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Dating of Icelandic Groundwater by Stable Water Isotopes, Tritium and ^{14}C

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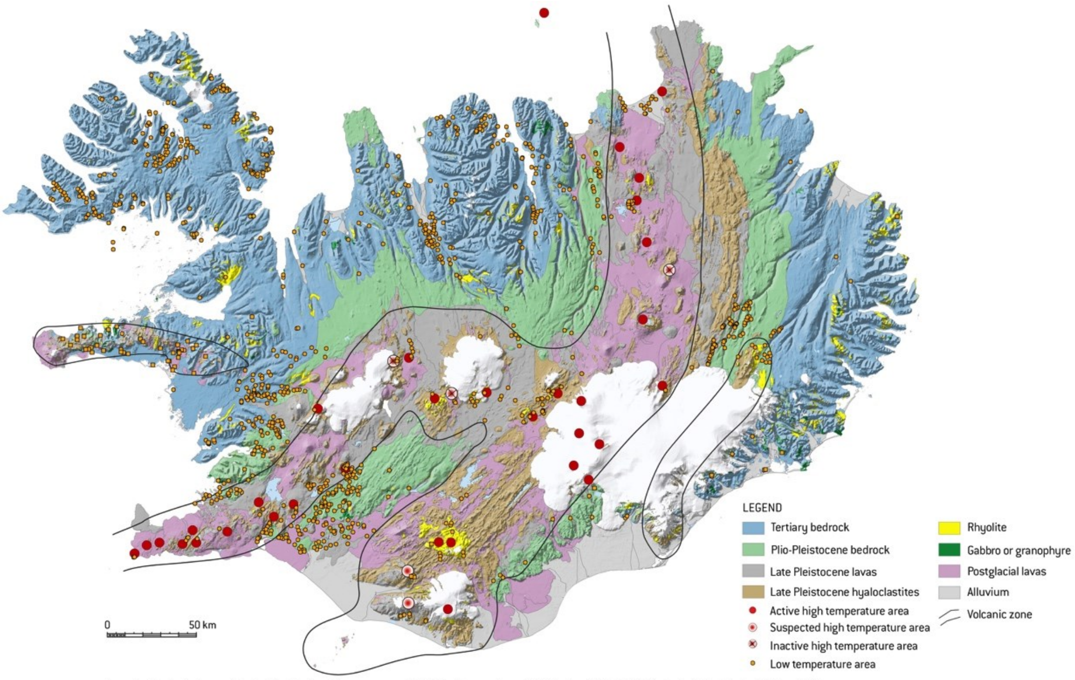
ABSTRACT

The use of water- and carbon isotopes to evaluate groundwater age is reviewed and methods to correct for the various sources of dissolved inorganic carbon in Icelandic groundwater are discussed. Stable water isotopes have revealed that a depleted pre-Holocene component is common within the Icelandic crust and thus offers the opportunity for relative age estimates. Additionally, differences in deuterium excess ($d=\delta^2H-8\delta^{18}O$) of low temperature groundwater have been interpreted as age dependent, either reflecting prolonged water-rock interaction or a change in the precipitation source area reflecting different climate regime.

Water age has also been estimated through carbon isotope measurements and in some instances supported by tritium analyses. Observed apparent ^{14}C ages range from modern to >40,000 yrs BP. Two methods have been applied to correct for dead carbon from the Icelandic basaltic bedrock; firstly the concentration of the incompatible element boron (B) has been used to estimate carbon concentration leached from the rock, and secondly geochemical modeling has been applied by estimating the different sources of dissolved inorganic carbon in the groundwater, identified as leaching from primary rocks, deep degassing of CO_2 (in case of geothermal water), as well as atmospheric and organic carbon.

1. INTRODUCTION

The regional geology of Iceland is characterized by interplay between a divergent plate boundary and a mantle plume. Volcanism is widespread and occurs along Neovolcanic rift zones characterized by volcanic systems comprised of a central volcano associated with fissure swarms (Saemundsson, 1978). Geothermal activity, often connected to the central volcanoes, has conventionally been divided into low- and high- temperature systems (Böðvarsson, 1961; Friðleifsson, 1979). The high temperature systems are associated with active volcanism and rifting whereas the low temperature areas are widespread in the Quaternary and Tertiary formations, often associated with active fissures and faults (Figure 1). More than 90% of the Icelandic bedrock is of basaltic origin and the oldest rocks, found in the western and eastern fjords, are ca 16 M years old. The permeability of the Tertiary lava pile is 1-4*10^{-14} m^2 but for geothermal areas the permeability is several orders of magnitude higher. The deeper crust has a very low permeability as pores and fissures are filled with secondary minerals.



Based on Geological map of Iceland by Haukur Jóhannesson and Kristján Sæmundsson 1999. Iceland. 1:1.000.000. Icelandic Institute of Natural History.

Figure 1: Simplified geological map of Iceland featuring the main rock types, age and the Neovolcanic rift zones. Also shown are geothermal areas, with the high temperature areas located within the active volcanic zones and the low temperature areas mainly outside the volcanic zones.

From around 1960 stable water isotopes have been measured in natural Icelandic waters. The pioneering work of Árnason (1976, 1977) led to comprehensive work on stable water isotopes on Icelandic groundwater and precipitation. His deuterium map of present day precipitation (Figure 2) has extensively been used to trace origin and delineate groundwater flow. For most waters the relationship between $\delta^{18}O$ and $\delta^{2}H$ follows closely the meteoric water line. In some instances an oxygen shift is observed and in case of high temperature groundwater the shift can be as high as 7‰. On rare occasions the isotopic compositions of the waters plot to the left of the meteoric water line, taking to indicate either a mantle/crustal CO_2 mixing with the groundwater in case of naturally carbonated springs or due to different origin of precipitation under a different climate regime (Johnsen et al., 1989). In natural waters in Iceland a large range is found both for $\delta^{18}O$ (-20.8‰ to +2.3‰) and $\delta^{2}H$ (-131‰ to +3.3‰). Some of the waters are more depleted than any present-day precipitation, suggesting a pre-Holocene water within the Icelandic crust.

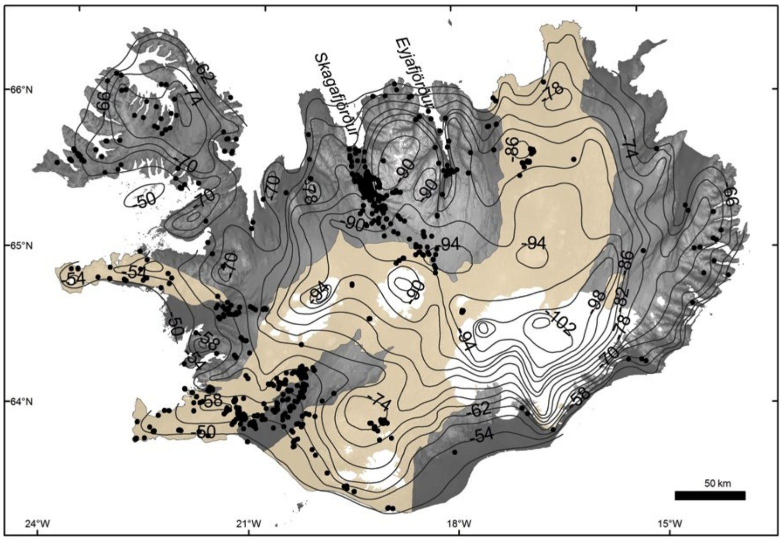


Figure 2: $\delta^{2}H$ contours of present-day precipitation (Árnason, 1976), sample locations (black dots) and the volcanic belts (light brown). Specially marked are the areas of Skagafjördur and Eyjafjördur, N-Iceland, which are specifically discussed in the text. Also specifically mentioned in text are the samples from the Southern Lowlands referring samples from between the volcanic zones in S-Iceland.

Comprehensive information on water chemistry is accessible for groundwater in Iceland. Temperature and Cl concentration are the independent variables that control the composition of Icelandic groundwater. It has been demonstrated that local chemical equilibria between primary fluids and geothermal minerals is approached for all major elements (except Cl) at temperatures as low as 100°C (e.g. Arnórsson et al., 1983).

Tritium has been measured for a limited number of water samples in Iceland (Arnórsson and Sveinbjornsdóttir, 2004; Theodórsson, 1967) both for age control and to estimate travel times of groundwater (Sveinbjornsdóttir and Johnsen, 1992).

Additionally, carbon isotopes have been measured in many Icelandic groundwater samples to evaluate carbon sources and reactions as well as water age (Sveinbjornsdóttir et al., 2010; Stefánsson et al., 2016, 2017). Observed apparent ^{14}C ages range from modern to >40,000 yrs BP. To correct for dead carbon from the Icelandic bedrock (mainly basalt) the concentration of the incompatible element boron (B) has been used to estimate carbon concentration leached from the rock (Sveinbjornsdottir et al., 2001). This B-based correction has been found to work well within well-defined watershed areas if insignificant CO_2 gas degassing of melt originating from the upper mantle or the lower crust affects the groundwater system. However, this method fails in areas where marine sediments are part of the bedrock (Sveinbjornsdottir et al., 2004) or where inflow of CO_2 gas from below plays a part in the carbon water budget. In recent years geochemical modeling approaches have been applied to correct apparent ^{14}C ages by estimating the different sources of dissolved inorganic carbon in the groundwater, identified as leaching from primary rocks, deep degassing of CO_2 (in case of geothermal water), as well as atmospheric and organic carbon (Stefánsson et al., 2016, 2017).

In this paper the use of water- and carbon isotopes to evaluate groundwater age for non-thermal and thermal water samples will be given and methods to correct for the various sources of dissolved inorganic carbon in Icelandic groundwater will be discussed.

2. METHODS

2.1 Sampling and analyses

Non-thermal and thermal groundwater samples were collected from springs and boreholes, in total over 300 samples. Sample locations are shown in Figure 2. The water samples were analyzed for major elements as described by Arnórsson et al. (2006). For dissolved inorganic carbon (DIC) analyses the thermal water samples were cooled down to avoid CO_2 degassing, upon sample storage using an in-line cooling coil, collected into gas-tight amber glass bottles and analyzed using modified alkalinity titration (Stefánsson et al., 2007). The pH was determined in untreated samples on site using pH electrodes (Arnórsson et al., 2006). The B concentration was measured spectrophotometrically on filtered samples (0.2μm cellulose acetate filter) or using ICO-OES, ICP-MS

(Wikner, 1981). The analytical precision for major elements based on duplicated analyses was found to be <0.3% at the 95% confidence level and for pH<±0.05.

2.2 Stable water isotopes

Samples for oxygen ($\delta^{18}O$) and hydrogen (δ^2H) isotope analyses were collected into 60 mL gas-tight amber glass bottles. Oxygen was extracted from the water samples by the method of Epstein and Mayeda (1953). Hydrogen isotope analysis based on the zinc reduction method (Coleman et al., 1982) was used until 1998 and later by the H_2-water equilibration method using a Pt-catalyst (Horita, 1988). The analyses were performed on a Finnigan MAT 251 mass spectrometer at the University of Iceland and the results reported in terms of the conventional δ-notation in ‰, relative to the VSMOW standard. Replicate analysis of the reference material yielded a standard deviation of ±0.05‰ and ±0.7‰ for oxygen and hydrogen, respectively.

2.3 Carbon isotopes

The samples for carbon isotope measurements ($\delta^{13}C$ and ^{14}C) on DIC were collected into a 1L gas-tight amber glass bottles, and 2-3 drops of $HgCl_2$ (3.7g/50mL) were added to the sample to prevent any photosynthesis upon sample storage. The DIC from the sample bottles was extracted for purification using a cryogenic extraction line (McNichol et al., 1994). The water samples were acidified in a vacuum system and CO_2 extracted directly by N_2 flowing through the water sample. The collected CO_2 was then partly used for $\delta^{13}C$ measurements and partly converted to graphite for AMS ^{14}C measurements (Sveinbjörnsdóttir et al., 1992).

The $\delta^{13}C$ analyses were performed on a Finnigan MAT 251 mass spectrometer at the University of Iceland and the results reported in terms of the conventional δ-notation in ‰, relative to the VPDB standard. Replicate analysis of the reference material yielded a standard deviation of ±0.1‰. The ^{14}C analyses were carried out using the HVEC EN tandem accelerator of the AMS ^{14}C Dating Centre at Aarhus University, Denmark. The ^{14}C results were normalized to a $\delta^{13}C$ value of –25‰ and expressed in percent modern carbon (pMC) relative to 0.95 times the ^{14}C concentration of the NBS oxalic acid standard (HoxI) or as conventional radiocarbon years BP. Replicate analysis of the reference material yielded a standard deviation of ±1.6 pMC.

2.4 Corrections for rock derived carbon

2.4.1 B-correction

Earlier studies have shown that it is possible to use the amount of the mobile element boron (B) in geothermal waters as a leaching indicator, i.e. its aqueous concentration is a measure of the amount of rock with which the water has reacted (Arnórsson et al., 1993). Sveinbjörnsdóttir et al. (1995) showed a negative, hyperbolic correlation between boron concentration and ^{14}C concentration of water samples, as expected if the boron concentration is a measure of dilution with ^{14}C-dead CO_2. Accordingly, they calculated the ^{14}C dilution, assuming the typical concentration of 1.2 ppm boron and 500 ppm CO_2 for the basaltic bedrock (Arnórsson and Andrésdóttir, 1995) and assuming the ratio of boron to CO_2 is the same in rock and groundwater. In the Skagafjordur region, N-Iceland, this correction methods works well as demonstrated in Figure 3, where after the B-correction the ^{14}C activity decreases in linear relation to increasing water-rock interaction, as measured by the rock derived Cl in the water (Sveinbjornsdóttir et al., 2001).

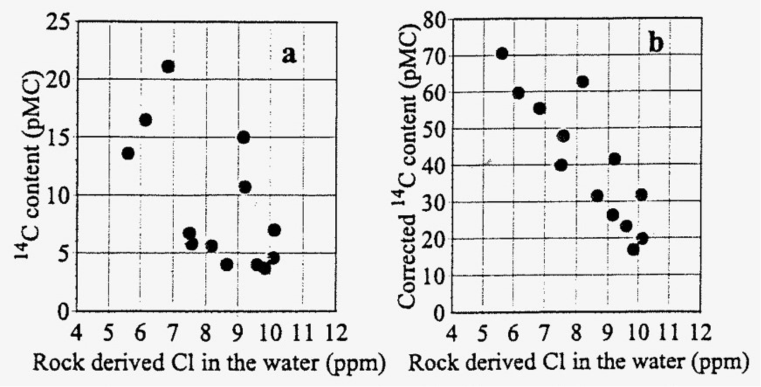


Figure 3: Correlation between the amount of water rock interaction as measured by the rock derived Cl in the water and the a) measured ^{14}C concentration and b) the ^{14}C concentration after the boron based correction (Sveinbjornsdóttir et al., 2001).

This B based correction seems to underestimate the age of groundwater with a considerable pre-Holocene marine component within the Southern Lowlands. It has been suggested that in these Cl rich waters boron is not conservative, as the B-based model assumes, but is incorporated into secondary clay minerals, probably illite (Sveinbjörnsdóttir et al., 2004). Another plausible explanation for the low B concentration and low^{14}C content after B-based correction is of some of the Southern Lowlands groundwater is due to significant deep gas input of ^{14}C dead carbon through the crust into shallower groundwater (Stefánsson et al., 2016).

2.4.2 Geochemical modeling approach

To better constrain the sources and reactions of DIC, an isotope modeling approach was developed (Stefánsson et al., 2016, 2017; Gunnarsson-Robin et al., 2018). The approach includes three steps: (1) development of a conceptual model, (2) quantitative isotope geochemical simulations of the conceptual models, and (3) comparison of data on natural waters with the results of the models. For Icelandic groundwater three major sources of CO_2 were identified 1) dissolution of partially degassed basaltic rocks formed at the surface or at shallow depths 2) atmospheric CO_2 through air-water exchange at surface and 3) input of gas at depth into the groundwater systems that has similar carbon and isotope composition as the pre-erupted melt of the upper mantle and lower crust beneath Iceland (Stefánsson et al., 2016). The reaction and isotope modeling were carried out using the programs PHREEQC (Parkhurst and Appelo, 1999) and IsoGem (Gunnarsson-Robin et al., 2018).

3. RESULTS

Sample locations are shown in Figure 2. Here we report results for waters < 150°C and with pH between 4.5 to 10.5 at 20°C. Most of the water samples are dilute, with chloride concentration < 50 ppm, explained by low Cl concentration of basaltic rocks that make up more than 90% of the Icelandic crust (Sigvaldason and Óskarsson, 1976; Arnórsson and Andrésdóttir, 1995). Some samples from low grounds showed signs of a seawater component with chloride concentration up to 20000 ppm. The analytical results are shown on Figures 4 and 5 for water isotopes and carbon isotopes respectively. The relation of δ^2H-δ^{18}O of the water samples mainly follows the World Meteoric Water Line (Craig, 1961), as demonstrated in Figure 4. Some waters show a slight oxygen shift mainly due to water-rock interaction. On Figure 4 water-rock reaction progress for 0.1 and 1 mol basalt per kg water is shown. Some of the waters are more depleted than any present-day precipitation, suggesting a pre-Holocene water within the Icelandic crust. Tritium was measured for a limited number of samples within the Skagafjordur region in N-Iceland, with the observed range of -0.4 to +13.8 TU (Sveinbjornsdóttir and Arnórsson, 1998; Arnórsson and Sveinbjornsdóttir, 2004). Figure 5 shows the large range in measured values of δ^{13}C (-27.4 to +2.0 ‰) and ^{14}C (0.6 to 118 pMC).

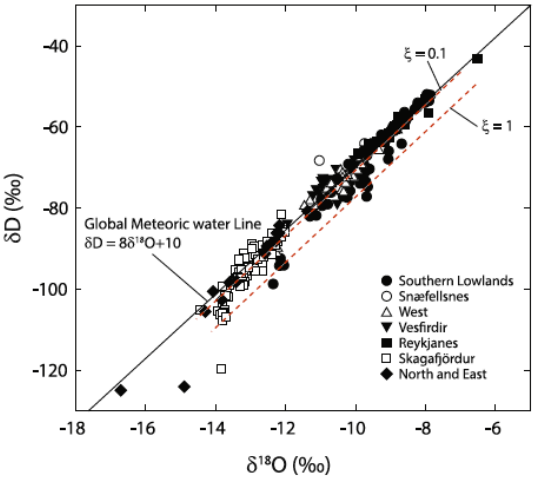


Figure 4: The relation of δ^2H-δ^{18}O mainly follows the World Meteoric Water Line (Craig, 1961). Some of the waters are more depleted than any present-day precipitation, suggesting a pre-Holocene water within the Icelandic crust. Some waters show a slight oxygen shift mainly due to water-rock interaction. Reaction progress for 0.1 and 1 mol basalt per kg water is also shown. Different symbols refer to different locations in Iceland.

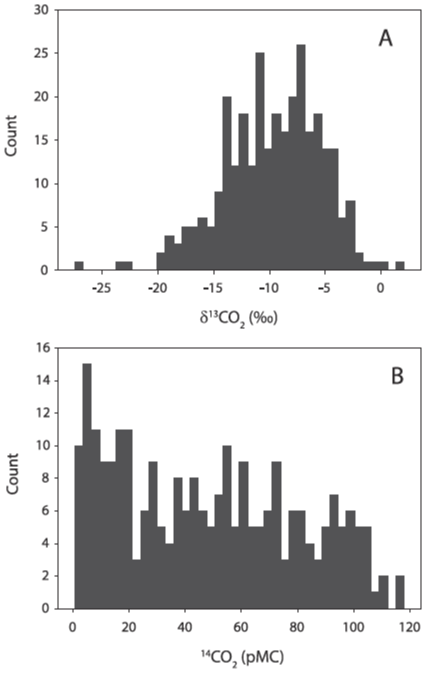


Figure 5: The measured range in carbon isotopes is large, both for A) δ^{13}C (-27.4 to +2.0 ‰) and B) ^{14}C (0.6 to 118 pMC).

4. DISCUSSION

Chemical and isotope compositions of groundwater often display a complex story. The waters are most often mixed with the components originating from different conditions and of different age and affected by water-rock interaction to a varying degree. These processes need to be considered in order to develop a hydrogeological model of groundwater systems. In this context dating is a key factor (IAEA, 2013; Kazemi et al., 2006). In case of Icelandic groundwater the observed age is most often the average age of mixed water of different origin and ages. It is however of great significance to be able to constrain a timescale (even just a relative timescale) to understand hydrogeology and hydrological history of a particular groundwater system.

4.1 Geographical distribution of groundwater with a pre-Holocene component

In Iceland stable water isotopes have been applied to estimate relative ages of groundwater, especially to assess if a pre-Holocene component is present in a specific groundwater system. Measurements have revealed that in the Icelandic crust more depleted water than modern precipitation can frequently been found. This has been interpreted to mean that the groundwater has a component of a depleted precipitation probably from the last glaciation (>12,000 yrs BP) when climate was colder than at present and precipitation thus more depleted. In Figure 6 the distribution of observed groundwater with a pre-Holocene component is shown. The figure demonstrates that these old waters are localized on low grounds and seem to be hydrologically stagnant. The most comprehensive study of these waters is from the Skagafjördur valley in N-Iceland. There the waters range in temperature form about 13-90°C and have a very distinct chemistry that reflects a maximum amount of water-rock interaction. They show extreme low values of tritium and the highest ^{14}C ages, which after boron-based correction for dead rock derived carbon due to interaction with the host rock, range mostly between ca. 3000 to 17,000 BP. This observed age range reflects mixing to varying extent of ice age water and more recent precipitation.

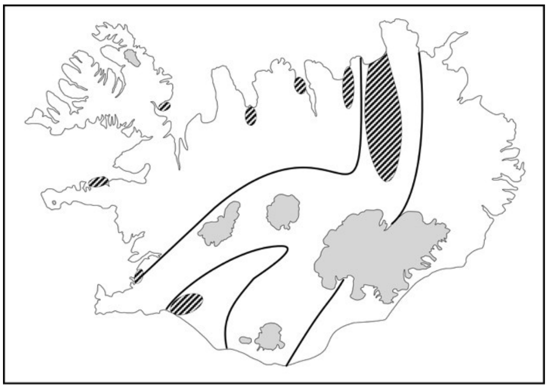


Figure 6: Locations of presently known water in Iceland with a pre-Holocene component shown in black.

Figure 7 displays the geographical distribution of δ^2H (A) and radiocarbon age (B) for the Skagafjördur waters. It demonstrates that in general the δ^2H of the waters gets more depleted from the cost and inland. Exceptions from this general rule are some low δ^2H values (ca -110‰) within the lowlands. These waters also display high ^{14}C ages (ca 15,000 BP) (Figure 7B). They are localized on low flat ground close to sea-water elevation. They originate, at least partly, from glacial melt-water from the last glaciation, which percolated into the ground and became stagnant. This glacial water has mixed with more modern precipitation to a varying degree.

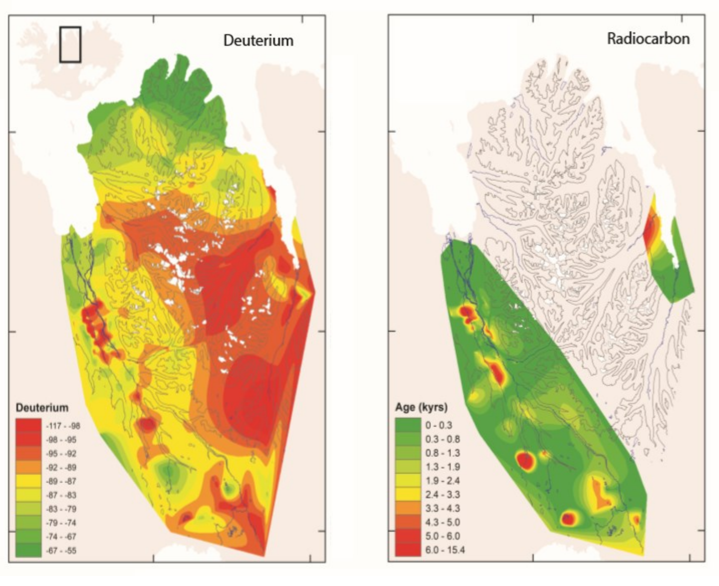


Figure 7: Maps showing the distribution of deuterium content of groundwater (left) and radiocarbon age of the water from the Skagafjördur-Eyjafjördur region, N-Iceland (right).

4.2 Data on d–excess in groundwater

Different deuterium excess ($d=\delta^2H-\delta^{18}O$) of Icelandic low temperature groundwater has been interpreted to be age related, either characterizing water-rock interaction over a long time or as changes in the origin of precipitation due to different climate regime (Johnsen et al., 1989). In the low temperature Mosfellssveit area in SW-Iceland the groundwater shows a distinct geographical distribution of deuterium excess, offering the possibility to divide the area into three different regions (Figure 8). This division can however not be seen in the stable isotope content of the water. Within the Helgadalur valley the d-excess is >13‰. These high d-values have been taken to indicate that the waters are from earlier times when climate was different. This interpretation is supported by ^{14}C age determinations where the water in Helgadalur (17,610±200 BP) is substantially older than in the other parts of the Mosfellssveit area, ranging from 3669 to 8312 BP (Figure 8) (Sveinbjörnsdóttir et al., 1995).

Some of the low-temperature geothermal waters in the Southern Lowlands show unusually low deuterium excess values relative to their temperature with an oxygen shift of about 1.5‰ (Sveinbjornsdóttir et al., 2004). However these waters show similar ^{14}C ages as water with normal d-values (around 10‰). These are waters with no pre-Holocene component. In this case the low d-values may indicate that the waters were hotter at some earlier times. As pointed out by Sveinbjornsdóttir et al. (2004) they have a clear geographical connection to the Flúdir hot thermal area (T=130°C), following a young tectonic fissure direction.

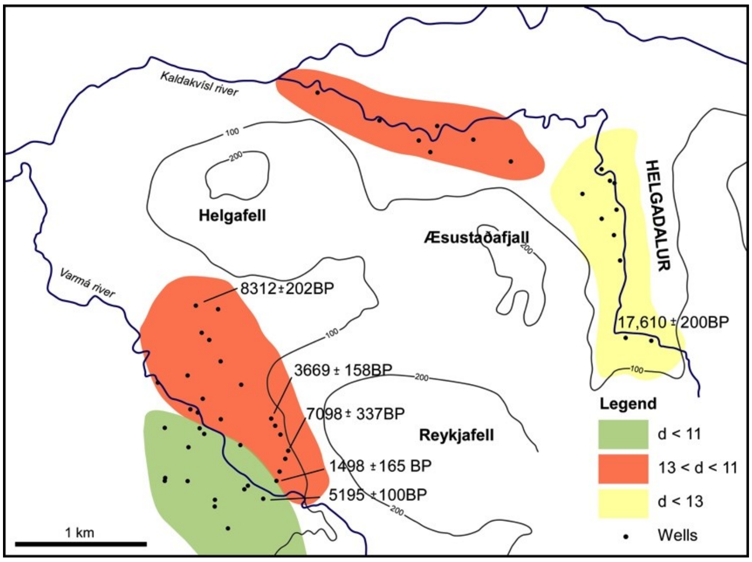
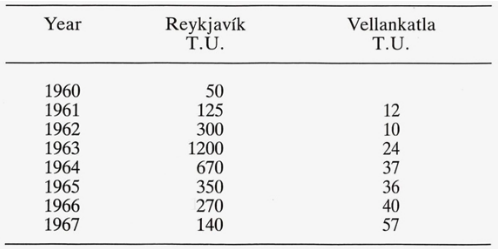


Figure 8: Geographical distribution of the observed d-excess in the Mosfellssveit low temperature area, SW-Iceland. Also shown are the apparent radiocarbon ages of water from drillholes, within the distinct geographical areas, demonstrating the different age of the Helgadalur groundwater in accordance with the interpretation of the high d-excess (see text)

4.2 Tritium and carbon datings

Tritium measurements have mainly been done on waters from the Skagafjördur area (Arnórsson and Sveinbjörnsdóttir, 2004) and in the Reykjavík city and the nearby Thingvellir area (Theodórsson, 1967; Sveinbjörnsdóttir and Johnsen, 1992). In Skagafjördur ground waters on low ground do not contain detectable tritium in accordance with the high ^{14}C age of these waters shown in Figure 7, considered to reflect a pre-Holocene component within this groundwater. Some of the waters at high ground show also low tritium content and an older radiocarbon age due to mixing of old glacier water with modern meteoric water. The tritium measurements from the Thingvellir area are from waters within the Vellankatla cold spring and collected in the years 1960 to 1967 (Table 1). Sveinbjornsdóttir and Johnsen (1992) estimated the age of the recent precipitation in the Vellankatla water by using stable isotope data together with the tritium data. Compared to local precipitation the Vellankatla water is depleted in ^{18}O by 2‰, suggesting that 75% of the Vellankatla water originate from the glacier Langjökull, some 50 km inland, and 25% from more recent precipitation. Assuming that the increase in tritium from 1962 and 1963 in the Vellankatla water was mainly due to the high tritium concentration values in the 1963 precipitation (Table 1 for Reykjavík) the age of the Vellankatla water which consists of recent precipitation, according to the stable isotopes, is younger than 10 yrs (Sveinbjornsdóttir and Johnsen, 1992). This is in general agreement with estimates compiled by Árnason (1976) based on tracer studies and Darcy's law calculations. This is also the lower limit for the travel time for the glacial water from the glacier Langjokull to the lake Thingvallavatn (ca 50 km), although it can be assumed to have longer travel times as the melt-water penetrates to greater depths than the local precipitation.



Year	Reykjavík T.U.	Vellankatla T.U.
1960	50	
1961	125	12
1962	300	10
1963	1200	24
1964	670	37
1965	350	36
1966	270	40
1967	140	57

Table 1: Tritium measurements for Reykjavík precipitation and the Vellankatla cold spring water in Thingvellir (data from Theodórsson, 1967)

The comprehensive database for carbon isotopes on Icelandic deeper groundwater (Sveinbjornsdóttir et al., 2010) can only be interpreted in terms of geochemical modeling if an input of CO_2 gas from below with similar isotopic composition as the pre-erupted melt of the upper mantle and lower crust beneath Iceland is assumed to contribute to the carbon budget of the waters, together with atmospheric-, organic- and rock leaching carbon (Stefánsson et al., 2016). This does not only apply for locations within the active volcanic zones in Iceland but also in some off-rift locations, where mantle-like $\delta^{13}C$ values are observed. The model that best fit the data from those areas involves interaction at shallow depth of basaltic rock (CO_2=70ppm, $\delta^{13}C$=-15‰, ±10% calcite) with air saturated surface water with atmospheric CO_2(g) at variable temperatures. Followed by inflow of CO_2 gas at depth ($\delta^{13}C$=-2.5‰) along a continuous w-r interaction path. For other off-rift areas the carbon isotopes are characterized by insignificant deep gas input and are dominated by shallow fluid-rock reactions.

5. CONCLUSIONS

In Iceland groundwater dating is complex as the water is most often mixed with components originating from different conditions, of different age and in some cases also affected by water-rock interaction. Thus it is of vital importance when age determinations are interpreted to understand the geology and hydrology of the specific groundwater system. Our research has shown that to succeed in understanding and defining a hydrological system interdisciplinary methods have to be applied and it is essential that isotopes and age estimates are interpreted together with geochemical- geophysical- and geological data. Age estimations are particularly important when defining a groundwater system. Several methods to estimate groundwater age have been applied in Iceland. We have demonstrated that stable water isotopes including the second order parameter; deuterium excess, can be used to estimate relative ages. Tritium has been used for a limited time span and radiocarbon age determinations have successfully been used when comprehensive corrections for “dead carbon” from the bedrock and CO_2 gas from the deep crust or mantle are applied together with $\delta^{13}C$ to correct for modern carbon of organic origin.

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