear repositories in Sweden

Maria J. Gimeno^{a,*}, Eva-Lena Tullborg^b, Ann-Chatrin Nilsson^c, Luis F. Auqué^a, Lino Nilsson^d

^a Earth Sciences Department, Sciences Faculty, University of Zaragoza, Pedro Cerbuna, 12, Zaragoza E-50009, Spain

^b Terralogica AB, Östra Annedärrsvägen 17, Gråbo SE-443 72, Sweden

^c Granitvägen 45, Täby SE-183 63, Sweden

^d Swedish Nuclear Fuel and Waste Management Co. (SKB), Box 3091, Solna SE-169 03, Sweden

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ABSTRACT

Numerous groundwater analyses from the crystalline bedrock in the Forsmark area have been performed between 2002 and 2019, together with thorough geological, geophysical, and hydrogeological studies, within the site investigations carried out by the Swedish Nuclear Fuel and Waste Management Company. The groundwater samples have been taken from boreholes down to ≈ 1000 m and the analysis include major- and trace-elements, stable and radiogenic isotopes, gases and microbes. The chemical and isotopic composition of these groundwaters evidences the presence of non-marine brackish to saline groundwaters with very long residence times (many hundreds of thousands of years) and a series of complex mixing events resulting from the recharge of different waters over time: glacial meltwaters, probably from different glaciations of which the latest culminated some 20,000 years ago, and marine waters from the Baltic starting some 7000 years ago. Later, meteoric water and present Baltic Sea water have recharged in different parts of the upper 100 m. These mixing events have also triggered chemical and microbial reactions that have conditioned some of the important groundwater parameters and, together with the structural complexity of the area, they have promoted a heterogeneous distribution of groundwater compositions in the bedrock. Due to these evident differences in chemistry, residence time and origin of the groundwater, several groundwater types were defined in order to facilitate the visualisation and communication. The differentiation (linked to the paleohydrological history of the area) was based on Cl concentration, Cl/Mg ratio (marine component), and $\delta^{18}\text{O}$ value (glacial component).

The work presented in this paper increases the understanding of the groundwater evolution in fractured and compartmentalised aquifers where mixing processes are the most important mechanisms. The model proposed to characterise the present groundwater system of the Forsmark area will also help to predict the future hydrogeochemical behaviour of the groundwater system after the construction of the repositories for the nuclear wastes.

1. Introduction

The radioactive waste programme of the Swedish Nuclear Fuel and Waste Management Co. (Svensk Kärnbränslehantering AB; SKB) includes the construction of a deep geological repository for the final disposal of the spent nuclear fuel (SFK) and the extension of the already existing repository for short-lived low and intermediate level radioactive wastes known as the SFR (e.g. SKB, 2008; SKB, 2013; SKB, 2022). Both repositories will be located in the Forsmark area (Fig. 1) on the Baltic

coast, 160 km north of Stockholm, the former in the Forsmark inland site and the latter in the SFR site. In order to characterise the area, thorough multidisciplinary site investigations have been ongoing since 2002. These investigations include geology, hydrogeology, hydrogeochemistry, ecology, and studies of thermal and mechanical properties of the bedrock (SKB, 2008; SKB, 2013; Ström et al., 2008; Andersson et al., 2013; and references therein).

Among all these disciplines, the hydrogeochemical characterisation of the groundwaters is one of the most important. The understanding of

* Corresponding author.

E-mail address: mjgimeno@unizar.es (M.J. Gimeno).

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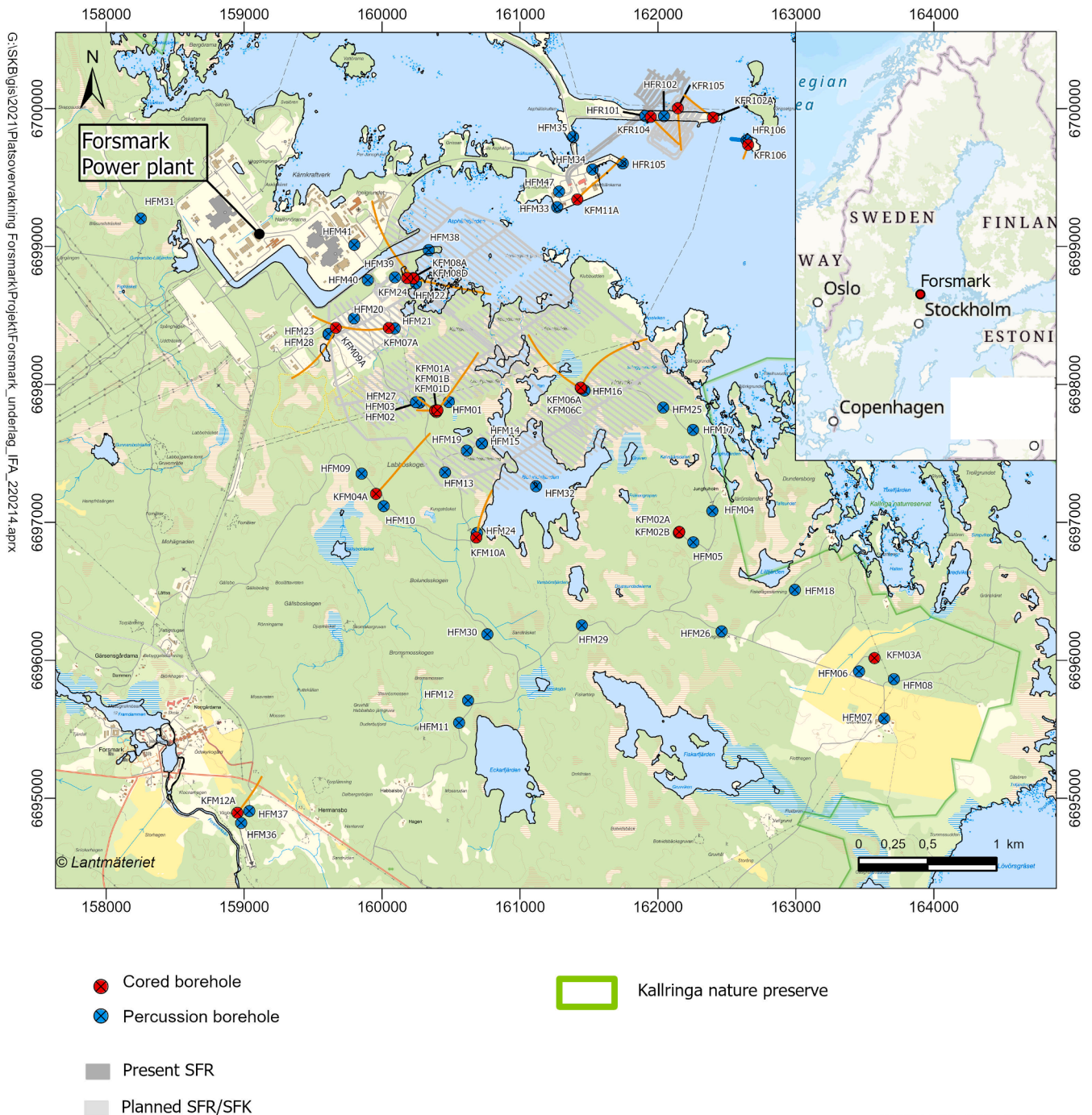
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the present, still fairly undisturbed, state of the groundwater system is fundamental to ensure suitable conditions of the candidate area. Moreover, it is necessary to predict the expected evolution of these groundwaters and its effect on the future performance of the repositories. The hydrochemical conditions that are potentially harmful to the safety of the repositories are those that affect the possible release and transport of the radionuclides to the biosphere. The knowledge of the paleohydrogeology of the site and the information on the residence times are of the utmost importance for the characterisation of both, the present and the future groundwater conditions.

As already established by previous authors (Follin et al., 2008; Hunter et al., 2008; Laaksoharju et al., 2008a, b; Tullborg et al., 2008;

Drake and Tullborg, 2009; Pitkänen et al., 2014; POSIVA, 2022), the northern and coastal location of the study area has conditioned a particularly complicated paleohydrological history, delimited by the existence of glaciations and marine transgressions (and their effects on meteoric water recharge; e.g. Edmunds, 2001) over the initial saline groundwaters present in the bedrock. The result has been a complex succession of water recharge and groundwater mixing events that have had important effects on the groundwater hydrogeochemistry. This kind of events have also been found in Olkiluoto, Finland (on the opposite side of the Baltic; Pitkänen et al., 2004) and in the Laxemar-Simpevarp-Äspö area, 500 km south of Forsmark in the Swedish coast (Gimeno et al., 2014). One of the characteristic features in all these systems is the



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Fig. 1. Map showing the entire Forsmark area and the location of the boreholes in the two sites Forsmark inland and the SFR.

important influence of Holocene marine recharge, which, in the case of the Äspö laboratory and the SFR, includes also the recharge of recent Baltic Sea water.

There are other groundwater systems with similar characteristics but located inland in the Canadian and the Fennoscandian Shields (e.g. Clark et al., 2000; Douglas et al., 2000; Gascoyne, 2004; Greene et al., 2008), and also in the sedimentary Cambrian-Vendian and Ordovician-Cambrian aquifers in the Baltic Basin, near the Baltic Sea (e.g. Raidla et al. 2009; Pärn et al., 2019). However, no Holocene marine recharge has occurred in these areas, only the mixing of the saline groundwaters present in the bedrock before the last glaciation (possibly influenced by much older marine waters), with glacial and/or meteoric water.

Many studies treating the hydrogeochemistry of the groundwaters in the Baltic area have been presented as technical reports over the years (see Pitkänen et al., 1999; Pitkänen et al., 2001; Pitkänen et al., 2004; Pitkänen et al., 2022; Laaksoharju et al., 2008c; Laaksoharju et al., 2009; Smellie et al., 2008; Pitkänen et al., 2014; Gimeno et al., 2008; Gimeno et al., 2009; Gimeno et al., 2011; Nilsson et al., 2011; Nilsson et al., 2013; POSIVA, 2022), and some scientific papers have also been published (Smellie et al., 1995; Gimeno et al., 2014; Gómez et al., 2014; Mathurin et al., 2012a; Mathurin et al., 2012b). The Forsmark area, has been particularly well studied and the hydrogeochemical results of the site investigations up to 2007 in Forsmark and up to 2011 in the SFR are available in technical reports (Laaksoharju et al., 2008c; Nilsson et al., 2011) and in several scientific papers (Auqué et al., 2008; Hallbeck and Pedersen, 2008a; Laaksoharju et al., 2008a, b; Rönnback et al., 2008; Ström et al., 2008; Waber and Smellie, 2008). After the site investigations, the monitoring of the groundwater chemistry has continued in both sites which has increased the amount of good quality data from new borehole sections as well as from already existing sections. Therefore, the main objective and contribution of this paper is the integration of the results obtained during the site investigations in the two sites (Forsmark inland and SFR) and the evaluation of the new data with the final purpose of the establishment of a common hydrogeochemical conceptual model for the entire Forsmark area.

The study focuses on the influence of several known mixing events and their effects on the present groundwater hydrochemistry. Especially important is the increased recognition of glacial meltwater injection to considerable depths, which has favoured the subsequent intrusion of brackish marine water. All these mixing events have in turn induced water-rock interactions in the mixed waters which affect some of the main hydrogeochemical parameters of the groundwater system (e.g. the carbonate and the redox systems). Mixing and reaction determine the resulting groundwater compositions and the understanding of the balance between these two processes is necessary to be able to predict the future hydrochemical evolution of the groundwater. A thorough characterisation of the associated water-rock interaction processes and their extension and importance as controlling factors, will be addressed elsewhere.

Apart from the main objective of this paper to present the integrated hydrogeochemical conceptual model for the groundwaters of the Forsmark area, there are two other important contributions: 1) the amount of high-quality groundwater analyses and the long sample series which makes the presented dataset unique and very useful to, e.g., verify results and assumptions made in other groundwater systems affected by mixing events (like those mentioned in the Canadian Shield) and to increase the understanding of the paleohydrogeology of the Baltic area; and 2) the methodology used in this study can be applied in analogous crystalline bedrock sites elsewhere which are considered for the construction of deep geological repositories (for e.g. nuclear wastes and CO₂ storage) and also in the study of the groundwater evolution in sedimentary aquifers of the coastal Baltic areas, importantly affected by continental glaciations and sea transgressions that control their use as drinking water supply.

2. General description, geological, hydrogeological and paleohydrogeological background

Fig. 1 shows the Forsmark area, where the two sites are located, and the relevant boreholes for the groundwater evaluation. The area is situated below the highest shoreline from the last glaciation, and has a flat topography. A general description of the area is provided elsewhere (SKB, 2008; SKB, 2013). A summary of the main geological, hydrogeological and paleohydrogeological characteristics is presented in this section and in Section SM1 in the [Supplementary Material](#) (henceforth Supp. Mat.).

2.1. Geology and hydrogeology

Sweden is part of the Baltic shield and, specifically, the Forsmark area is part of the Svecofennian province. The bedrock consists largely of crystalline rocks of granitic to granodioritic composition formed and affected by deformation under amphibolite-facies conditions 1.9 to 1.8 Ga ago (Stephens, 2008; Stephens, 2010; Curtis et al., 2011; Fig. S1; Supp. Mat.). During the Palaeozoic this crystalline basement was covered by several hundreds of meters of sediments including sandstones, organic-rich shales and limestones and, on top of that, several kilometers of molasse sediments from the Caledonides (Cederbom et al., 2000; Fredén, 2002; Calner and Ahlberg, 2011). After the denudation of these deposits, the bedrock surface became covered by several meters of glacial (till) and post-glacial deposits containing limestone fragments (up to 20 % volume; Hedenström and Sohlenius, 2008).

Steeply dipping WNW-ESE striking ductile and brittle regional structures dominate the area (Stephens et al., 2008; Stephens et al., 2015) and they are regarded as significant recharge/discharge features, e.g. the Forsmark-, Eckarfjärden- and Singö-zones (FDZ, EDZ and SDZ) as well as Zone 8 bordering the SFR site (Figs. S1.1 and S1.2; Supp. Mat.). Perpendicular to these are the hydraulically important gently dipping ENE to NNE fracture zones from which the most relevant are zones A2-F1, in the Forsmark inland, and H2, in the SFR site (Fig. S1.2; Supp. Mat.). The zones A2-F1 split the bedrock within the Forsmark inland candidate site into two blocks referred to as hanging and footwall bedrock, the first one characterised by a series of outcropping gently dipping fracture zones of high transmissivity (similar to zones A2-F1) and the second, by a significant difference between the upper very transmissive 150–200 m and the low transmissivities at greater depth. This difference facilitates the flushing out of shallow bedrock water. In the SFR area, the most important gently dipping zone is H2 which dips to the SSE and runs in the SE-NW direction between 50 to, at least, 200 m depth. This zone acts as a flow pathway with less transmissive bedrock volumes above and below.

2.2. Paleohydrogeology

As indicated above, the crystalline basement was under a thick cover of partly marine sediments during the Palaeozoic and that made recharging groundwaters saline and rich in organic material creating reducing conditions. They might be the origin of the very deep and old waters found in the bedrock of this and other Scandinavian areas. The sedimentary cover remained well into the Tertiary (Lidmar-Bergström, 1996).

During the Quaternary many glacial stages have been recorded (cf. the Marine Isotope Stages MIS sequence; Lisiecki and Raymo, 2005). Periods of temperate conditions, permafrost and glaciations have occurred repeatedly in the Forsmark area also during the last and most well-studied glacial stage (Weichsel). The Weichselian ice cover reached at its maximum some 20,000 y ago into northern Germany. The subsequent deglaciation and complex evolution of the Baltic Sea (cf. Fredén, 2002, and references therein) implicate that recharge to the groundwater has varied in intensity, flow paths and groundwater chemistry over time (Fig. 2).

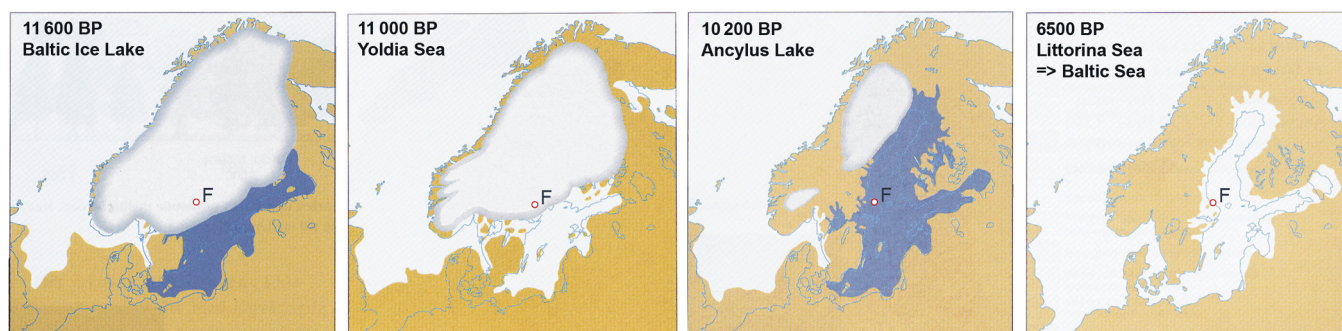


Fig. 2. Map of Fennoscandia illustrating the four main stages since the last glaciation (the Holocene period): the Baltic Ice Lake, the Yoldia Sea, the Ancylus Lake and the Littorina Sea. Fresh water is symbolised with dark blue and marine/brackish water with light blue. The Forsmark area (notated 'F') was probably at or close to the rim of the retreating ice sheet during the Yoldia Sea stage (modified from Fredén, 2002). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Considering these paleo-events, it was expected to find remains of different groundwaters in the bedrock of the Forsmark area: old saline groundwaters, glacial meltwaters, marine waters (Littorina and modern Baltic) and modern meteoric recharge.

Old saline groundwaters. These groundwaters may have been present in the bedrock before the Quaternary glaciations and they were certainly present before the last glaciation (Weichsel) especially in the deeper and less well-connected parts. This type of saline waters (TDS >20 g/L) have been detected in boreholes exceeding some 300 to 700 m depth in other studied areas of Sweden and Finland (cf. Pitkänen et al., 1999; Pitkänen et al., 2004; Laaksoharju et al., 2009). Although with some differences among them (like the total dissolved solids, the SO_4^{2-} contents or the Ca/Na ratios) all these saline waters have a Ca-Na-Cl composition, non-marine signature, and long residence times as revealed by e.g. their ^{36}Cl and He contents (Mahara et al., 2008).

Glacial meltwater. The pattern of glaciations and transgressions/regressions have occurred repeatedly in the past, however, the most evident remains and effects correspond to the last glacial period and the subsequent deglaciation. Due to the pressure from the ice the rock stress was different and fractures that are not transmissive today may have been open and allowed the penetration of large volumes of glacial meltwater through the ice and further into the bedrock fractures. This water was low in $\delta^{18}\text{O}$ (lower than -16‰) due to the cold climate conditions and it has been assumed to be a freshwater with relatively low content of dissolved solids from the interaction with till materials at the base of the glacier.

Littorina Sea water. Due to the presence of the glacial meltwater in the bedrock, during the period when the Forsmark area was covered by the Littorina Sea, density driven intrusion of the brackish Sea water can be assumed. The salinity of the Littorina Sea waters during its maximum was twice as high as the present Baltic Sea. We recognise this water by its relatively high $\delta^{18}\text{O}$ (close to -4‰) and its marine signature in some major components like high Mg, K and SO_4^{2-} and a marine Br/Cl ratio.

Modern Baltic Sea water. The isostatic rebound (ca 7 mm/y at present) has continued to decrease the inflow of Atlantic seawater into the Baltic, decreasing its salinity and producing a regression of the shoreline. Since the investigated SFR site, including the present SFR facility, is located below the sea and the operational tunnels have existed for about 30 years already, it is necessary to consider a drawdown of present Baltic Sea water via the vertical fracture zones. Forsmark inland has been emerged for a long period and therefore, the possibility of finding modern Baltic seawaters in the bedrock is much lower.

Meteoric recharge. The ongoing isostatic rebound results in a regression and allows the recharge of meteoric water through the regolith and further into the shallow fractures of the bedrock in the inland areas. It is expected to be a fresh Na-Ca- HCO_3 water with an environmental isotopic composition like recent average precipitation in the area and a low TDS content.

These five original waters are, therefore, assumed to have been present at the Forsmark area at some stage over the time and they are considered as the end members of the different mixing events (Gimeno et al., 2008; Gimeno et al., 2009; Gimeno et al., 2014; Nilsson et al., 2011; Gómez et al., 2014). The waters have been plotted, for information, in some of the figures included in the sections below. The selected end-member compositions are explained in the Supplementary Material (Section SM2).

3. Materials and methods

A total of 2079 groundwater samples, taken during the years 2002 to 2019, were evaluated for the hydrogeochemical modelling of the Forsmark area. The samples represent borehole sections in 19 core drilled (76 mm) boreholes and 39 percussion drilled (140 mm) boreholes in the Forsmark inland, and 5 core drilled and 3 percussion drilled boreholes at the SFR site (Fig. 1). The samples from the Forsmark inland cover a depth range from the surface to approximately 1,000 m depth (~ -1000 m a.s.l. as the area is quite flat and it is located at the sea level) and the ones from the SFR represent depths down to 400 m. The applied methods for the drilling, sampling and analyses of the water samples is described in detail in Nilsson et al. (2020) and references therein.

The groundwater dataset from Forsmark is unique in the number of analyses covering initial sampling and subsequent yearly monitoring. The time series, spanning over more than a decade, help to show the stability in the groundwater system. The parameters analysed include not only major, minor and trace elements, but also stable and radiogenic isotopes as well as Eh, pH, gases and microbes. All these analyses have made it possible to make a thorough quality categorisation (Smellie et al., 2008; Nilsson et al., 2020) and to exclude less representative samples from subsequent detailed evaluations.

In brief, after a careful sampling procedure, analytical protocols and quality assurance, the chemical and isotopic data are rigorously assessed with respect to their representativity based on a categorisation protocol followed for all the samples. The protocol consists of an evaluation of the degree of accomplishment (from 1 to 5, of which 1 is the best) of the following quality criteria: a) available data for the main major elements and some isotopes, b) charge balance, c) amount of drilling water still present, d) number of samples taken during a sampling campaign and the position of the specific sample in that series, e) the length of the sampled section, f) the sampling method and g) the possible disturbances during sampling. The final quality category for one sample is defined by the worst possible grade obtained for the individual criteria. A more detailed explanation of the categorisation criteria can be found in Nilsson et al. (2020).

In terms of numbers, from the total of 2079 groundwater samples:

- 1265 samples were assigned to quality categories 1 to 4 which means that they are accepted/approved and used in the explorative analyses performed in the following stages of interpretation and modelling. The definition of the water types has been made over this set of samples.
- The 814 category 5 samples are considered representative of the “perturbed groundwater system” and, therefore, they are not used for the definition of the conceptual model. However, they are important when evaluating, for instance, the effect of the drilling or the sampling conditions and their effects on the chemistry of the groundwaters (see Nilsson et al., 2020).
- Only 66 samples were selected to be shown in most of the plots and figures. They correspond to every isolated section sampled for groundwater (15 sections in 13 percussion boreholes and 51 sections in 22 core boreholes). The number of samples from each sampling location varies between 1 (3) to 76 and the reduction to one sample per section was done to avoid biased, misleading and unclear x/y plots and 3D visualisations. Although all the approved groundwater data from one sampling location show similar chemical and isotopic values, the selected sample for each section is usually the one with the higher category grade. Two sections are represented by samples of quality category 5 since there were no better samples available. The chemical and isotopic composition of the 66 samples selected for the plots in this paper is shown in Table S3 (Supp. Mat.).

Explorative analysis is performed on the category 1 to 4 data and consists of a general examination of the groundwater compositions using traditional geochemical approaches, including the use of ion-ion plots and some statistical analyses (PCA using OriginPro 2022®), to describe the main chemical characters, discriminate the different water types and provide an early insight and understanding of the sites. The following step is the interpretation in terms of chemical reactions, residence time and palaeohydrogeological events like mixing. Speciation-solubility calculations have been performed with PHREEQC (Parkhurst and Appelo, 2013) and the WATEQ4F thermodynamic database (Ball and Nordstrom, 2001, with the modifications reported in Auqué et al. (2006).

4. Presentation of the groundwater types

4.1. The criteria for the subdivision

Since the beginning of the site investigations, it was recognised that a separation into groups or water types was necessary to facilitate the description and interpretation of the figures and diagrams showing the chemical and isotopic composition of the groundwaters (Smellie et al., 2008; Laaksoharju et al., 2008c; Nilsson et al., 2011; Mathurin et al., 2012b). The main objective of introducing these water types was to facilitate the visualisation and communication of the differences in chemistry, residence time and, in turn, origin of a complex groundwater system. The approach used to define the water types is the same as in the previous two separate investigations in the Forsmark inland and the SFR sites, but with some modifications to include the particularities of both sites under the same scheme.

Based on the paleoclimatic considerations (cf. section 2.2) it was recognised that Cl, Mg and $\delta^{18}\text{O}$ in the groundwaters were the key parameters to differentiate the various groundwater types:

Chloride is one of the main components in these groundwaters and it represents the salinity evolution in the Forsmark area. As a conservative element, it has also been considered an indicator of the possible mixing lines (related to the input of marine waters or with the existence of very old saline waters).

$\delta^{18}\text{O}$ is another conservative parameter (with the possible exception of nearly stagnant waters with very long residence times) which has helped to differentiate recharge waters from cold or warm periods and to separate the groundwaters affected by glacial influence from the rest.

The dissolved Mg in the groundwaters of the studied area has proved to be a useful indicator of marine waters (Gimeno et al., 2008; Gimeno et al., 2009; Nilsson et al., 2011) with concentrations as high as 300 mg/L for the most saline marine groundwaters, whilst the contents are around 10 mg/L in other waters with the same salinity but with a clearly non-marine origin.

Fig. 3 represents the two conservative parameters, Cl and $\delta^{18}\text{O}$, for the 1,265 groundwater samples with categories 1 to 4, together with the theoretical end members assumed from the paleohydrogeological model (Meteoric Recharge -MR-, Baltic, Littorina, Glacial, and Deep Saline; Table S2; Supp. Mat.). Different mixing pathways are expected to be shown in this plot considering how the groundwater chemistry may have responded to the changes in climate and the transgressions and regressions over time (cf Section 2.2). The location of the samples in the plot with respect to the location of the end members shows the presence of waters with clear influences of meteoric recharge (grey rectangle), marine waters (blue rectangle), glacial meltwaters (yellow rectangle) and even some non-marine waters with higher salinities (black rectangle). In all the cases, except for the waters with meteoric recharge influence, the groundwaters samples do not reach the pure composition of the theoretical end members.

Apart from these four groups, it is evident that there are some samples with intermediate values that indicate an even more complex origin (e.g. mixing among three or even more end members) that made the separation of additional types necessary.

Starting with the already existing water types for Forsmark inland and SFR, multiple tests were made changing the limits of the considered parameters (other parameters were also tested) to be able to get the final definition of the water types to characterise the waters from both sites. The final distinguished major water types (and the abbreviations used in the paper) are indicated in Table 1 together with the chosen values for their definition.

The two first types correspond to the waters mainly affected by the meteoric recharge and they represent the modern recharge waters (Meteoric) with progressively more interaction with the regolith and/or the bedrock or with some mixture with marine waters (Brackish Meteoric; BrMet). The group of waters with an important marine influence show higher Cl concentrations, and the upper limit is defined by the maximum concentration deduced for the Littorina Sea (6500 mg/L Cl; Pitkänen et al., 2004; Fig. 4a). However, the most characteristic parameter that separates these waters from the rest is the Cl/Mg ratio

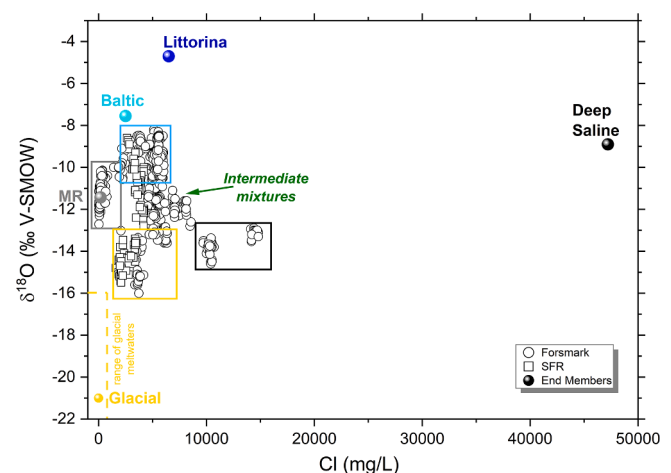


Fig. 3. $\delta^{18}\text{O}$ vs Cl in the studied groundwaters and in the end members assumed to have influenced the groundwaters over the paleohydrogeological history (Deep Saline, Glacial, Littorina, Baltic and Meteoric Recharge, MR; their composition can be found in the Table S2 of the Supplementary Material). The boxed areas indicate groups of groundwaters with clear influences of one end member.

Table 1
Main chemical and isotopic criteria used for the definition of the different water types.

Water Type	Abbreviation	Cl (mg/L)	Cl/Mg	$\delta^{18}\text{O}$ (‰ V-SMOW)
Meteoric	Meteoric	$\text{Cl} < 200$	$\text{Cl}/\text{Mg} < 30$	
Brackish Meteoric	BrMet	$200 \leq \text{Cl} < 2,000$	$\text{Cl}/\text{Mg} < 30$	$-13 \text{‰} \leq \delta^{18}\text{O}$
Brackish Marine Baltic	BrMarBal	$2,000 \leq \text{Cl} < 3,500$	$14 < \text{Cl}/\text{Mg} < 40$	$-9 \text{‰} \leq \delta^{18}\text{O} \leq -7 \text{‰}$
Brackish Marine Littorina	BrMarLitt	$3,500 \leq \text{Cl} < 6,500$	$14 < \text{Cl}/\text{Mg} < 40$	$-11.5 \text{‰} \leq \delta^{18}\text{O} \leq -7 \text{‰}$
Brackish Mixed	BrMix	$2,000 \leq \text{Cl} < 6,500$	$14 < \text{Cl}/\text{Mg} < 40$	$-13 \text{‰} \leq \delta^{18}\text{O} \leq -9 \text{‰}$
Brackish Glacial	BrGl	$1,500 \leq \text{Cl} < 9,000$	—	$\delta^{18}\text{O} \leq -13 \text{‰}$
Brackish Transition	BrTrans	$2,500 \leq \text{Cl} < 9,000$	$40 \leq \text{Cl}/\text{Mg} < 190$	$-13 \text{‰} \leq \delta^{18}\text{O}$
Brackish Non-Marine	BrNonMar	$4,000 \leq \text{Cl} < 9,000$	$\text{Cl}/\text{Mg} > 190$	$-13 \text{‰} \leq \delta^{18}\text{O} \leq -10 \text{‰}$
Saline	Saline	$9,000 \leq \text{Cl}$	$\text{Cl}/\text{Mg} > 500$	$-15 \text{‰} \leq \delta^{18}\text{O} \leq -10.5 \text{‰}$

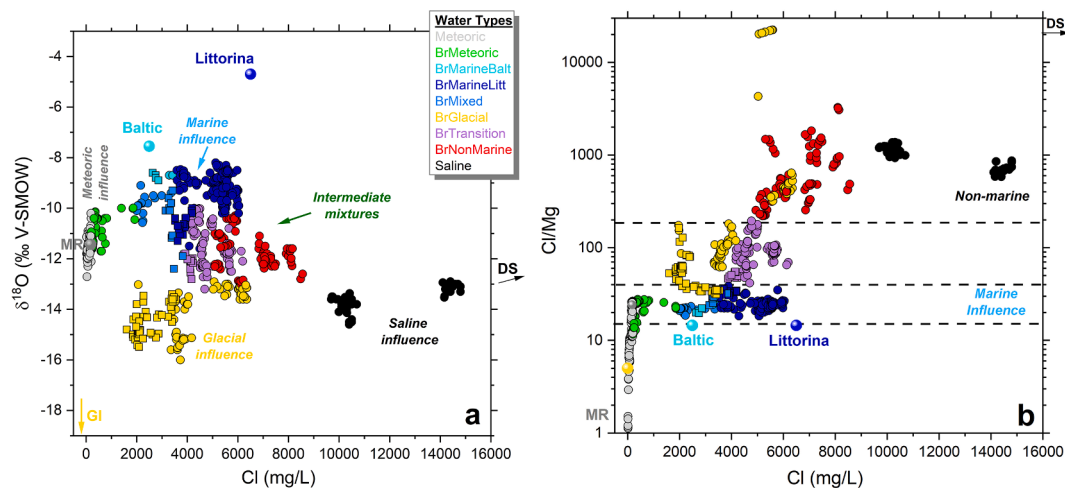


Fig. 4. Representation of the parameters used for the definition of the water types in the studied groundwaters: $\delta^{18}\text{O}$ vs Cl (a) and Cl/Mg vs Cl (b). Also shown in the plots are the theoretical composition of the end members (the Cl concentration of the Deep Saline end member is too high to be plotted at the scale of interest for the Forsmark groundwaters, therefore from now on, only the indication of where it would be is shown with an arrow). The samples are colour coded by the water types defined in Table 1.

(Fig. 4b). The marine group has been divided in two types that represent groundwaters affected by the waters from either the Littorina Sea stage, Brackish Marine Littorina (BrMarLitt), or from the present Baltic Sea, Brackish Marine Baltic (BrMarBal).

The groundwaters significantly affected by glacial meltwaters (from the last or from previous deglaciations), the Brackish Glacial (BrGl) type, are separated from the rest basically by their $\delta^{18}\text{O}$ value, however, the salinity range accepted for this group is quite broad as there are several possible mixtures with very different waters.

The group of samples that are considered intermediate mixtures, has been separated in three water types: BrMixed (BrMix), BrTransition (BrTrans) and BrNonMarine (BrNonMar). The BrMix type represents the mixture between marine waters and glacial or meteoric waters. The BrTrans is generally deeper and comprises degrees of mixing between brackish marine and non-marine waters (Fig. 4b). The BrNonMar waters show intermediate Cl values but their Mg values indicate the clear non-marine origin that differentiates them from the other intermediate mixtures. They show a trend towards the saline group indicating the possible mixing and water-rock interaction evolution over time. The limit between the BrNonMar and the Saline waters has been set to 9000 mg/L Cl with the additional difference of generally lower $\delta^{18}\text{O}$ values in the saline group.

The groundwater subdivision presented above was also tested using a principal component analysis to consider all the main compositional variables (Ca, Mg, Na, K, Cl, HCO_3^- , SO_4^{2-} , Br, $\delta^{18}\text{O}$ and $\delta^2\text{H}$). The results can be found in the Supp. Mat. (section SM4) and they show that the definition of the water types is quite successful in separating groups with different chemical and isotopic compositions and also in indicating the trends and connections among them.

4.2. Distribution of the groundwater types with depth

Fig. 5 shows the depth location of the water types as displayed by the 66 selected samples representative of each sampled borehole section (cf. section 3). The Cl distribution with depth shows that the uppermost 400 m display a wide variability in the concentrations (up to 6,000 mg/L; Fig. 5a) associated to the presence of different groundwater types. Even more variability is shown by the $\delta^{18}\text{O}$ values at those depth from around -16‰ in the BrGl groundwaters to -8‰ in the waters with some marine component (Fig. 5b). The shallower depths in Forsmark inland are characterised by Meteoric and BrMet waters down to 60 and 150 m depth, respectively. There are also a few exceptions of BrMarLitt or BrMix waters at these depths. BrMarBal and BrMix waters characterise the shallowest part in the SFR site. Below 150 m depth, BrMarLitt and BrGl are present at both sites. The shallowest BrTrans type waters have been found at 250 m depth in Forsmark inland and at 400 m in the SFR site (400 m is the deepest sampled location in SFR and these BrTrans water represent the most saline groundwater type in that site).

Below 500 m depth (where the BrMarLitt waters disappear), the waters from Forsmark inland show an increasing trend in the Cl concentration and a decrease in the variability of $\delta^{18}\text{O}$ to between -12 and -14‰ . These changes are associated to the transition from waters with marine influence to waters without marine signature (with Cl higher than 7000 mg/L; Fig. 5a) and with an important influence of glacial meltwater. Notably, the samples with the highest Cl contents (around 15,000 mg/L) are located between 650 and 850 m depth whereas the deepest samples from approx. 1000 m depth only reach around 10,000 mg/L Cl. This agrees well with the rest of the observations of variable Cl contents at similar depths and this irregular distribution supports the bedrock heterogeneity and the presence of isolated bedrock

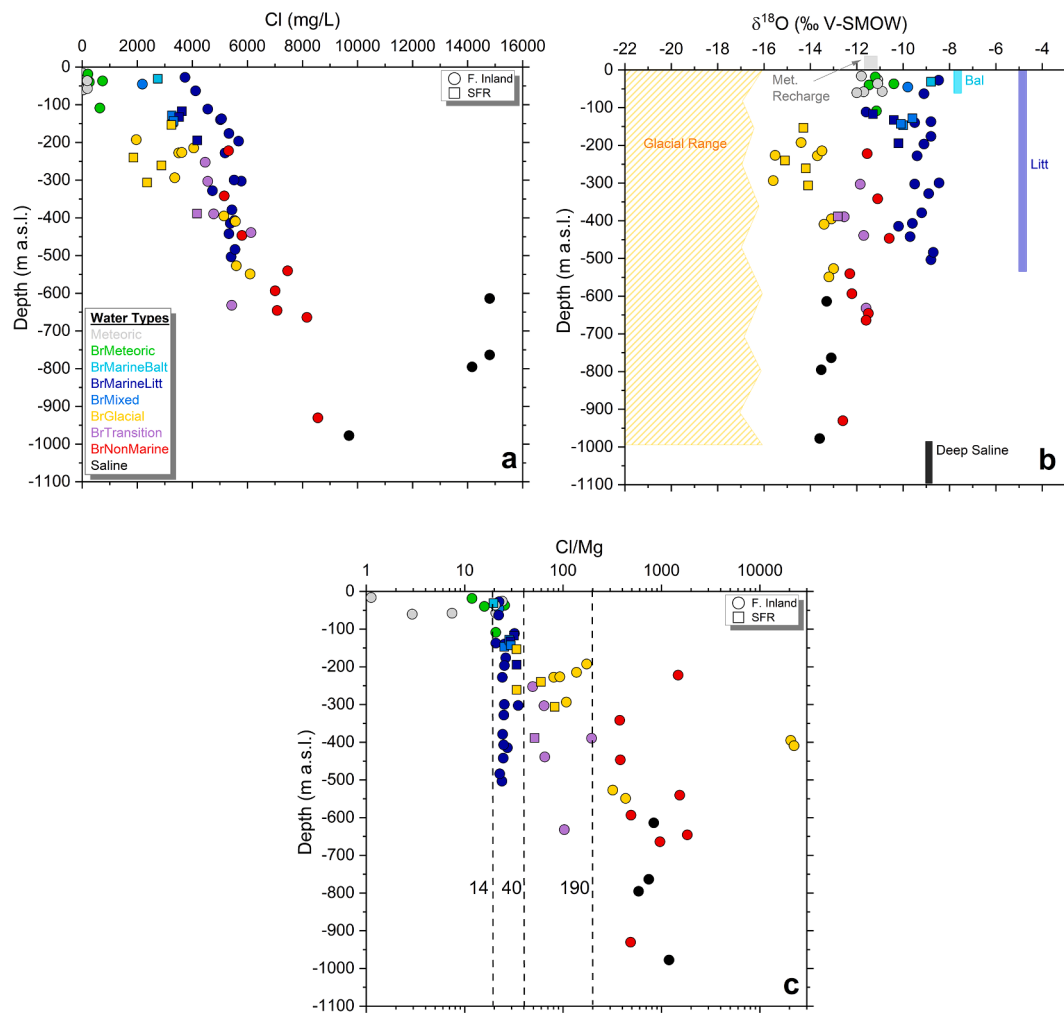


Fig. 5. Distribution with depth of Cl (a), $\delta^{18}\text{O}$ (b) and the Cl/Mg ratio (c) in the 66 selected groundwaters representative of each sampled section. The vertical dashed lines in panel c represent the values Cl/Mg 14, 40 and 190 which are the limits established for the marine, waters (BrMarBal and BrMarLitt), the BrTrans and the BrNonMar water types. The theoretical ranges of the isotopic composition of the end members (Deep Saline, Littorina Seawater, Baltic Seawater, Glacial Meltwater and Meteoric Recharge) are shown in panel (b).

compartments in the less connected parts of the rock, irrespective of the depth.

The Cl/Mg ratio (Fig. 5c) confirms the observation from the other two plots that the waters inside each group appear at very different depths. The water type with the largest variability in the Cl/Mg ratio is the BrGl, with ratios from around 30 up to over 20,000 due to the fact already pointed out, that glacial meltwaters have mixed with marine and non-marine waters. The marine groundwaters are the ones clearly restricted to values between 14 and 40 and the waters with no marine influence show Ca/Mg ratios over 200.

5. Results and discussion

5.1. Characterisation of the mixing processes

The chemical components Na, Ca, Br, Mg, K and SO_4^{2-} are evaluated to complete the picture of the mixing processes discussed in section 4. Their concentrations are mainly controlled by mixing but they can also be affected, to various extent, by heterogeneous chemical reactions.

These elements show two different distribution trends with respect to salinity and depth. One is followed by typical marine indicators, like Mg, K, SO_4^{2-} , with maximum concentrations in the brackish marine waters, at between 5000 and 6000 mg/L of Cl and down to 500 m depth (Fig. 6 and Fig. S5.1; Supp. Mat.). The other trend, followed by elements like Ca, Na

and Br (Figs. 7 and 8), is parallel to Cl with a general increase in concentrations with salinity and depth.

Fig. 6 shows the distribution of Mg and SO_4^{2-} with respect to depth and salinity (the plots for K can be found in Fig. S5.1; Supp. Mat.). Despite the clear marine influence shown by the samples with the higher contents of these elements, it is also clear that the Mg/Cl and $\text{SO}_4^{2-}/\text{Cl}$ ratios in the BrMarBal and BrMarLitt waters are slightly lower than the original marine signature (below the Sea Water Dilution Line, SWDL) indicating that additional processes have affected (lowered) the Mg and SO_4^{2-} concentrations in these waters, either by mixing or by chemical or microbial reactions.

Figs. 7 and 8a show the evolution of Na, Ca and Br with the significant enrichment in the more saline groundwaters and the overall positive correlation with chloride, indicating that mixing is the main process controlling the dissolved content of these elements. In the case of Na two different trends can be seen: one of them is parallel although slightly below the seawater dilution line, indicating the mixing with a marine end member; the other trend follows the theoretical mixing line from the dilute waters to the deep saline groundwaters (DSML), although slightly above. These deviations from the mixing lines indicate possible effects of some reactions on the dissolved Na concentrations (see below).

The Ca distribution versus Cl is also parallel to the mixing line towards the deep saline groundwaters (although in this case slightly

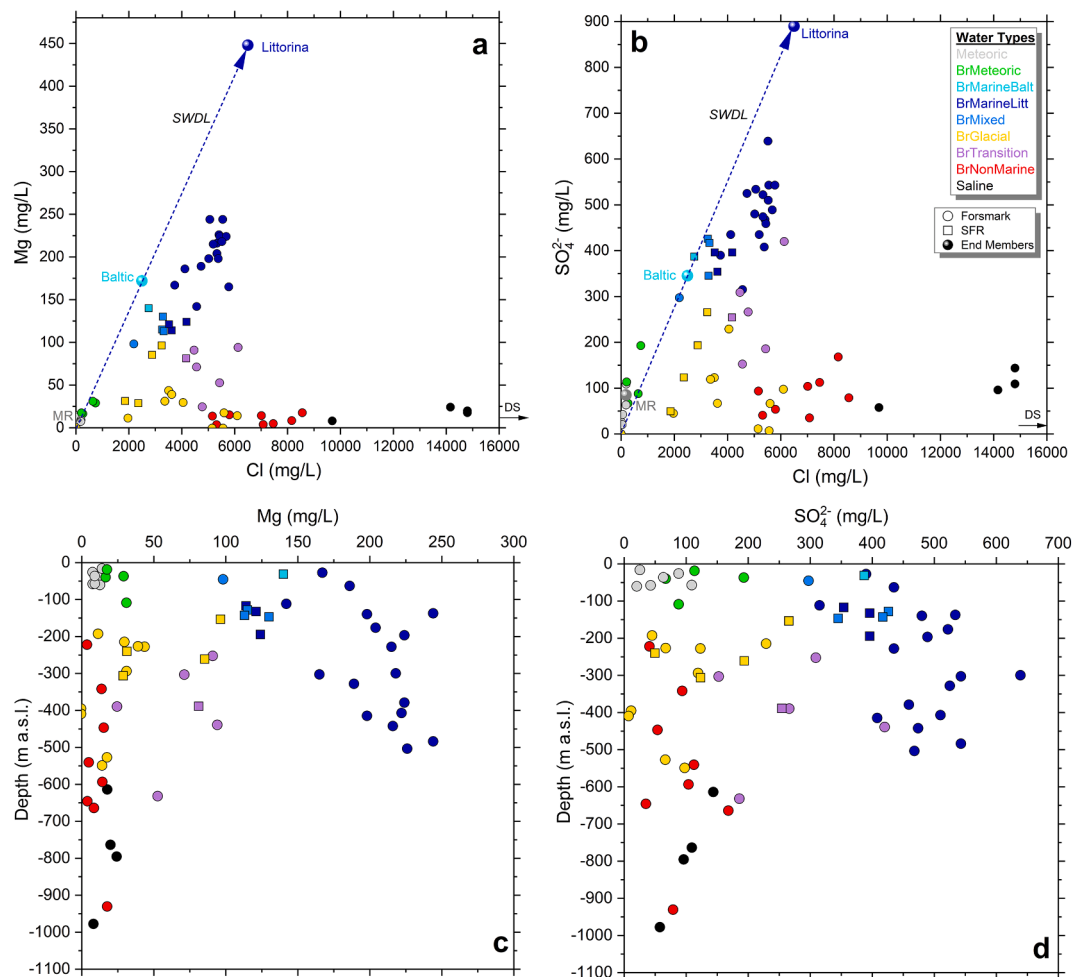


Fig. 6. Distribution of Mg (a, c) and SO_4^{2-} (b, d) with salinity and depth in the different groundwater types. The theoretical composition of some of the end members (Littorina Seawater, Baltic Seawater and Meteoric Recharge) are shown in the plots against Cl. SWDL line in panels a and b corresponds to the Sea Water Dilution Line.

below; Fig. 7d). From all the elements described in the section, Ca is the most affected by heterogeneous reactions (calcite dissolution/precipitation and cation exchange) but its high contents due to the mixing with more saline waters, mask the effect of the small mass transfers caused by these reactions.

The distribution of the Br values with salinity (Fig. 8a) is much closer to the mixing lines than the distributions of Na and Ca. The almost perfect fit with the Sea Water Dilution Line supports the fact that Br can be considered a conservative element controlled mainly by mixing in this system. Br/Cl ratios (Fig. 8b and c) show that the BrMarLitt and BrMarBal groundwaters have values from 0.003 to 0.0045, supporting their marine origin whilst the deeper waters show a progressive increase in the Br/Cl ratio towards values around 0.01 suggesting increased influence of water/rock interaction (e.g. with mica minerals) and supporting a non-marine origin and longer residence time. This is also seen in the plot of Br/Cl against the Ca/Mg ratio (Fig. 8c) where the waters show a mixing trend from a cluster of recent Met, BrMet, BrMarine and BrMix groundwaters with low Ca/Mg and Br/Cl ratios, towards older and more saline, BrNonMar and Saline, with much higher values. Between these two extremes there are some BrGl and all the BrTrans groundwaters with intermediate ratios indicating their mixed origin. Also, the Na/Ca ratio (Fig. 8d) shows a clear distribution according to the water types. The highest values correspond to the Met, BrMet and BrMarBal groundwaters; the intermediate values are represented by the BrMix, BrMarLitt and some BrGl groundwaters; finally, the rest of the waters (BrTrans, BrNonMar and Saline) show values around or below 1

indicating the effects of more intense water-rock interaction and mixing with a saline non-marine component.

Although mainly influenced by mixing, all these parameters can, to some extent, be affected by water-rock interaction processes involving cation-exchange and/or dissolution-precipitation of aluminosilicates and calcite (see section 5.2 and Section SM5.2; Supp. Mat.), and even microbial reactions in the case of SO_4^{2-} . These reactions agree well with what was found in the Laxemar area (Gimeno et al., 2014). The cation exchange processes can explain the values of Na, K and even Mg slightly below (and Ca above) the seawater dilution line as a result of a salinisation scenario where the marine waters enter into a system with a more dilute groundwater. The Na and K values slightly over (and Ca slightly below) the mixing line with the deep saline could be explained by the cation exchange resultant of a dilution scenario where dilute glacial/meteoric waters evolve towards the brackish non marine and saline groundwaters present in the bedrock.

Especially in the waters with longer residence times, the dissolution-precipitation of aluminosilicates, although much slower processes than the cation exchange, can also be important in the control of some of these cations. This can be seen in the mineral stability diagrams used for the evaluation of the aluminosilicate system (Fig. S5.2; Supp. Mat.). According to those results, and in agreement with the main Na, K and Mg-bearing minerals in the bedrock and fracture minerals (albite, adularia, chlorite and different mixed-layer clays, smectite/illite, chlorite/smectite, chlorite/vermiculite; Sandström et al., 2008; Sandström et al., 2011; Sandström et al., 2014), it is expected that the

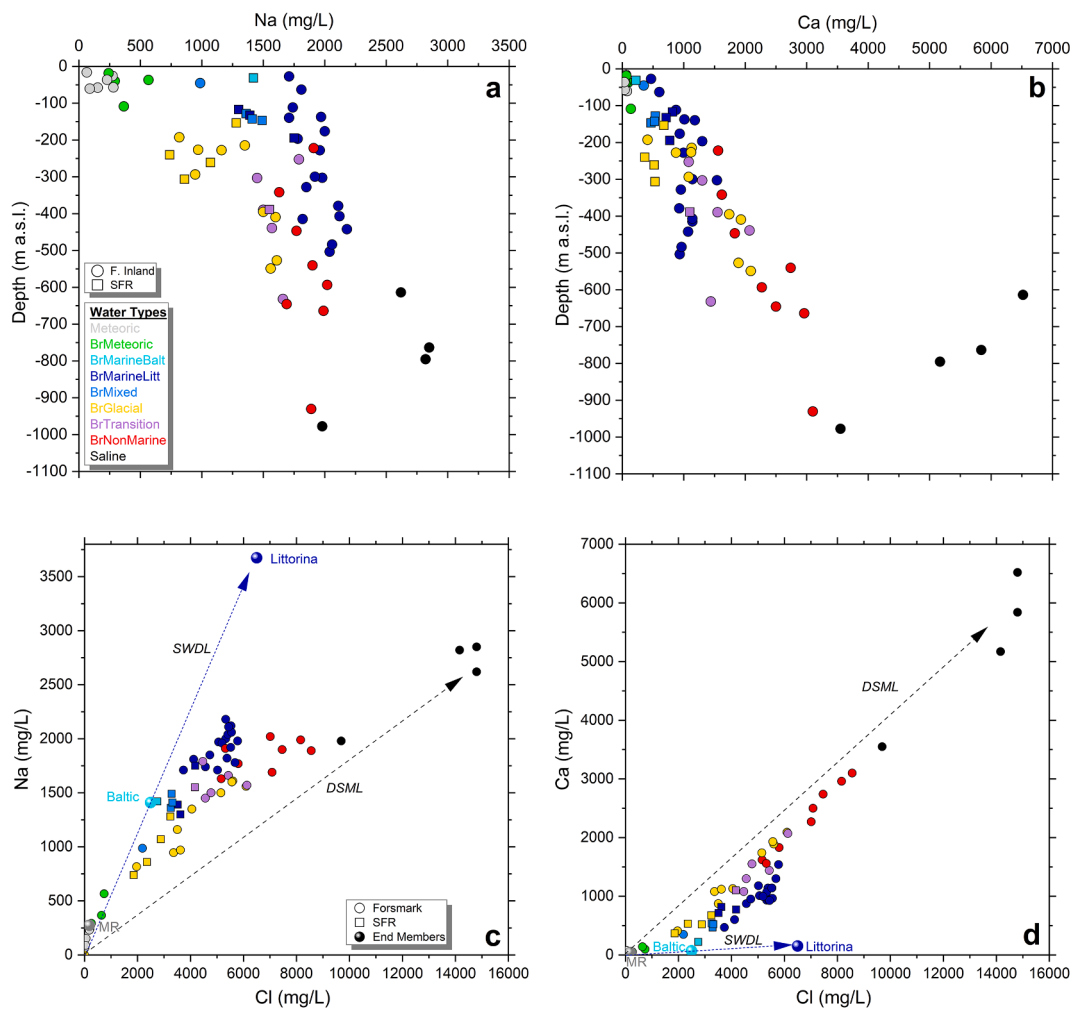


Fig. 7. Distribution with depth and Cl of Na (a, c) and Ca (b, d). The arrows in panels c and d show the theoretical Deep Saline Mixing Line (DSML; black arrow) and the Sea Water Dilution Line (SWDL; blue arrow). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

heterogeneous reactions include also their release from primary minerals and their partial or total incorporation into secondary ones. However, all these mineral reactions are superimposed, in most cases, on different mixing processes.

Finally, with respect to SO_4^{2-} , although its main source in these groundwaters is of marine origin, its concentration in the brackish marine waters is below the SWDL (Fig. 6b), and the $\delta^{34}\text{S}_{(\text{SO}_4)}$ values are between 24 and 27 ‰ CDT, higher than expected for marine waters (Fig. S5.3.1, Supp. Mat.). The solubility-control of sulfate minerals like gypsum, celestite and barite, on the dissolved SO_4^{2-} can be discarded in these waters (Fig. S5.3.2; Supp. Mat.; see also Gimeno et al., 2008). Therefore, the most probable reason for the chemical and isotopic values seems to be the SO_4^{2-} reduction mediated by Sulfate Reducing Bacteria (SRB, reported as active in some Forsmark inland groundwaters; Hallbeck and Pedersen, 2008b) which, apart from lowering the SO_4^{2-} content in the original marine waters has modified their $\delta^{34}\text{S}_{(\text{SO}_4)}$ values. This must have occurred during partly open conditions when the marine waters intrude into the bedrock through sea sediments, or directly through the bedrock but in both cases not entirely isolated to make the $\delta^{34}\text{S}_{(\text{SO}_4)}$ values slightly over the typical marine ones. At greater depth or in isolated pockets of the bedrock (BrGl, BrTrans, BrNonMar and Sal) with higher Cl contents, the SO_4^{2-} reduction must have happened under closed condition resulting in very low SO_4^{2-} contents and high $\delta^{34}\text{S}_{(\text{SO}_4)}$ values (>30 ‰ CDT).

5.2. Characterisation of the chemical and microbial reactions

This second subsection deals with SiO_2 , F and the carbonate and redox systems which, although affected by mixing, are mainly conditioned by water-rock interaction and microbial processes.

5.2.1. The carbonate system

Besides bicarbonate and pH, Ca is an important component of the carbonate system that has been described above, together with the components that are mainly controlled by mixing (Section 5.1). The bicarbonate concentrations show a clear decrease with depth and salinity (Fig. 9a and Fig. S5.4a; Supp. Mat.). The highest values are found in the first 100 m in the Meteoric and BrMet groundwaters (up to 500 mg/L) where the carbonate system and the microbial production of CO_2 are very active (Gimeno et al., 2008). The concentrations are still quite high (between 100 and up to 200 mg/L; Fig. 9a) below 100 m depth in the waters with marine component (BrMarBal, BrMarLitt and BrMix). This seems to be due to the interaction of the marine waters (Littorina or Baltic) with seabed sediments during infiltration (Gimeno et al., 2014). Below 500 m depth, the HCO_3^- values are very low (Fig. 9a).

The pH values do not show any clear trend with depth or salinity (Fig. 9b and Fig. S5.4.1b; Supp. Mat.) as also seen in other studied crystalline rock systems (Laxemar, Olkiluoto or Lac du Bonnet; Gimeno et al., 2014; Pitkänen et al., 2004; Gascoyne, 2004). Many samples, at almost all depths, have pH values in the range between 7 and 8.

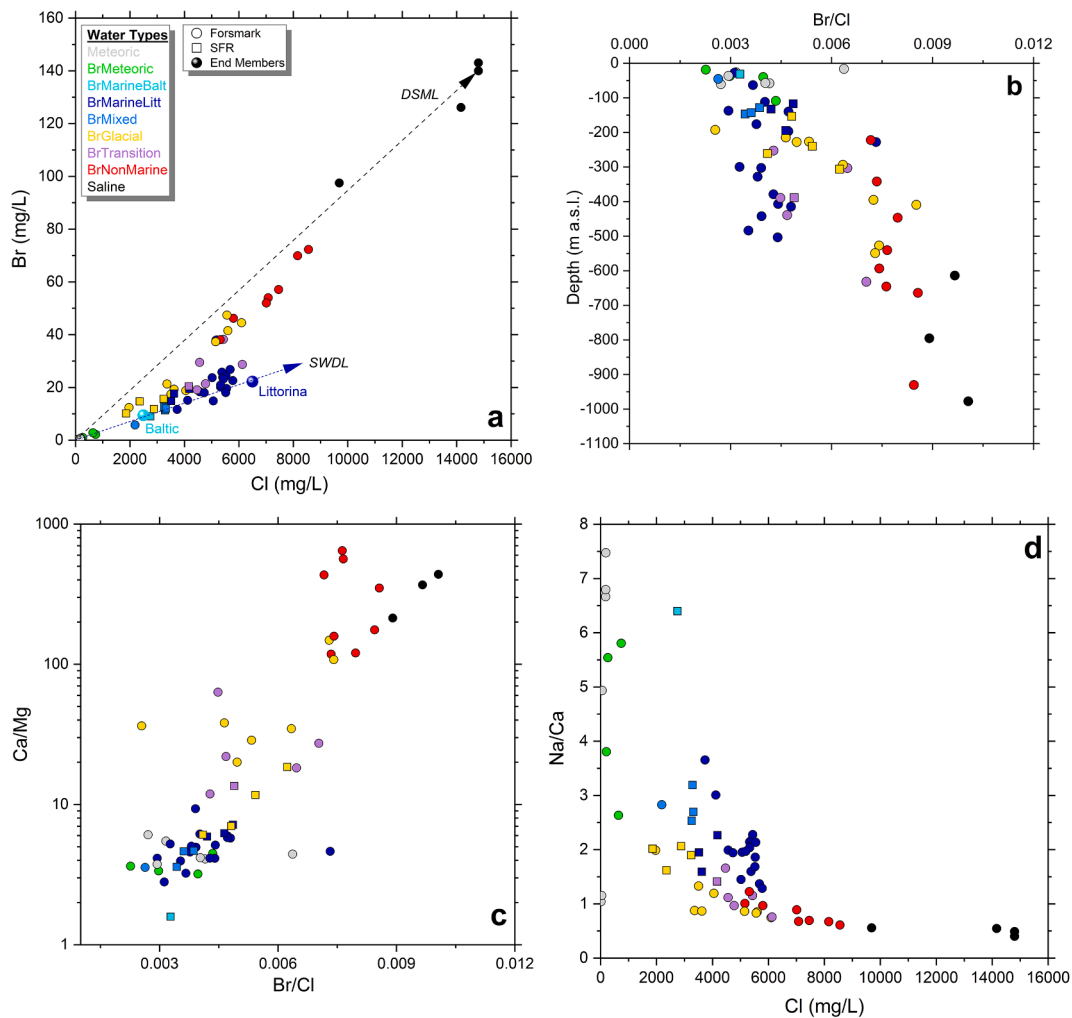


Fig. 8. Plots of Br vs Cl (a), Br/Cl vs depth (b) and vs Ca/Mg (c) and Na/Ca vs Cl (d). The arrows in plot a show the theoretical mixing line with the deep saline waters (DSML) and the sea water dilution line (SWDL).

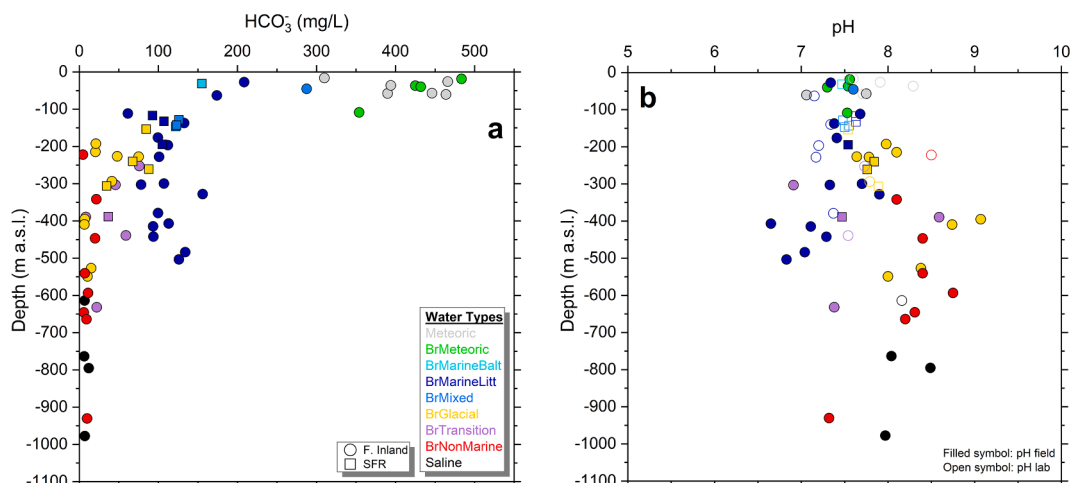


Fig. 9. Distribution of HCO₃⁻ (a) and pH (b) with depth. The groundwaters samples are colour coded by the water type.

However, most of the BrNonMar, the Saline and some BrTrans and BrGl, show higher pH values (between 8 and 9) corresponding to the samples with the highest Ca and lowest HCO₃⁻ concentrations (Fig. 9a). This seems to be related to the saturation state of the waters with respect to calcite (Fig. S5.4.2a; Supp. Mat.).

Calcite is, together with chlorite/corrensite, the most common fracture mineral in the Forsmark area (Sandström et al., 2008) and it has an important role in the control of pH and HCO₃⁻ whereas its control on Ca is completely masked by the effect of mixing. Most of the waters are in equilibrium or near-equilibrium with this mineral including the dilute

shallow groundwaters. However, in terms of their isotopic signatures only a few observations were made of fracture coating calcites in apparent equilibrium with the present groundwater. Instead, Precambrian and Palaeozoic origins are frequent and some findings of Mesozoic calcites are reported (Drake et al., 2017). Calculated CO₂ partial pressures (Fig. S5.4.2b; Supp. Mat) show values higher than the atmosphere in all the shallow groundwaters (Meteoric and BrMet) and in the BrMarLitt waters at all depths. In general, the pCO₂ decreases with depth and salinity due to the mixing with other waters with very low carbon contents and/or to its consumption by microbially-mediated reactions or by water/rock interaction.

The degree of calcite oversaturation displayed by many groundwaters at all depths is between +0.5 and +1.0 (Fig. SM5.4.2a; Supp. Mat), which was also observed in Laxemar (Gimeno et al. 2014; and references therein). Apart from the possible problems derived from the pH measurements in waters with high pCO₂ (possible outgassing), the oversaturation state might be real and necessary to overcome the kinetic barrier to precipitation. This oversaturation can be the result of the presence of anaerobic bacteria like IRB, SRB, and methanogens (all of them present in this fractured rock system; Hallbeck and Pedersen, 2008a; Hallbeck and Pedersen, 2008b) or the result of the dissolution of aluminosilicates, which, in both cases, would promote an increase in pH and alkalinity (and in dissolved calcium contents in the case of the dissolution of some aluminosilicates; Gimeno et al., 2014; and references therein).

5.2.2. Silica and fluoride

Dissolved SiO₂ contents in the groundwaters from Forsmark inland and the SFR do not show a clear trend with depth (Fig. S5.5.1a; Supp. Mat.). The greatest variability is evident in the groundwaters with Cl between 4000 and 6000 mg/L (Fig. S5.5.1b; Supp. Mat.) present at around 300 m depth, where the high SiO₂ values seem to derive from mixing with marine waters (Littorina). As already indicated for the Laxemar site (Gimeno et al., 2014), variable but high dissolved SiO₂ contents (up to 60 mg/L) are expected in the Littorina Sea waters during the infiltration into the basement through the seabed sediments which are very rich in highly soluble diatom skeletons (Burke and Kemp, 2002 and references therein).

Some shallow meteoric groundwaters also show high SiO₂ contents but the rest of the groundwater system have values around 12 mg/L with a progressively narrower range with depth and salinity. The same behaviour has been observed in other crystalline rock systems such as Laxemar, Olkiluoto, Palmottu and the Canadian Shield (Blomqvist et al., 2000; Pitkänen et al., 2004; Gascoyne, 2004; Gimeno et al., 2008). This constant value (independent of the salinity) indicates that, despite the potential marine influences on many groundwaters, there is a mineral phase whose solubility is limiting the dissolved SiO₂ contents. Most of the waters are in equilibrium with chalcedony (Fig. S5.5.1c and d; Supp. Mat.), which indicates that this is the silica phase controlling the SiO₂ contents, however, the clay minerals and the feldspars seem to have an important role in the control of SiO₂ through incongruent dissolution reactions in the shallow groundwaters.

The fluoride concentrations also show an important dispersion at shallow depths, while the contents in the deeper and more saline groundwaters show a narrow range around 1.5 mg/L (Fig. S5.5.2a and b; Supp. Mat.) despite the varying Cl concentrations and depths. This suggests the existence of a mineral solubility control on dissolved F in the groundwaters with a long residence time. The dominant source of F in groundwaters, especially in crystalline rock systems (Deshmukh et al., 1995; Saxena and Ahmed, 2001) is fluorite (CaF₂) which has been reported in Forsmark inland and in the SFR at very different depths (Pettersson et al., 2004; Sandström et al., 2008; Sandström et al., 2011). The speciation-solubility calculations (Fig. S5.5.2c and d; Supp. Mat.), indicate that most of the Forsmark inland and the SFR groundwaters are in equilibrium with this mineral almost irrespective of depth and salinity. This behaviour of F and its control by fluorite has also been

reported in other crystalline rock systems (Laxemar, Olkiluoto and Palmottu, as shown in Gimeno et al., 2014).

5.2.3. Redox systems

Potentiometric Eh measurements were performed in a number of sampled sections following the methodology developed by SKB (Auqué et al., 2008; Gimeno et al., 2008). The measured values range from -143 to -281 mV with a heterogeneous distribution with depth. This indicates that although sampling (or drilling-induced) perturbations may have influenced the original redox conditions (Gimeno et al. 2008) the rock-water system and the microbial reactions keep a considerable buffering capacity (Sandström et al. 2008) for maintaining a significant reducing character.

Although the contents of Mn, NH₄⁺, Fe, S²⁻, and U have contributions from inorganic and/or microbial reactions, they show a general trend (with depth and Cl; Figs. 10 and 11 and Fig. S5.6.1; Supp. Mat.) similar to other marine indicators like Mg, K and SO₄²⁻. The low values are associated to the BrNonMar and Saline waters and the maximum contents to the BrMarLitt samples from Forsmark inland. The clear association of these elements with the BrMarLitt groundwaters was also found in Olkiluoto (Pitkänen et al., 2004), in Laxemar-Simpevar-Äspö, and in Finsjön (reviews by Gimeno et al., 2008; Gimeno et al., 2009).

The evolution of Mn, Fe, NH₄⁺ and S²⁻ is frequently linked to bacterial activity (manganese, nitrogen, iron and sulfide reducing bacteria – MRB, NRB, IRB and SRB) and their presence has been reported in the Forsmark inland and the SFR sites at almost all depths (Hallbeck and Pedersen, 2008a; Hallbeck and Pedersen, 2008b). However, additional inorganic reactions, many of them induced by the microbial activity, can also be important in the control of their dissolved contents in the different groundwater types. For example, the fact that the highest contents of these redox elements are found in the BrMarLitt waters seems to be associated to the interaction of the Littorina sea waters with the marine sediments during their infiltration into the bedrock. In this type of sediments, minerals like rhodochrosite, siderite, and/or amorphous Fe²⁺-monosulfides can precipitate and the waters will reach the corresponding equilibrium situation (Gimeno et al., 2008 and references therein). Additionally, those groundwaters can contain significant NH₄⁺ concentrations most probably inherited from the production by bacterial activity in the marine sediments (Pitkänen et al., 2004 and references therein). The Littorina waters could have reached an equilibrium with these minerals and kept the solubility controlled concentration for the rest of their passage into the bedrock (cf. Gimeno et al., 2008; Gimeno et al., 2011 for further discussion). This is what has been observed in the groundwaters with marine component which are in equilibrium with rhodochrosite and siderite irrespective of their location (Fig. S5.6.2a, b; Supp. Mat.) even though these minerals have not been found in the fractures sampled at the Forsmark area.

Other processes like the dissolution of Mn-bearing minerals and the reductive dissolution of Mn-oxyhydroxides may increase the dissolved Mn concentrations in the marine sediments and, therefore, justify the observed increase in the brackish marine groundwaters. There is also a positive correlation between dissolved Mn and dissolved Fe²⁺ that can be due to the presence of Fe phases with traces of Mn (oxyhydroxides, clays) or of Mn sorbed on their surfaces.

Fe and S²⁻ are interrelated through inorganic processes, such as sulfide precipitation and reductive dissolution of Fe³⁺-oxyhydroxides by H₂S (cf. Gimeno et al. 2009 and references therein), which may exert an important control on the dissolved Fe²⁺ and S²⁻ contents. The main source of dissolved Fe²⁺ appears to be the inorganic or microbially-induced reductive dissolution of Fe-silicates (e.g. Fe³⁺-bearing clay minerals) or Fe³⁺-oxides and oxyhydroxides in the fracture fillings.

Under undisturbed conditions S²⁻ seems to be controlled by the amorphous Fe²⁺-monosulfides solubility in the waters with sufficient SO₄²⁻ contents and marine signature (Fig. S5.6.2c and d; Supp. Mat.). More groundwaters are in equilibrium with respect to mackinawite (a crystalline and less soluble iron monosulfide) which could be

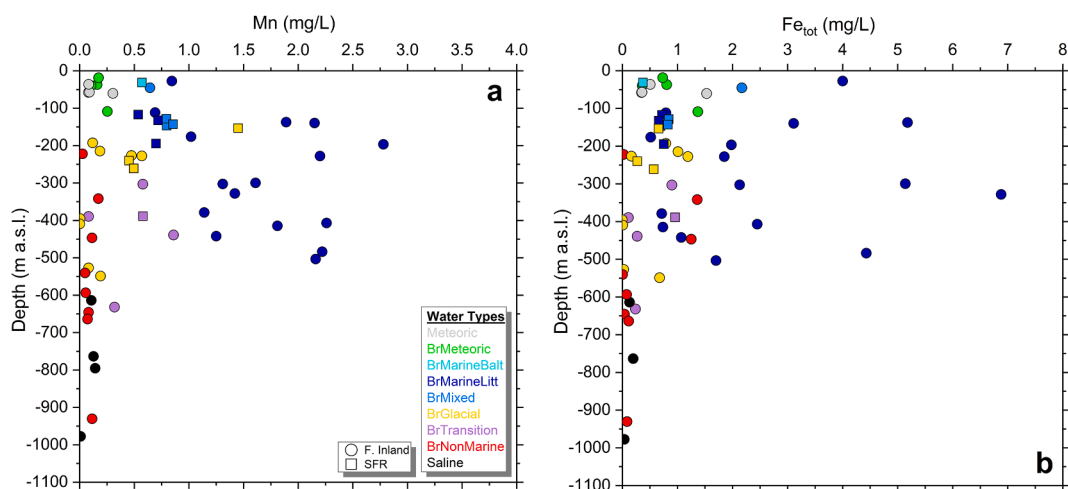


Fig. 10. Distribution of Mn (a) and Fe (b) with depth in the selected groundwaters. The maximum concentrations are associated to the BrMarLitt groundwaters.

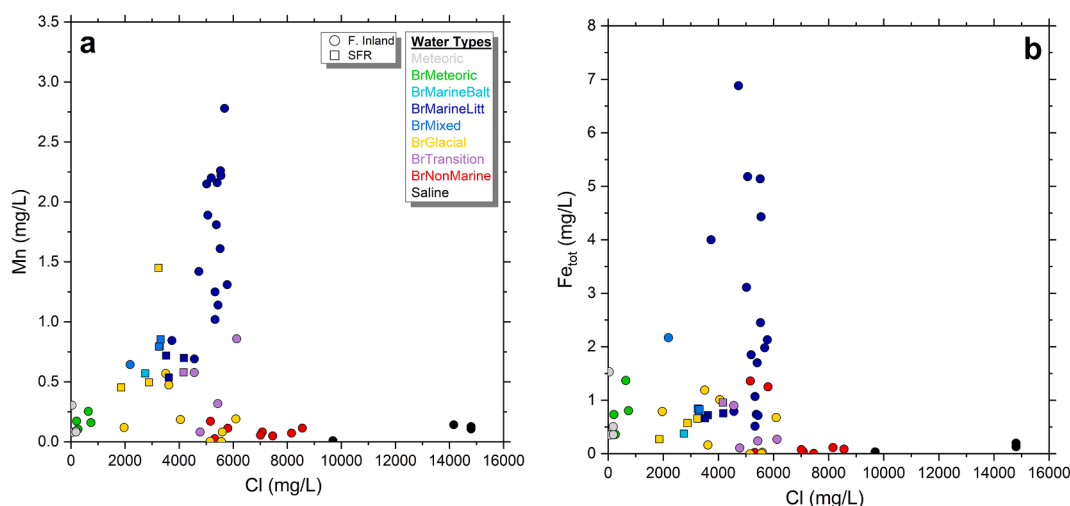


Fig. 11. Distribution of Mn (a) and Fe (b) with chloride in the selected groundwaters. The maximum values are associated to the BrMarLitt groundwaters with Cl contents between 5,000 and 6,000 mg/L.

interpreted as due to a lower SRB activity at present producing enough H_2S to reach the mackinawite solubility product but not enough to reach amorphous monosulfide's. Another possibility is the presence of an important but past SRB activity, no longer existent, which produced the original amorphous phase that has subsequently recrystallised (cf. Gimeno et al. 2011). The latter might be the case for the long term hydraulically isolated groundwaters with very high isotopic $\delta^{34}\text{S}$ values indicating SO_4^{2-} reduction under closed conditions. The information found in the fracture fillings indicates a common occurrence of Palaeozoic pyrite, but recent deposition of sulfides has been difficult to identify, therefore suggesting minor occurrences or already aged amorphous sulfides.

Uranium concentrations higher than $10 \mu\text{g/L}$ were found in the BrMarBal, BrMix and BrGl groundwaters in the SFR and in some of the BrMarLitt and BrTrans samples in Forsmark inland (Fig. S5.6.1e; Supp. Mat.). This seems to be related to the chemical reactivity of recharging marine waters (rich in CO_2) which promotes uranium mobilisation of, especially, U^{6+} by carbonate complexation like the identified species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^0$ in groundwaters from 500 m in KFM02A (Tullborg et al., 2017). Towards even greater depth, the HCO_3^- content and the redox potential decrease and the solubility of U becomes increasingly reduced.

The mineralogical background to the U supply from the bedrock has been thoroughly investigated by Krall et al., (2015), Krall et al. (2017),

Krall et al. (2019). It was shown that e.g. oxidised U present in Ca-U^{6+} silicates precipitated around ~ 1.25 Ga and has survived despite the overall indicated reducing conditions (e.g. formation of pyrite) which resulted in the formation of the uranophane and haiweeite, of Paleozoic ages (400–300 Ma), detected in some fractures.

U-series isotopes of fracture coatings and groundwater samples have been used to understand how the recent evolution (<1 Ma) both, in terms of the flow system and the hydrogeochemistry, has influenced the observed U distribution. The results support that periodic water intrusions, driven by glaciation and deglaciation events and subsequent intrusions of brackish marine waters during the last 120,000 y, can explain the U anomaly and the U isotope distribution in the groundwaters (Suksi et al., 2021).

5.3. Residence time

An overall qualitative evaluation of the groundwaters residence time can be carried out assuming that the longer the time, the greater the mineralisation/salinity of the waters will be, due to longer water-rock interaction. More qualitative information can be obtained from the values of stable isotopes, such as $\delta^2\text{H}$ and $\delta^{18}\text{O}$ since they represent the conditions (e.g. climate or marine/terrestrial) during recharge. More solid time constraints are given by the radioactive isotopes ^3H , ^{14}C , ^{36}Cl

and radiogenic He all of which have been measured to various extent in the groundwaters of the Forsmark area. Irrespective of the method to gain information on residence times it is important to keep in mind that the groundwaters from the Forsmark area are affected by important events that have resulted in a mixture of residing groundwaters of different ages and origins.

5.3.1. $\delta^{18}\text{O}$, $\delta^2\text{H}$ and tritium (^3H)

Starting with the more qualitative indicators, Fig. 12 shows the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values in the selected groundwaters and in the end members. These values confirm the extensive mixing of waters. Still many signatures have been preserved like the signs of evaporation with a position below the Global Meteoric Water Line (GMWL) for the marine water. The samples found above the GMWL are Saline and BrNonMar, with the maximum value found in KFM01D at -445 m depth which, as it will be seen below, is also the water with the highest He content (cf Fig. 15b). This deviation towards the left of the GMWL is well known in shield brines and it is usually explained by water/rock interactions over substantial time spans and under near-stagnant conditions (Frape and Fritz, 1987; Clark and Fritz, 1997; Kloppmann et al., 2002; Gimeno et al., 2014). Notably, the Saline waters from Forsmark inland have relatively low $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values indicating a probable mixing with glacial waters, which can be from the last glaciation or even older.

The tritium values (Fig. 13a) show a characteristic decrease with depth. Values higher than 4 TU can be regarded as a result of recharge from the last 60 years and are only found in surface waters and near-surface groundwaters (not included in the plot) and in the shallow groundwaters of the Meteoric and BrMet type in Forsmark inland and of the BrMarBal and BrMix type in the SFR. Below 150 m depth the ^3H values are in general <2 TU with a few exceptions in the interval 2–4 TU.

Due to today's low ^3H content in the atmosphere (now recovered from the high bomb ^3H added during the 60's) the background is low, and the waters are, therefore, sensitive to very small additions of ^3H like e.g. *in situ* production of ^3H in the bedrock of up to 1 to 2 TU as the one discussed for Stripa by Andrews et al (1989). Furthermore the contamination of a few TU in waters otherwise tritium-free, is a possibility especially considering the vicinity to the nuclear power plant. These two possible sources may explain why waters with obviously long residence times in the bedrock (based on e.g. mineralisations and/or other dating methods) still show ^3H values slightly above the detection limit.

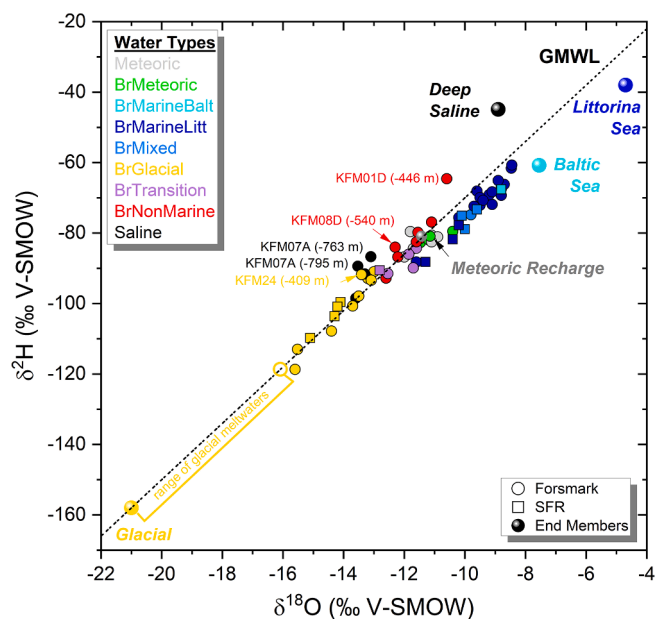


Fig. 12. Location of the studied samples and the end members in the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ plot. The Global Meteoric Water Line (GMWL) is also shown.

5.3.2. $\delta^{13}\text{C}$ and ^{14}C

The range of detection for the radiocarbon (^{14}C) with a half-life of 5730 y, theoretically allows determination of waters up to an age of at least 30,000 years and therefore, should cover the period since the last deglaciation. However, radiocarbon dating is complex with the major problem being to constrain the ^{14}C input to the bedrock, and the extent of reactions involving carbonate dissolution and breakdown of recent and old organic material which will affect the $^{14}\text{C}_{(\text{TIC})}$ content in the recharge waters (see Smellie et al., 2008 for more details). This is exemplified in the plot of ^{14}C versus ^3H (Fig. 14a) which shows that the young ^3H -containing waters (in the order of <60 years) have gained carbon from sources diluting the atmospheric ^{14}C signal. This, in turn, results in apparent ^{14}C ages in the order of thousands of years or even more (<80 pmC). A possible correction for this will be highly uncertain and all the plots with ^{14}C therefore show uncorrected values (Fig. 14). The apparent decreasing trend of radiocarbon in the waters from today's Baltic Sea and Meteoric water towards the BrMarLitt waters agrees with the understanding of the system (Fig. 14b).

From the plot of $^{14}\text{C}_{(\text{TIC})}$ versus HCO_3^- (Fig. 14c) it is obvious that BrGl and BrNonMar (all having $\text{HCO}_3^- <20$ mg/L) show unexpectedly high radiocarbon contents. This has been interpreted as due to the uptake of atmospheric CO_2 at some point during the sampling or analytical procedures which is very difficult to avoid in waters with extremely low alkalinity. It was therefore decided not to interpret these data from a residence time perspective and not to continue with ^{14}C measurements in waters with bicarbonate contents below 20 mg/L.

Analyses of the stable carbon isotopes, $\delta^{13}\text{C}$, show distinctly higher values for the BrMarLitt samples which agrees with the presence of a significant portion of marine carbonate in these samples (Fig. 14d). On the other hand, all the BrMarLitt have $\delta^{13}\text{C}$ values lower than the Baltic Sea samples from outside the Forsmark coast (values in the order of 0 to -3 ‰ $\delta^{13}\text{C}_{(\text{PDB})}$). This indicates an uptake of organic or microbial mediated carbon (with low $\delta^{13}\text{C}$) during the passage through the seabed sediments or the upper part of the rock. Assuming an addition of 30 to 60 % of the carbon from reactions (microbial or dissolution of calcite) contributing low or non ^{14}C , it yields to residence times from the present to around 5000 to 10,000 years for the Littorina waters. The lowest radiocarbon contents (around 10 to 15 pmC) were measured in two BrGl samples from the SFR and in a few BrTrans and BrMarLitt from both sites. This information strengthens the view that the marine waters with higher salinity than the present Baltic Sea are the Holocene Littorina Sea waters and that at least part of the glacial waters are from the last deglaciation.

5.3.3. ^{36}Cl and He

The contribution of the cosmogenically produced ^{36}Cl with a half-life of around 300,000 y is relatively high and variable in the surface waters and the near-surface groundwaters (Fig. 15a; all the samples with ^{36}Cl data have been plotted in this figure since the number of analyses is considerably low). In contrast, marine waters are very low in ^{36}Cl ($^{36}\text{Cl}/\text{Cl}$ 5×10^{-15}) and this is reflected in the brackish marine groundwaters in the Forsmark area (BrMarBal and especially BrMarLitt). At greater depth and with longer residence times the subsurface production of ^{36}Cl becomes evident, and it is assumed that after ca. 1.5 Ma the dissolved chloride is in isotopic equilibrium with the rock. A possible equilibrium situation is shown by the BrGl, BrNonMar and Saline groundwaters (Fig. 15a). However, due to e.g. mixing with porewaters and/or small portions of very old and saline waters, the values can end up in the interval calculated for equilibrium although the entire water body has not been isolated for 1.5 Ma. The BrGl waters show different paths in the two sites, with a more distinct marine portion in the ones from the SFR whereas the BrGl from Forsmark inland tend to have a mixing line towards the BrNonMar. Finally, the BrTrans groundwaters show values between the equilibrium and the values measured in the BrMarLitt, further supporting a mixture between BrMarine and BrNonMarine components for this water type.

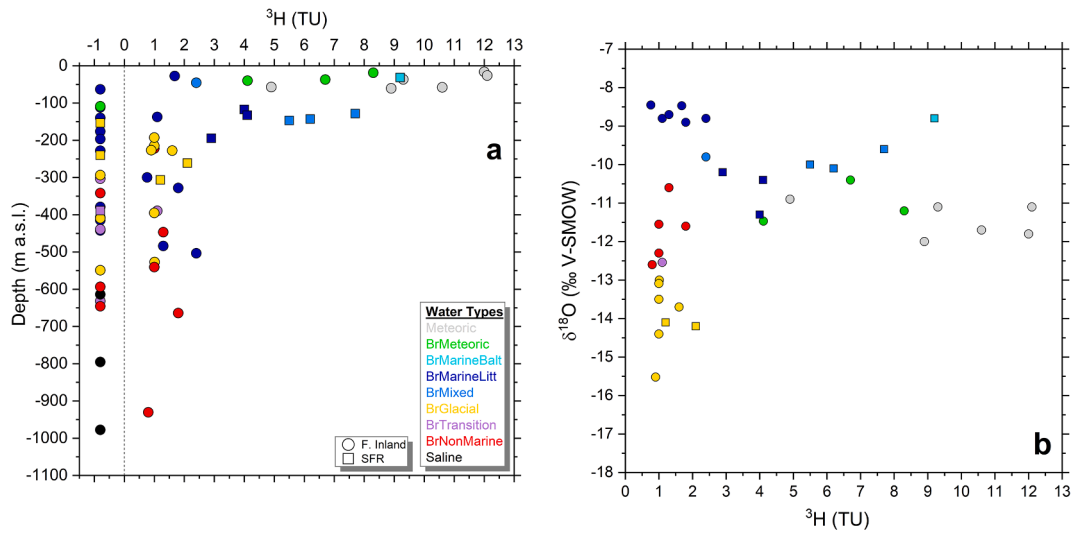


Fig. 13. Tritium versus depth (a) and $\delta^{18}\text{O}$ (b). The values below zero in panel (a) correspond to the tritium detection limit of 0.8 TU.

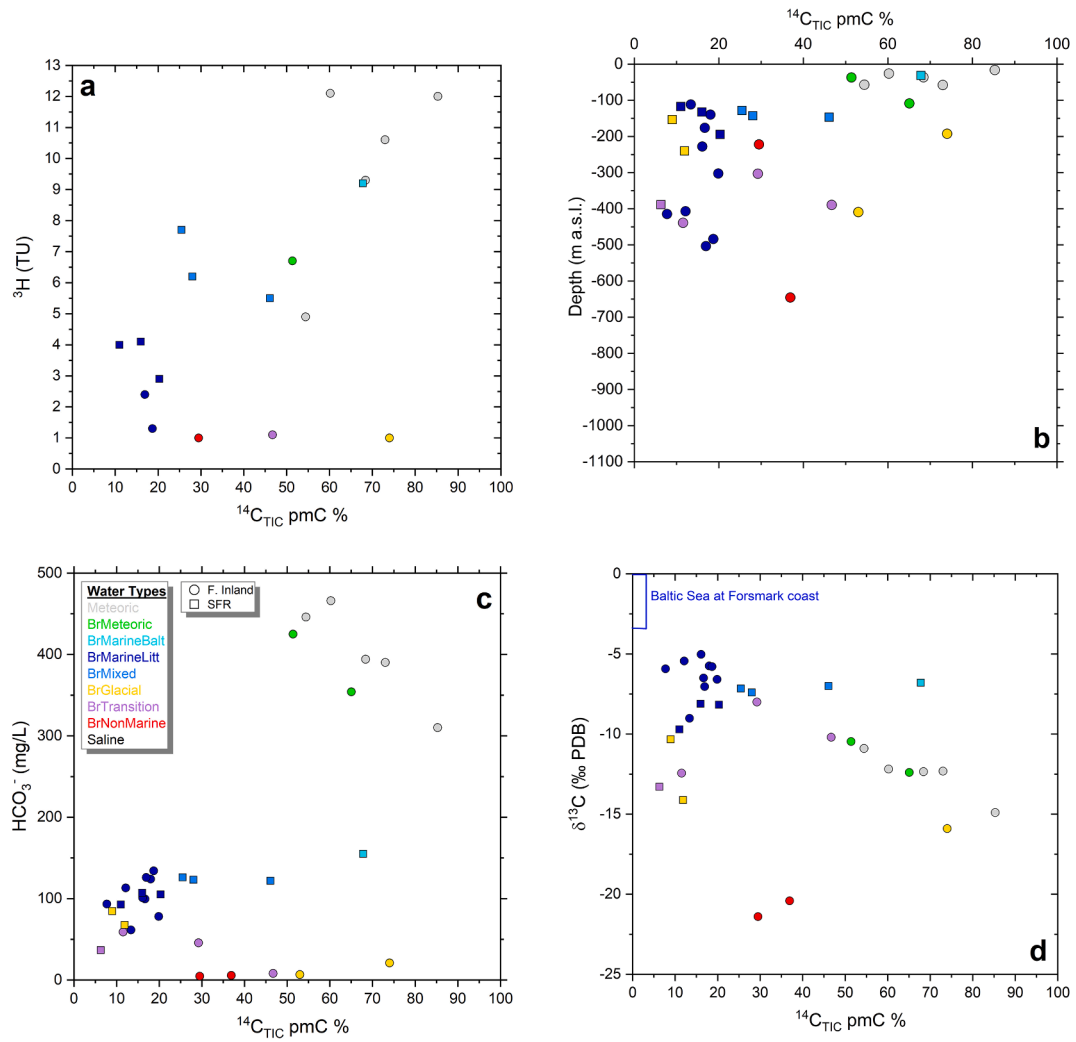


Fig. 14. $^{14}\text{C}_{\text{TIC}}$ versus ^3H , depth, HCO_3^- and $\delta^{13}\text{C}$ (in this last plot, the range of values measured in the present Baltic Sea outside the Forsmark coast, are shown for comparison). Note that there are no carbon isotopes data for the saline waters due to their very low HCO_3^- content.

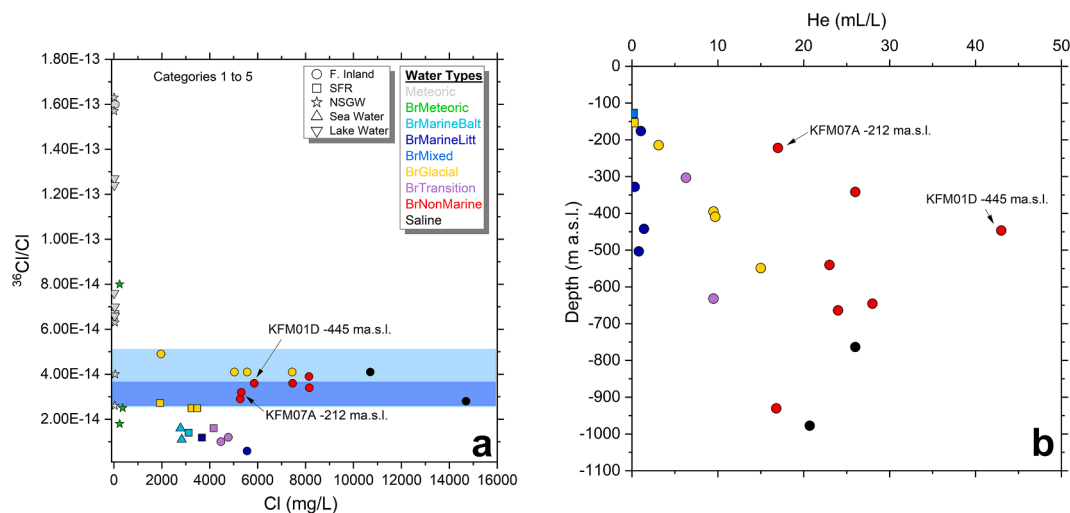


Fig. 15. (a) $^{36}\text{Cl}/\text{Cl}$ (atomic ratio) is plotted versus Cl content in all the waters where the value has been analysed (including category 5 values and some surface waters, Sea and Lake, and near surface groundwaters, NSGW). The blue fields represent calculated equilibrium values with the host rock (the entire field representing granodiorite to late granites of the Forsmark area and the darker blue part represents only the two most common rock types in Forsmark inland (meta-granodiorite and metagranitoid; calculation of equilibrium provided by J. Byegård, Pers. Com.). (b) Distribution of He versus depth. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Helium-4 is assumed to grow in crystalline bedrocks due to alpha decay of the U and Th present in the rocks and, therefore, it is expected that the longer the residence time the higher the ^4He content. Helium isotopes have not been measured in the Forsmark groundwaters but total He is assumed to roughly correspond to ^4He . The He content in the groundwaters (Fig. 15b) increases from BrMar to BrGl and BrTrans and finally to BrNonMar and Saline, in all the cases irrespective of the depth. For the BrNonMar and Saline groundwaters the He values are in the interval of 15 to 30 mL/L with the exception of an even higher value (42 mL/L He) in borehole KFM01D at -445 m depth. This section was resampled 8 years after the first sampling and the measured value for He was equally high (39 mL/L). Another interesting fact is that even the shallowest BrNonMar water (from KFM07A at 212 m depth) shows a $^{36}\text{Cl}/\text{Cl}$ value (Fig. 15a) in the expected range for equilibrium with the rock and a He content of 17 mL/L supporting a very long residence time, probably older than Weichsel.

Modelling of residence times based on He can also be done using the U and Th contents in the host rock, the rock porosity and the diffusion coefficients. Such calculations were reported in Smellie et al., (2008) indicating ages from 50,000 to 100,000 y for BrMarLitt samples and in the order of 500,000 y to 1,500,000 y for BrNonMar samples. Trinchero et al. (2014) made alternative calculations and reported even older ages based on the same material.

The lack of He-isotope measurements, the variations in U and Th contents in the different rock types and the different assumptions on portion of degassing of He from great depth compared with the *in situ* production, make the age calculations *sensu stricto* highly uncertain. For example, the BrMarLitt waters show ^{14}C contents that indicate a Holocene origin, i.e. some thousand to ten thousand years in accordance with the present understanding of the site, whereas the He age calculations end up with much older ages. The uncertainty in He age calculations has also been addressed by Gerber et al., (2017) and Purtchert et al. (2023) pointing to e.g. the need for basal He flux information. Nevertheless, the He contents in the groundwaters at Forsmark show a sequence of relative ages (Fig. 15b) that fits with the paleohydrogeological model of the site and, as such, it helps to confirm the groundwater types and their origins.

5.3.4. Summary of residence times

Table 2 shows a compilation of all the residence time parameters and they are described briefly next. Young fresh to brackish groundwaters

(tritium > 4TU; Fig. 13) affected by the meteoric or the Baltic Sea waters recharge are only present in the upper 100 to 150 m of the bedrock. These recharge waters are assumed to have resided in the rock only for decades. Older waters affected by marine waters more saline than today's Baltic, follow at greater depths and most of them show ^{14}C values compatible with Holocene ages (Fig. 14) supporting the suggested connection with the Littorina transgression some 7000 y ago.

A few waters with glacial components can be clearly associated to the last glaciation-deglaciation whereas most of the BrGl groundwaters were not possible to date due to their low HCO_3^- contents. Nevertheless, the He content measured in the BrGl and the BrTrans puts them in a time span between the Littorina period and the long residence time characteristic of the BrNonMar and Saline waters with the later showing ages in the order of hundreds of thousand of years, validated by $^{36}\text{Cl}/\text{Cl}$ (Fig. 15a).

The age evolution does not follow a clear depth trend which is shown by the distribution of waters with very different residence times (e.g. Fig. 15b). While some groundwaters have been able to intrude deep into the bedrock system (i.e. detected Holocene waters at 500 m in some sections), others have remained immobile at shallow depths for very long times (i.e. the BrNonMar waters with long residence times at around 200 m) leaving isolated groundwater pockets and giving a heterogeneous compartmentalisation in the bedrock system.

6. Hydrogeochemical model for the groundwater evolution

All the results and interpretations presented in the previous sections, including the qualitative and quantitative evidence of the groundwaters residence times, have been integrated in the hydrogeochemical model that is presented below. There still exist uncertainties mainly due to the limited number and uneven distribution of the sampling points in the whole bedrock volume. However, the model presented here can be considered representative of the Forsmark area groundwater system at present thanks to the combination and integration of the understanding of the physicochemical characteristics of the groundwaters and of the hydrogeology and paleohydrogeology.

Fig. 16 shows the present distribution of the water types in a 3D view. The four panels show different orientations to facilitate the detailed view of different parts of the rock mass. The location of the 66 selected borehole sections is shown in the figures coloured by the water type code. In some of the panels, the preliminary layout of the future repository in Forsmark inland and the existing SFR facility are shown,

Table 2
Summary of the origin, residence time and depth location of the different groundwater types.

Groundwater Type	Origin	Residence time	Depth/Site
Meteoric	Meteoric recharge	Modern water from the last 60 years; TU > 4	SFR: absent Fors. Inland: max 50 m
BrMet	Met. Recharge + water rock interaction	Modern water from the last 60 years; TU > 4	SFR: absent Fors. Inland: max 100 m
BrMarBal	Modern Baltic infiltration	Modern water from the last 60 years; TU > 4 Low ³⁶ Cl	SFR: max 50 m Fors. Inland: almost absent
BrMix	SFR: Mixture of Marine (old and new) and glacial Fors. Inland: Mixture of littorina, glacial and/or meteoric	Components of modern water from the last 60 years	SFR: 150 – 200 m Fors. Inland: 50 m
BrMarLitt	Littorina sea infiltration, reaction with marine sediments and mixture with the previous waters	<ul style="list-style-type: none"> • ¹⁴C: from present to 5,000–10,000 y (Holocene) • Low ³⁶Cl • He < 2 mL/L 	SFR: 100 to 200 m Fors. Inland: 30 – 500 m
BrGl	Glacial meltwater from different deglaciation periods	Some of them are from the last glaciation-deglaciation (11,000 to 20,000 y), others are possibly from older glaciations based on: <ul style="list-style-type: none"> • ³⁶Cl: equilibrium with the rock • 3 < He < 15 mL/L • ³⁶Cl: between marine and non-marine waters. • 3 < He < 15 mL/L 	SFR: 150—300 m SFR Fors. Inland: 200 – 550 m
BrTrans	Mixture of marine and non-marine waters.	<ul style="list-style-type: none"> • ³⁶Cl: between marine and non-marine waters. • 3 < He < 15 mL/L 	SFR: ≈ 400 m Fors. Inland: 250 – 650 m
BrNonMar	Old non-marine waters including components of old meteoric waters (from warm and cold climates) and even older non-marine groundwaters.	<ul style="list-style-type: none"> • Older than the last deglaciation (>15,000 y) • ³⁶Cl: equilibrium with the rock • He: 15 to 30 mL/L 	<ul style="list-style-type: none"> • Only sampled in Fors. inland: • 200—950 m
Saline	The oldest and more saline non-marine groundwaters.	<ul style="list-style-type: none"> • Residence times in the order of > 100,000 y • Older than the last deglaciation (>15,000 y) • ³⁶Cl: equilibrium with the rock • He: 15 to 30 mL/L • Residence times in the order of > 100,000 y 	<ul style="list-style-type: none"> • Only sampled in Fors. inland • 600 – 1000 m

together with some of the more transmissive gently dipping fracture zones (ZA2-ZF1 and ZH2, in purple colour as in Fig. S1.1; Supp. Mat.) and some of the vertical ones that separate important parts of the rock system: the regional Singö zone (DZ Singö) and the local zone 60 (Z60; both in black as in Fig. S1.1; Supp. Mat.). To understand the present groundwater conditions, and to illustrate the description of this understanding, Fig. 17 shows a simple sketch of the succession of mixing events over time and the depth distribution of the groundwater types. From up to down: a) situation prior to the last deglaciation, b) last deglaciation and intrusion of Late Weichselian meltwater, c) the Littorina Sea water penetration caused by density intrusion, and d) and e) the present situation in Forsmark inland and SFR, respectively.

The presence of saline groundwaters (Cl values higher than 10,000 mg/L) in the deeper parts of the area seems to reflect the groundwater conditions before the last deglaciation (Fig. 17). The behaviour of Cl, Mg and $\delta^{18}\text{O}$ reflects the mixing and dilution of a deeper, older and more saline groundwater, with other less saline and younger groundwaters from shallower depths. That is, prior to the last deglaciation, dilute waters must have entered the bedrock during warm and cold periods (including previous glaciations) and mixed with the already present old and saline non-marine groundwaters producing a hydrochemical transition from brackish (Brackish non-marine type; BrNonMar) to saline (Saline type) groundwaters towards depth (Fig. 17). This general trend is, however, inhomogeneously distributed in the bedrock system supporting the compartmentalisation of the fractured bedrock and the presence of isolated pockets of older waters at shallower depths than expected (as confirmed by the residence time results). At present, the Saline water type has only been sampled at depths below 600 m but the BrNonMar waters have been found as shallow as 200 m and down to depths of 950 m (Fig. 17).

During the glaciation and deglaciation phases of the Weichselian, dilute glacial meltwaters with very low $\delta^{18}\text{O}$ penetrated the Forsmark area mainly along the highly transmissive deformation zones, but also into presently less conductive or dead-end fractures that were kept open by the different stress regime prevailing beneath the ice (Fig. 17). Some of these fractures may have become less transmissive when the ice load disappeared and that led to the formation of 'pockets' of glacial meltwater heterogeneously distributed within the rock mass (Figs. 16 and

17). This is also supported by U-series measurements of the fracture coatings (Suksi et al., 2021). The $\delta^{18}\text{O}$ values indicate that the glacial meltwaters, that can be from the Weichselian and/or previous glaciations, penetrated down to 550 m depth and even deeper in some places. Mixing with the older non-marine saline to brackish groundwaters gave rise to the Brackish Glacial (BrGl) groundwater type. These groundwaters are observed in the Forsmark inland between 200 and 550 m depth, and in low transmissive bedrock volumes above and below the gently dipping zone H2 at the SFR (150 to 300 m; Figs. 16 and 17). The lower contents of Cl, Ca, Mg, Na, K, SO_4^{2-} and mainly the lower $\delta^{18}\text{O}$ values in the SFR samples than in Forsmark inland for the same depths, indicate the presence of higher portions of glacial meltwater in the SFR site. However, there is a relatively deep penetration of glacial meltwater in certain zones in Forsmark inland as interpreted from the relatively low $\delta^{18}\text{O}$ (< -13 ‰) values in the saline waters, compared with similar waters from Laxemar, Oskarshamn and Olkiluoto which are generally > -12 ‰ for the same salinity (Pitkänen et al., 1999; Pitkänen et al., 2004; Smellie et al., 2008; Gimeno et al., 2014).

The presence of dilute glacial meltwater filling the upper several hundred meters of the bedrock fractures made the subsequent density driven infiltration of the Littorina seawaters possible producing varying degrees of mixing with the earlier brackish-glacial groundwaters and deeper non-marine waters (Fig. 17). The result of this mixing event is the groundwater type named Brackish Marine Littorina (BrMarLitt). Being a mixture with the Littorina Sea, these waters are characterised by high concentrations of typical marine components such as Mg, SO_4^{2-} , HCO_3^- and SiO_2 and an important enrichment in redox elements like Mn, Fe, NH_4^+ and U due to the interaction with the marine sediments. Additionally, considering that the estimated $\delta^{18}\text{O}$ value for the Littorina Sea waters is -4.7 ‰ SMOW (Pitkänen et al., 1999), the BrMarLitt groundwaters show a wide range of $\delta^{18}\text{O}$ values due to the mixing with BrGl waters with depleted isotopic signatures.

The density-driven penetration of the Littorina water stopped at the depths where it met non-marine groundwaters with similar density (meaning salinity). In those places another mixed water type was produced, the Brackish Transition (BrTrans) which is quite common at an intermediate depth (250–650 m) in the Forsmark inland while it is only found at the deepest sampled location (around 400 m) in the SFR site.

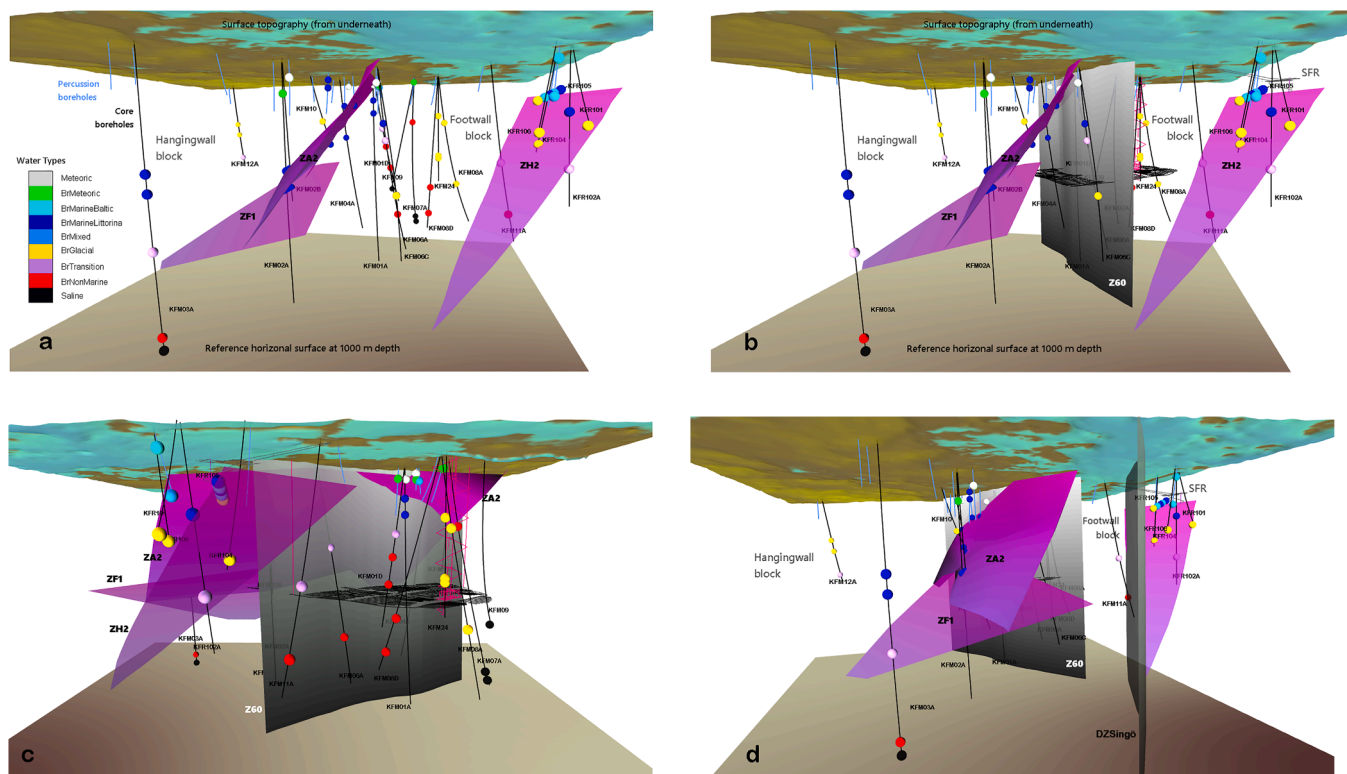


Fig. 16. 3D block of the Forsmark area showing the location of the selected samples coloured by their water type. a) View of the rock volume from the SE (the sea). b) Same orientation of the view; note how the local deformation zone 60 (Z60; Supp. Mat. SM1) divide the repository layout in two parts which have distinctive characteristics: the presence of more BrMarLitt waters in the southern side of zone 60 (panel b), and of more BrNonMar and BrGl in the northern side (panel c). c) View from the NE. d) View from the S showing the main characters of the hanging wall. Here the Deformation Zone Singö is plotted to show the separation of the two sites, Forsmark inland and SFR. The upper surface shows the topography (land and sea) seen from underneath and the lower surface has been drawn at 1000 m depth for reference.

There were also minor fracture systems where mixing did not occur and where the BrGl groundwaters have remained at shallower levels in the bedrock ('pockets') shielded from the passage of the infiltrating Littorina seawater. This is the case for most of the BrGl waters in the SFR (Figs. 16 and 17).

The BrMarLitt type groundwater is primarily associated to the gently dipping fracture zones like H2, A2-F1 (Figs. 16 and 17) and a series of other gently dipping fracture zones characteristic of the hanging wall in Forsmark inland (Fig. S1.1 and 1.2; Supp. Mat). The transition from these waters, with a strong marine signature, to the non-marine waters occurs at different depths in different parts of the Forsmark area (see Figs. 16 and 17) but the maximum penetration seems to be around 500 m. Similar situations were found in Laxemar (Sweden; Smellie et al., 2008; Laaksoharju et al., 2008; Gimeno et al., 2014) and Olkiluoto (Finland; Pitkänen et al., 1999; Pitkänen et al., 2004).

Following the Littorina stage (and the subsequent uninterrupted transition to the present Baltic Sea conditions) the gradual land uplift formed the present Forsmark inland while the SFR area continued to be submerged so the hydrogeochemical evolution has been slightly different (Fig. 17). The SFR excavation/construction phases have resulted in the drawdown of modern Baltic Seawaters giving rise to the Brackish Marine Baltic groundwater type (BrMarBal) in the upper parts of the highly transmissive deformation zones that previously hosted BrMarLitt groundwaters and now are influenced by drawdown. These waters are more dilute than the preceding BrMarLitt groundwaters and less affected by water-rock interaction.

As a result of the mixing of these recent (BrMarBal) or previous (BrMarLitt) marine waters with BrGl groundwaters, a new mixed water type, Brackish Mixed (BrMix) appears in different parts of the SFR, being most probably a product of additional anthropogenic mixing due to the

increased flow caused by drawdown. BrMix groundwaters also occur at a few shallow locations in Forsmark inland (around 50 m depth) close to the sea where some mixture with meteoric water is also a possible explanation. Their main hydrogeochemical features are the mixed character of marine (old and new) and dilute (glacial or meteoric) waters.

In the case of the Forsmark inland, the meteoric recharge is responsible for the very dilute groundwaters presently found in the upper part of the rock (down to about 60 m) with the lowest chloride contents and $\delta^{18}\text{O}$ isotopic values around -11‰ i.e., the Meteoric groundwater type. The groundwater is influenced by reactions in the overburden and the composition differs from meteoric/surface waters. Further down (to around 100 m depth) some mixing and additional water-rock interactions have occurred and the groundwater is slightly more saline i.e., the Brackish Meteoric type (BrMet). At these depths, because the hydraulic system is more dynamic due to the higher frequency of open fractures, climatic changes have resulted in the cyclic introduction and flushing out of different groundwater types. This is indicated by ^3H and ^{14}C which show that the groundwaters at this depth range have got contributions from recharge during the last decades, whereas the main water body may reach up to hundreds or even thousand years. Still, this agrees with the palaeohydrogeological evidence that points to the emergence from the Baltic Sea starting at Forsmark some 2500 years ago and therefore subsequently facilitating meteoric water recharge.

The effects of these mixing events can be seen in the contents and distribution of many dissolved chemical and isotopic components that are clearly controlled by mixing. However, as a result of these mixing processes, water-rock interaction and microbial mediated reactions also became effective in the complex evolution of the groundwaters in larger

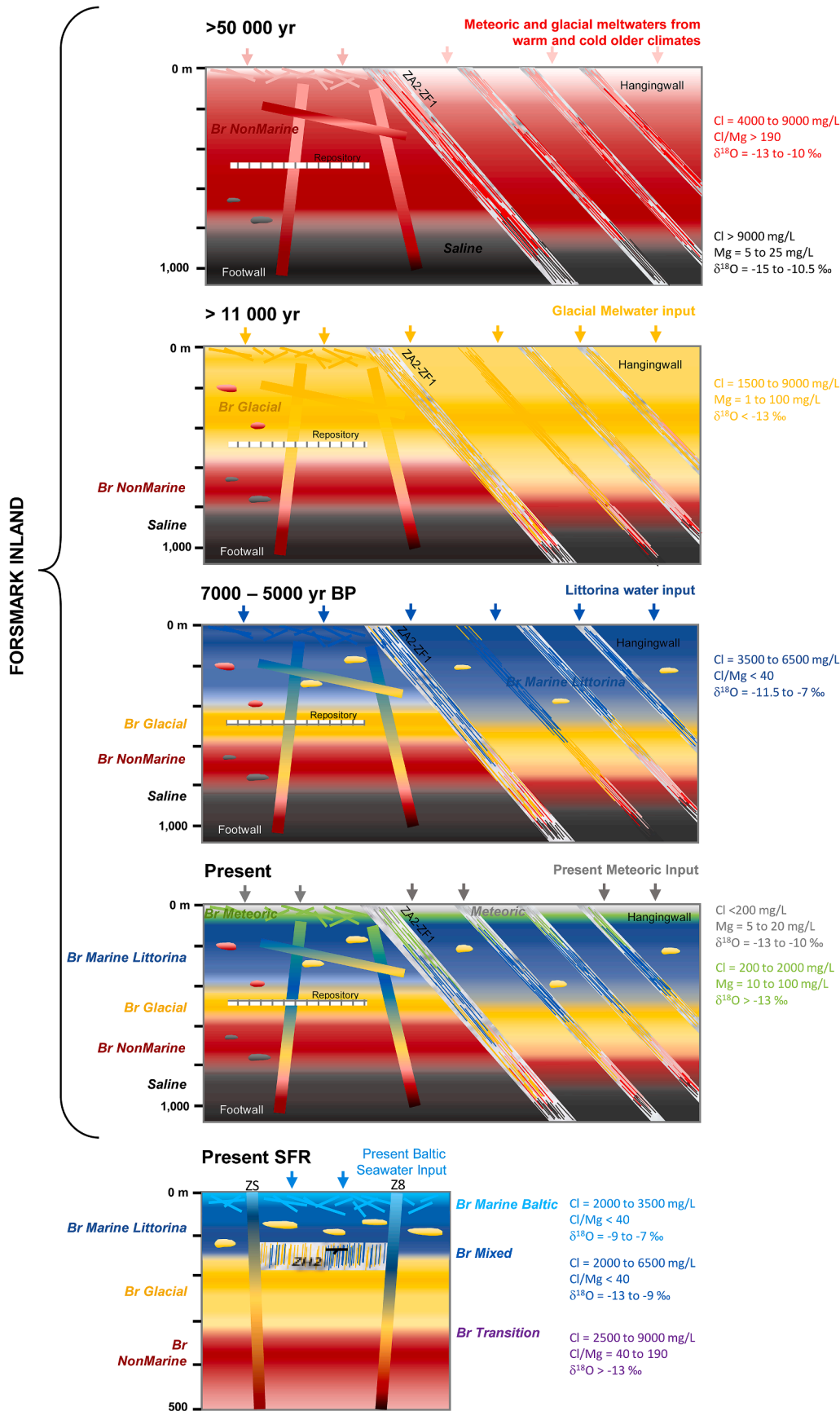


Fig. 17. Idealised conceptual model of the different recharge and mixing events and the distribution of the resulting groundwaters. The first four schemes represent different periods in the Forsmark inland (including the present) and the last scheme represents the present situation in SFR site. The three main criteria used for the definition of the water types are indicated for each of them. In the cases in which the Cl/Mg is not used as a criterion, the range of Mg composition typical of the water type is indicated. There are no sharp limits between the water types and that is represented in the plots as fading colours. The two groundwater types that represent important natural or anthropogenic mixing situations (BrMix and BrTrans) are specifically indicated in the SFR profile. The vertical fracture zones represented in that profile, ZS and Z8, correspond to the regional Singö zone and Zone 8.

or smaller degree, on some groundwater constituents.

One of the main reactions triggered by mixing is cation exchange. The dilution or concentration scenarios associated to the different mixing events control the directionality of the heterovalent cation exchange processes (Appelo and Postma, 2005; Gimeno et al., 2008) affecting Na, K, Mg and Ca. Another important set of reactions is the dissolution-precipitation of aluminosilicates (adularia, albite and several clay minerals identified in the fracture fillings), especially in the groundwaters with the longest residence times where equilibrium or near equilibrium situations with these minerals can be reached. These reactions participate in some degree in the control of dissolved Na, Mg and K and Ca. They also contribute to the control of alkalinity and pH although these parameters are also importantly affected by the calcite equilibrium. Silica contents are controlled by the reactions involving aluminosilicates and, in the last term, by the equilibrium with chalcidony. Equilibrium with calcite (even with slight oversaturation) is rapidly attained at shallow depths and it is a very important and ubiquitous process in the groundwaters of the Forsmark area. It is the main control of alkalinity and pH and also participates in the control of the dissolved calcium.

Despite the possible effects of the above discussed reactions on the Na, Mg, K and Ca contents, it is important to keep in mind that the progressive mixing with marine waters or with the deeper Ca-Na-rich groundwaters masks most of the effect of the mass transfers caused by all these reactions.

The microbially-mediated reactions linked to the activity of MRB, IRB, NRB and SRB, are very important in the behaviour and evolution of Mn, Fe, NH_4^+ and S^{2-} . But there are also some inorganic reactions that affect their contents:

- the dissolution of Mn(II)-bearing minerals, Mn and Fe oxydes and oxyhydroxides, Fe-silicates, ferrous iron sulfides, and U-bearing minerals;
- the surface processes on Fe oxyhydroxides; and
- the equilibrium conditions with ferrous iron monosulfides, rhodochrosite and siderite.

The equilibrium with the last two minerals seems to be an inherited character from the infiltration of the Littorina waters through marine sediments (the same could be said about the NH_4^+ enrichment) and it underlines the importance of microbially-mediated reactions and water–rock interactions of the marine waters in the sea sediments, prior to their entrance into the groundwater system, as some of their effects remain as tracers of the existence of a marine component in the subsequent mixing processes.

One of the main conclusions for the conceptual understanding of the hydrogeochemistry is that the concentrations of redox components, together with the potentiometrically measured Eh values, show that reducing conditions prevail in all the groundwaters although without a clear trend with depth. These reducing conditions indicate that the inorganic and/or microbially-mediated reducing capacity of the groundwater–rock system is enough to compensate for the possible episodic disturbances associated to the input of oxidising waters (e.g. glacial or meteoric waters) along the palaeohydrological history of the area. This is also supported by the observations of unaltered pyrite in fractures almost up to the bedrock surface (Sandström et al., 2008; Sandström et al., 2014).

The identification of the sequence of mixing events along the history of the studied area and the characterisation of the groundwater types produced due to those events that has been presented here will allow the quantification of the involved mixing proportions and of the associated water–rock interaction processes that will be addressed in a future paper.

7. Conclusions

The hydrogeochemistry of the groundwaters present down to ≈ 1000

m depth in the crystalline bedrock of the Forsmark area is mainly a product of 1) the recharge of glacial meltwater from the last and most probably also from former glaciations; 2) the subsequent evolution of the Baltic region during the last 10,000 years, which has led to intrusions of both, more saline Littorina Sea waters and present Baltic Sea waters (this last in the tunnels of the SFR); and 3) the recharge of recent meteoric water in the upper 50–100 m of the Forsmark inland. These different types of recharge waters have mixed either with each other or with preexisting non-marine brackish to saline waters with very long residence times in the bedrock (in the order of many hundreds of thousands of years). It is also clear that even if chemical and microbial reactions have occurred over time, it is still possible to recognise the influence of the different waters that have entered the rock system especially during the last glaciation and thereafter. This is because mixing is the main controlling process of several groundwater components.

The geology of the area and the changes in the hydraulic head over time have produced the characteristic heterogeneous interconnection of different parts of the rock system and have conditioned the distribution of the groundwaters. This compartmentalisation of the bedrock is responsible for the presence of waters with very different residence times and compositions at similar depths.

The understanding of this complex fractured crystalline rock system has been achieved thanks to the thorough site characterisation of the area performed by SKB during the last 20 years. The integration of all the geoscientific studies gives a high confidence to the proposed hydro-geochemical model.

The model of the area shows the successive inputs of the different recharge waters conditioned by the climate evolution of the area in the past. Since this paleoclimate evolution is expected to be repeated in the future, the conclusions obtained here will be the key for (1) the development of possible hydrochemical evolution scenarios that can affect the repository after closure, and (2) the evaluation of their consequences, at the necessary time scale, in the safety assessments of the future performance of the repositories.

Finally, these results provide a paleohydrogeochemical record of events in line with those found in similar fracture systems (e.g. in the Canadian or Fennoscandian Shield; Clark et al., 2000; Douglas et al., 2000; Pitkänen et al., 2004; Pitkänen et al., 2022) or in the sedimentary aquifers of the Baltic Basin (Raidla et al. 2009; Pärn et al., 2019; Malov and Tokarev, 2019).

Declaration of Competing Interest

The authors declare that they have no known competing 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.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jhydrol.2023.129818>.

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