O, H and C isotopic systematics of Icelandic groundwater

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Abstract. Stable water isotopes of oxygen and hydrogen have been studied in Icelandic natural waters since 1960 for hydrological and geothermal research. All the waters are of meteoric and seawater origin. The measured range in δD and $\delta^{18}O$ is large -131 to +3.3‰ and -20.8 to +2.3‰ respectively. Some of the waters are more depleted than any present-day precipitation suggesting a pre-Holocene component in the groundwater. Carbon isotopes of streams, rivers, soil and groundwater have been studied since 1990 in order to evaluate the carbon sources and reactions that possibly influence the carbon systematics of the water. Results show large range of values, for $\delta^{13}C_{DIC}$ -27.4 to +4.5‰ and for $^{14}C_{DIC}$ +0.6 to +118 pMC. Apart from atmospheric, organic and rock leaching, input of gas at depth with similar isotopic composition as the pre-erupted melt of the upper mantle and lower crust beneath Iceland have been identified as sources for carbon in the deeper groundwater.

1 Introduction

Oxygen and hydrogen isotopes are commonly used in geothermal studies to identify the source(s) of thermal fluids and to study the physical properties of the geothermal reservoir. Deuterium contour map of mean annual present-day precipitation [1] has been used extensively to trace the origin and flow of groundwater in Iceland, including geothermal water. However, in recent years measurements have revealed that some of the groundwater is more depleted than any present-day precipitation, taken to indicate a pre-Holocene component in the water [2 - 4]. The groundwater flow in Iceland is most often made of several water components, with different age and origin and mixed to a variable degree. Thus the isotopic content of a water sample may coincide with present day precipitation in Iceland, especially if the pre-Holocene component is small and/or the Holocene component(s) is relatively enriched in the heavier isotopes. It is therefore emphasized that using the deuterium contour map of the present day precipitation to trace origin of groundwater requires detailed understanding of water chemistry, hydrology and the geological history of the area studied.

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Inorganic carbon (DIC) in natural waters may originate from various sources including the atmosphere, organic matter, bedrock and the mantle [e.g. 5 - 7]. As Iceland is situated on a divergent plate boundary, mantle and crustal rock dissolution are likely to dominate the source of CO_2 in thermal and non-thermal groundwater [e.g. 6, 8 - 11].

Here an overview is given on the water- and carbon isotopes in Icelandic non-thermal and low temperature groundwater (T<130 °C) and how they can be used to reveal sources and reactions that influence the isotopic systematics of the groundwater.

2 Sampling and analytical methods

Samples for water- and carbon isotope analyses were sampled into gas tight 60mL and 1L amber glass bottles, respectively. For the carbon samples 2-3 drops of $HgCl_2$ were added to the sample to prevent photosynthesis during storage. The CO_{2DIC} was extracted from the water samples by the method of [12] as described in [13]. Water isotopes and $\delta^{13}C$ were measured on a Finnegan MAT 251 at the University of Iceland [10]. The results are defined in the conventional δ–notation in ‰ relative to SMOW and VPDB standards respectively. The standard deviation is 0.05‰, 0.07‰ and 0.15 ‰ for repeated measurements of oxygen, hydrogen and stable carbon. The ^{14}C measurements were carried out at the Aarhus AMS Centre, Aarhus University, Denmark using an HVEC EN Tandem accelerator [14]. Replicate analyses on a reference material yielded a standard deviation of 1.6 pMC.

The geochemical and isotopic modelling is based on simulating chemical reactions for a given system as a function of reaction progress. Comparison of the results with measured $\delta^{13}C$ and ^{14}C data is then used to evaluate sources and reactions of dissolved inorganic carbon in groundwater [7]. For the carbon isotopes three models were constructed 1) Model 1 (water-rock (w-r) ± cc) involved interaction at shallow depth of basaltic rock (CO_2 =70ppm, $\delta^{13}C$=-15‰) with air saturated surface water with atmospheric CO_2 (g) at variable temperatures. The basalt was considered either to have no carbonates or 10% calcite. 2) Model 2 (w-r/r) same as Model 1 followed by interaction with less degassed intrusive rock (CO_2=250ppm, $\delta^{13}C$=-5‰) at greater depth 3) Model 3 (w-r/CO_2) same as Model 1 followed by inflow of CO_2 gas at depth ($\delta^{13}C$=-2.5‰) along a continuous w-r interaction path. Both low (10^{-6} bar) and high (1 bar) CO_2 gas fluxes were considered [7].

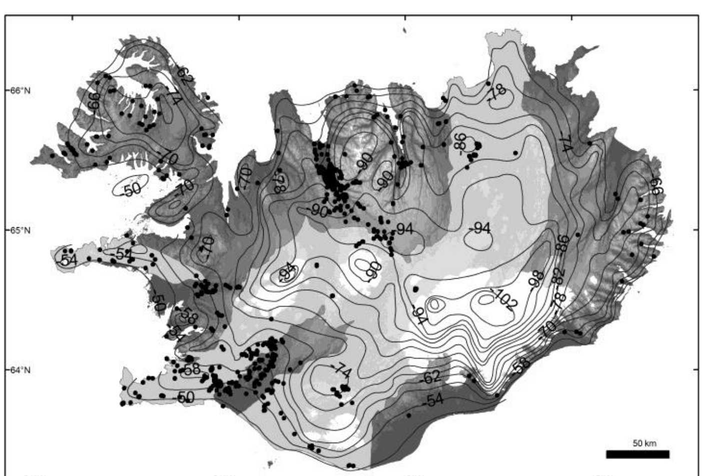

Fig. 1. Sample locations (black dots), volcanic belts (light gray) and δD contours of present-day precipitation [1].

3 Results and discussion

Iceland is characterized by active volcanic belts going from S to N, shown on Fig. 1. Also shown on the Figure are the groundwater sampling locations. The samples were collected away from active volcanic geothermal systems. Furthermore the distribution of δD in present day precipitation in Iceland [1] is shown on the Figure. All the waters follow closely the Global Meteoric Water Line as demonstrated in Fig. 2 suggesting a meteoric origin for the water samples. Some of the waters lie slightly to the right of the line, possibly suggesting water-rock reaction. In recent years groundwater with more depleted isotope values than any present day precipitation in Iceland has commonly been observed in the lowlands where groundwater flow is very slow [2]. An example is the valley of Skagafjördur, N-Iceland, where water isotopes, tritium and carbon dating have demonstrated different sources and age for the groundwater. The highland waters and the mountain water surrounding the Skagafjördur valley are of modern age with δD values of modern precipitation in accord with geographical location. The old and isotopically depleted waters are considered to be from a pre-Holocene time when the climate was colder than today with more depleted precipitation. These waters are found in the valley plain where groundwater flow is very low. They show the highest ^{14}C age [3], reflect the highest amount of water-rock interaction and the lowest tritium values [15].

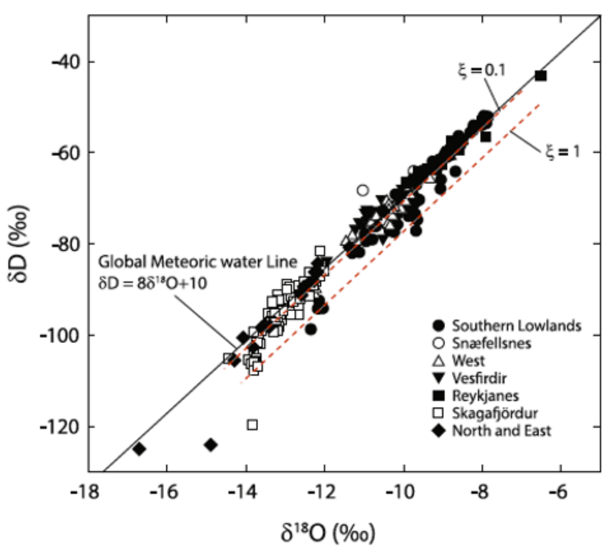

Fig. 2. $\delta^{18}O$ vs δD compared to the Global Meteoric Water Line. Reaction progress for 0.1 and 1 mol basalt per kg water is also shown. Different symbols refer to different locations in Iceland.

The measured range in carbon isotopes $\delta^{13}C_{DIC}$ and $^{14}C_{DIC}$ in Icelandic non-thermal and low temperature groundwater (<130°C) are from -27.3 to +2.0‰ (average = -9.7‰) and from 0.6 to 118 pMC (average = 48 pMC) respectively. The range in CO_2 concentration is also large, though most of the waters have <100ppm. The measured CO_2 concentration corresponds to a very variable partial pressure of CO_2 (p_{CO2}), ranging from ca 10^{-7} to ca 1 bar as demonstrated in Fig. 3. Most of the waters have lower pCO_2 than the atmosphere, suggesting a removal of CO_2 relative to surface waters into secondary carbonate minerals in accordance with previous findings that Icelandic groundwater is calcite saturated [16,17].

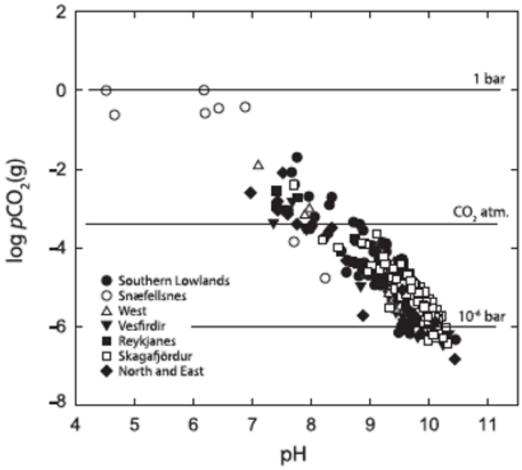

Fig.3. pH vs the logarithm of the partial pressure of CO_2. The partial pressure of CO_2 in the atmosphere corresponds to 399 ppm. Different symbols refer to different locations in Iceland.

Fig. 4 represents a typical mixing plot for the two components $^{14}C_{DIC}$ and $\delta^{13}C_{DIC}$. It shows the measured data in comparison with the three different model simulations, described above. Three major trends are observed suggesting multiple CO_2 sources in the groundwater: 1) Atmospheric CO_2 through air-water exchange 2) Rock derived CO_2 from water-rock interaction with CO_2 degassed basalt at shallow depth followed by calcite formation 3) input of deep CO_2 gas with P_{CO2} of <10^{-6} to 1 bar, with 0 pMC and $\delta^{13}C$ value of the Icelandic mantle (-2.5%) [7].

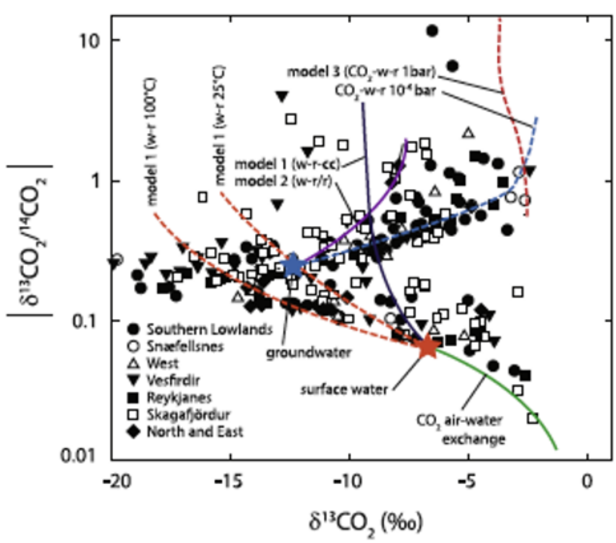

Fig. 4. The relationship between the numerical value of $\delta^{13}CO_2/^{14}CO_2$ and the $\delta^{13}CO_2$ values of DIC in the water sampled. Also shown are the results of the three isotope geochemical models, described in the text. The measured data fits three major trends suggesting three different CO_2 sources; atmospheric, rock derived due to basalt dissolution at shallow depth and input of mantle/crustal CO_2.

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