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Isotope Systematics of Volatile Elements in Icelandic Thermal Fluid

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ABSTRACT

Thermal fluids in Iceland are dominated by water (>97 mol%), have wide temperature range (<10 to >440°C) and variable Cl concentration (<10 to >20,000 ppm). Previous studies spanning over half a century have revealed a large range of values for volatile element isotopes for δD (-131 to +3.3‰), ^{3}H (-0.4 to +13.8 TU) and $\delta^{18}O$ (-20.8 to +2.3‰) for water, $^{3}He/^{4}He$ (+3.1 to +30.4 R_A), $\delta^{11}B$ (-6.7 to +25.0‰), $\delta^{13}C\text{-}CO_2$ (-27.4 to +4.6‰), $^{14}C\text{-}CO_2$ (+0.6 to +118 pMC), $\delta^{13}C\text{-}CH_4$ (-52.3 to -17.8‰), $\delta^{15}N$ (-10.5 to +3.0‰), $\delta^{34}S\text{-}H_2S$ (-10.9 to +3.4‰), $\delta^{34}S\text{-}SO_4$ (-2.0 to +21. ‰) and $\delta^{37}Cl$ (-1.0 to +2.1‰) in both liquid and vapor phases. The isotope systematics reveal the source(s) and transport processes of the volatiles from the mantle beneath Iceland, through the crust and to surface. Based on available data it can be concluded that the thermal fluids in Iceland originate from meteoric and/or seawater whereas selected volatile elements have variable and sometimes mixed sources including degassing of mantle-derived melts contributing to He, CO_2 and Cl in the fluids, water-rock interaction contributing to CO_2, H_2S, SO_4, Cl and B in the fluids and air-water interaction mainly controlling N_2. The large range of many non-reactive volatile isotope ratios, such as δ37Cl and $^{3}He/^{4}He$, are considered to indicate heterogeneity of the mantle and derived melts beneath Iceland. In contrast, the large range of many reactive isotope elements, such as CO_2 and H_2S, are heavily affected by processes occurring within the geothermal systems, including fluid-rock interaction, depressurization boiling, and isotopic fractionation between secondary minerals and the aqueous and vapor species. Variations due to these geothermal processes may exceed any differences observed among various sources highlighting the importance and effects of chemical reactions on the isotope systematics of reactive elements.

1. INTRODUCTION

Volatile elements are commonly found within planetary crusts and atmospheres and include for example H, He, B, C, N, O, F, S, Cl and other noble gases. Collectively, they are derived from the atmosphere, mantle, and crust and are typically influenced by processes occurring within geothermal systems, such as water-rock interaction, degassing and boiling and fluid mixing (e.g., Giggenbach, 1992; Stefánsson et al., 2017). Some volatiles, for example He, undergo limited interactions and are effective tracers of source provenance whereas other volatiles such as C, S, H and O are chemically reactive, and their isotope characteristics may reflect both sources and secondary processes. Thermal fluids in Iceland provide a unique opportunity to study the variable source(s) and secondary processes of volatile elements at divergent plate boundaries, as it is located on land whereas in most cases they are placed at the oceanic bottom with seawater typically overprinting other possible volatile element sources. Moreover, geothermal activity is widespread, both within the rift zones of Iceland and off-rift away from modern volcanic activity.

Isotopes of volatile elements in thermal fluids in Iceland have been studied since the 1960s. Early on, considerable effort was made in water sources and flow paths using δD systematics (e.g., Friedman et al., 1963; Árnason and Sigurgeirsson, 1968; Árnason, 1976, 1977) as well as deep mantle degassing and mantle source provenance using He isotopes (Polak et al.,1976; Torgersen and Jenkins, 1982; Sano et al., 1985; Hilton et al.,1990, 1998; Marty et al., 1991; Poreda et al., 1992; Füri et al., 2010). Despite some early work related to reactive volatiles like carbon and sulfur (Arnórsson and Barnes, 1983; Sakai et al., 1980; Torssander, 1986), less was known about their sources in the thermal fluids until recently with studies focusing on boron ($\delta^{11}B$) (Aggarwal et al., 2000), carbon ($\delta^{13}C$ and ^{14}C) (Stefánsson et al., 2016; Thomas et al., 2016), sulfur ($\delta^{33,34,36}S$) (Stefánsson et al., 2015; Gunnarsson-Robin, 2017) and chlorine (Stefánsson and Barnes, 2016) isotopes.

In this study, we aim to summarize available data on the isotope systematics of volatile elements in thermal fluids in Iceland and to trace their source(s) and reactions in geothermal systems.

2. GEOTHERMAL ACTIVITY AND THERMAL FLUIDS IN ICELAND

The regional geology of Iceland is the result of both extension and migration of the Mid-Atlantic divergent plate boundary relative to the Iceland mantle plume. In the Eastern and Northern Volcanic Zones and the flank zones, central volcanic complexes have formed typically characterized by a central volcano, caldera structure and a fissure swarm parallel to spreading. In the Western Volcanic Zone, such volcanic complexes are less obvious (e.g., Sæmundsson,1974).

Geothermal activity in Iceland has been classified into low- and high-temperature systems (Bödvarsson, 1961). Most of the high-temperature geothermal systems are located in central parts of the belts of active volcanism and rifting. In the Eastern and Northern Volcanic Zones, the high-temperature geothermal systems are typically associated with the volcanic complexes whereas in the Western Zone several high-temperature systems are present, these not always associated with volcanic complexes. Low-temperature geothermal activity is widespread in the Quaternary and Tertiary formations of Iceland with the main activity mostly confined within the North American Plate and the Southern Lowlands. The low-temperature activity is frequently associated with active fractures and faults (e.g., Arnórsson et al., 2008).

Thermal fluids of low- and high-temperature geothermal systems in Iceland are commonly divided into primary and secondary fluids (Arnórsson et al., 2007). Primary or reservoir fluids are those occurring within the geothermal system at depth where secondary fluids are formed upon chemical and physical changes occurring when fluids ascent to surface including boiling, condensation and mixing with non-thermal water. The geothermal fluid composition in Iceland is dominated by H_2O generally accounting for >99 mol% (Stefánsson et al., 2017). Thermal waters in Iceland typically have Cl concentrations <200 ppm, presumably because of low Cl content of basaltic rocks which make up the bulk of the Icelandic crust. Geothermal systems that have a seawater component, such as Reykjanes and Svartsengi and within the Southern Lowlands, display much higher Cl concentration, up to ~20,000 ppm, similar to seawater salinity values (Arnórsson and Andrésdóttir, 1995; Ármannsson, 2015). It has been demonstrated that the concentration of major rock forming elements (Si, Na, K, Ca, Mg, Al and Fe) is controlled by temperature dependent equilibria between the primary fluids and secondary minerals observed in the geothermal systems (e.g., Arnórsson et al.,1983). In contrast, the concentrations of many volatile elements are highly variable. Non-reactive elements like He, are considered to largely represent their source characteristics and/or mixing with atmospheric-derived components (e.g., Füri et al., 2010), whereas the concentrations of reactive volatiles such as CO_2, H_2S and H_2 may be close to gas-mineral equilibrium (e.g., Stefánsson, 2017) whereas in other cases gas-mineral and gas-gas equilibria is not observed suggesting that the source exerts a significant control on the gas concentration (e.g., Stefánsson and Arnórsson, 2002). Secondary fluids are generally formed upon boiling of primary fluids and mixing with non-thermal water. Vapor condensation and mixing lead to the formation of steam-heated water with low pH and rich in SO_4 whereas the boiled liquid commonly forms hot springs at surface with alkaline pH values. Carbonate springs have also been suggested to form by mixing of have CO_2-rich vapor or gas with non-thermal water (Arnórsson and Barnes, 1983; Stefánsson et al., 2017). Hot springs formed by mixing of boiled reservoir water and shallow non-thermal water are also common, these having variable chemical characteristics depending on the fluid sources and mixing ratios.

3. ISOTOPE SYSTEMATICS OF VOLATILE ELEMENTS

3.1. Water origin and age traced by water and carbon isotopes

δD and $\delta^{18}O$ values of precipitation and non-thermal and thermal water in Iceland vary greatly, with δD values from −131 to +3.3‰ and $\delta^{18}O$ values from −20.8 to +2.3‰ (Craig, 1963; Friedman et al., 1963; Árnason and Sigurgeirsson, 1968; Árnason, 1976, 1977; Ólafsson and Riley, 1978; Arnórsson, 1985; Darling and Ármannsson, 1989; Sveinbjörnsdóttir et al., 1986; Ármannsson et al., 2014; Pope et al., 2015). This wide range and comparison with the Global Meteoric Water Line (GWML) is considered to indicate both meteoric and seawater sources of low- and high-temperature waters in Iceland, either originating locally or by regional groundwater flow from high- to low-ground (Árnason, 1976). Many of the high-temperature fluids are observed to

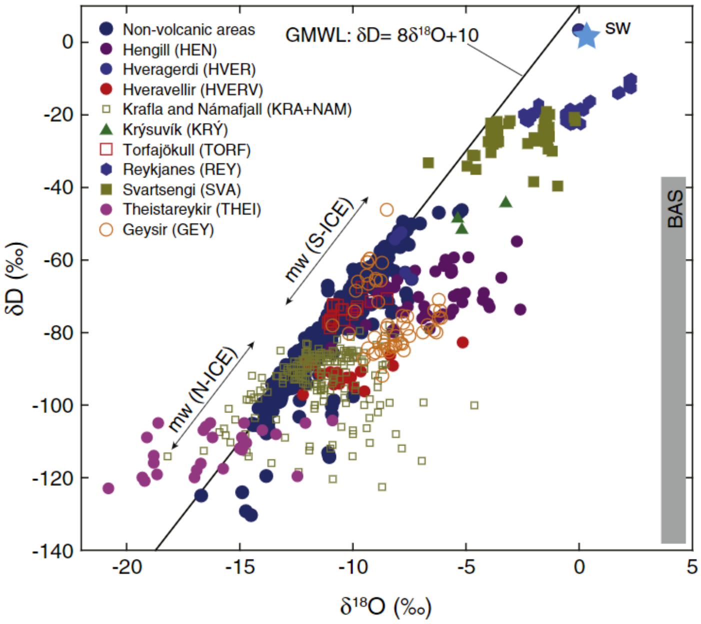

Figure 1: The relationship between δD and $\delta^{18}O$ values for thermal fluids in Iceland. For low-temperature systems, the values in the liquid phase are shown; whereas for high-temperature systems both values of the vapor and liquid phases are shown. Most systems display low chlorine concentration with the source of the thermal water considered to be meteoric water. Two systems, Reykjanes and Svartsengi, have seawater or seawater-meteoric water mixtures as the source fluid. Many of the high-temperature areas are shifted towards higher $\delta^{18}O$ values relative to the global meteoric water line (GMWL) due to fluid-rock interaction. The values for thermal fluids are from Ólafsson and Riley (1978), Arnórsson (1985), Darling and Ármannsson (1989), Sveinbjörnsdóttir et al. (1986), Ármannsson et al. (2014), Pope et al. (2015) and Stefánsson et al. (2017).

be shifted to higher $\delta^{18}O$ values relative to the GMWL, this considered to result from water-rock interaction and leaching of oxygen from the primary rocks (Stefánsson et al., 2017) (Fig. 1).

Many low-temperature geothermal areas in Iceland have δD and $\delta^{18}O$ values lower than those of the nearby lowland and highland areas. In some cases, the values are lower than observed for present-day precipitation throughout Iceland, for example at Skagafjörður and Eyjafjörður areas, North Iceland. Springs and streams with modern water according to tritium and ^{14}C content have similar δD and $\delta^{18}O$ values of the local precipitation, with lower values at high elevation and higher values at low elevation close to coastal areas. In the valley floor of Skagafjördur, water with much lower δD and $\delta^{18}O$ values compared with the values for modern local and sometimes highland precipitation are sometimes observed. These waters also display low water age according to tritium and ^{14}C content. This water is considered to represent times when the air temperature was cooler and precipitation was isotopically lighter, i.e., last glacial times ~12,000 years ago. The waters are found where low hydrologic flow may be expected in valley bottoms at altitudes close to sea level.

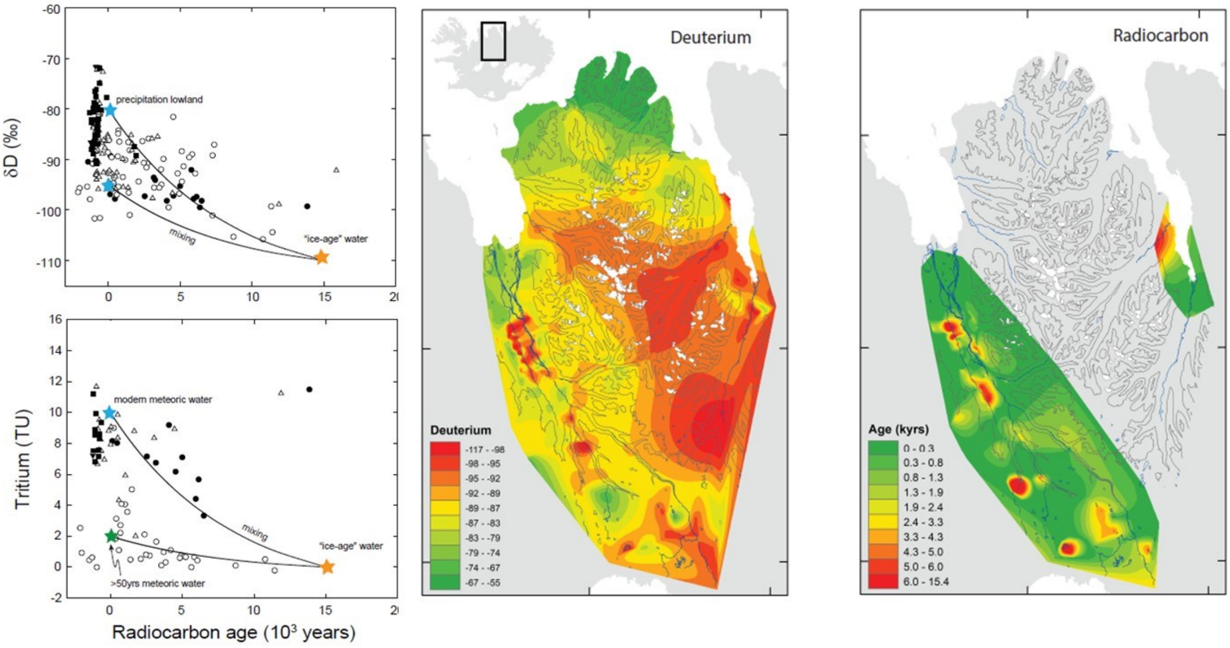

Figure 2: The relationship between δD and radiocarbon age and tritium and radiocarbon age for waters in Skagafjörður and Eyjafjörður, N-Iceland. Also shown are the geographical distribution of δD and radiocarbon age of the waters. The radiocarbon age was calculated based on the measured ^{14}C content corrected for rock derived carbon (Stefánsson et al., 2016). Also shown are the mixing trends between two water components, old water of meteoric origin from the last glacial times >12000 years ago with δD lower (<-110 ‰) than today's precipitation and meteoric water of recent origin (modern to >50 years old). Most surface water (rivers and streams) and soil waters and many ground waters within the highlands are close to be modern age (~0-20 years old) and of local meteoric origin. In contrast, many ground waters at low-ground display mixing trends between old "ice-age" water and more recent water that is however likely to be >30-50 years old based on the tritium content, these waters samples also showing considerable effects of rock leaching. Similarly, some ground-waters and surface waters within the highlands display mixing between old water most likely originating from old-ice glacial melt and modern meteoric water, these waters showing insignificant effects of rock leaching, consistent with their old glacial and modern precipitation source.

3.2. Fluid origin,mixing and progressive fluid-rock interaction traced by boron, chlorine and sulfur isotopes

Boron, chlorine and sulfur in thermal fluids is considered to originate from the source fluid, fluid-rock interaction and magma degassing (e.g., Arnórsson and Andrésdóttir, 1995; Stefánsson and Barnes, 2016; Gunnarsson-Robin et al., 2017). These variable sources and processes can be traced using the B, Cl and S isotopes. Boron isotope ratios ($\delta^{11}B$) in low- and high-temperature thermal water in Iceland range from −6.7‰ to +25.0‰ (Aggarwal et al., 2000), chlorine isotope ratios ($\delta^{37}Cl$) are between −1.0 and +2.1‰ (Kaufmann and Arnórsson, 1986; Stefánsson and Barnes, 2016) and sulfur isotope values ($\delta^{34}S$) varies from -1.0 to +24.9 ‰ for SO_4 and -11.6 to +10.5 ‰ for H_2S (Sakai et al., 1980; Torssander, 1986; Stefánsson et al., 2015; Gunnarsson-Robin et al., 2017). By comparing the data with results of isotope modeling, the source(s), mixing trends and effect of fluid-rock interaction can be assessed (e.g., Stefánsson et al., 2015; Stefánsson et al., 2016, 2017; Stefánsson and Barnes, 2016; Gunnarsson-Robin et al., 2017).

The $\delta^{11}B$ ratio of the thermal source fluid, meteoric and/or seawater, is similar or upto +39.6 ‰ (Foster et al., 2010) whereas for basaltic rocks it is much lower or between −1.5 to−16.9‰ (e.g., Brounce et al., 2012). Boron is considered to be a mobile element upon fluid-rock interaction, i.e. does not enter secondary minerals, and is therefore an effective parameter of primary rock dissolution. Inspection of the $\delta^{11}B$ and B concentration relationship reveal indeed such a trend with B in water showing the effect of source water B and progressive basalt dissolution (Fig. 2). Similarly, Cl is considered to be mobile upon secondary mineral formation under geothermal conditions

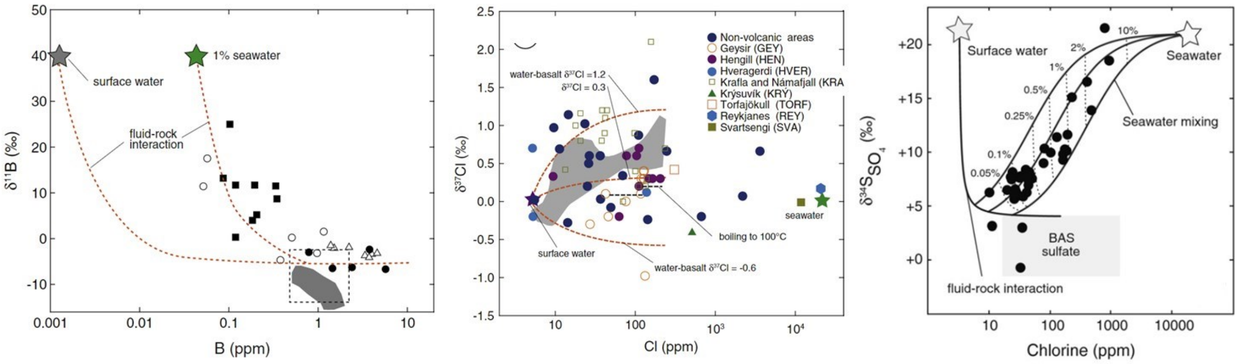

Figure 3: The relationship between δ11B and B concentration, δ37Cl and Cl concentration and δ34S-SO4 and Cl concentration. As observed, all isotope ratios and elemental concentrations show the effect of the source water being meteoric, seawater or mixture thereof, progressive primary rock dissolution and in the case of SO4, mixing with seawater. The figures are based on data reported by Aagerwald et al. (2000), Stefánsson and Barnes (2016) and Gunnarsson-Robin et al. (2017).

(Arnórsson and Andrésdóttir, 1995; Stefánsson and Barnes, 2016), and following similar trends are observed for Cl as B, i.e. the isotope and chemical composition is mainly controlled by the source fluid and progressive primary rock dissolution (Fig. 3). In the case of sulfate, the relationship between δ^{34}S-SO$_4$ ratios and Cl concentration may reveal the source fluid, rock leaching and mixing with seawater as can been observed for low-temperature geothermal waters in South Iceland (Fig. 3).

3.3. Mantle degassing and secondary crustal processes traced by carbon and helium isotopes

Kononov and Polak (1975) and Polak et al. (1976) were the first to report helium isotope data from Icelandic thermal fluids. These pioneering studies were followed by later studies of Hauksson and Goddard (1981) and Torgersen and Jenkins(1982), Sano et al. (1985), Marty et al. (1991), Poreda et al. (1992), Hilton et al., (1990, 1998) and the extensive study of Füri et al. (2010). All these studies were recently summaries by Harðardóttir et al (2018). Helium like other noble gases are geochemically nonreactive and generally interpret to represent source provinces. These studies demonstrated significant variability in the isotopic composition of helium with ^{3}He/^{4}He ratios as high as ~30 R$_A$ (where R$_A$ is the ^{3}He/^{4}He of air) in thermal fluids in Iceland. Significantly, several region in Iceland are activity degassing fluids characterized by high ^{3}He/^{4}He ratios which are generally associated with deep-mantle plumes under hotspots. The ^{3}He/^{4}He ratios in thermal fluids from both low- and high-temperature areas across Iceland are shown in Fig. 4. The highest helium isotope ratios are found not only in central Iceland but also in NW Iceland. A cluster of samples, located in low-temperature areas in the Southern Lowlands, have also high ^{3}He/4He ratios which are mostly characterized by values of 14-20 R$_A$. In summary, helium isotope ratios in thermal fluids clearly reflect deep mantle degassing as well as mantle heterogeneity below Iceland.

Carbon isotopes reveal deep origin of CO$_2$ in thermal fluids but also secondary processes including boiling and phase separation and fluid-rock interaction. The graphical distribution of δ^{13}C in thermal fluids southern and western Iceland is shown in Figure 4. Within the rift zone and associated with volcanic centers like Reykjanes, Svartsengi, Krýsuvík and Hengill, δ^{13}C are typically >5‰ suggesting mantle gas as the major source of CO$_2$. The gas is formed by either deep or shallow magma degassing, or both. In off-rift areas, the δ^{13}C values are usually much lower, between −20 and −7‰, suggesting water-rock interaction being the dominant source of CO$_2$ in these waters with the range of carbon isotope values being controlled by CO$_2$ and δ^{13}C variation in the basalts in Iceland (Barry et al., 2014) and isotope fractionation between secondary minerals and aqueous species up on fluid-rock interaction (Stefánsson et al., 2016). However, at some off-rift locations (e.g., Grímsnes) mantle-like δ^{13}C values dominate. The source of the CO$_2$ in these thermal waters is the same as within the rift, i.e., CO$_2$ degassing of melts originating in the upper mantle and the lower crust and the percolation of CO$_2$ through the crust and partitioning into shallower thermal groundwater systems (Stefánsson et al., 2016). The off-rift δ^{13}C mantle values correlate to some extent with the ^{3}He/^{4}He ratios. For example, within the rift zone at Reykjanes to Hengill, high δ^{13}C values are typically associated with ^{3}He/^{4}He ratio of <14 R$_A$. Slightly higher ^{3}He/^{4}He ratios are observed towards east in the Southern Lowlands, with the exception of the areas of high δ^{13}Cvalues that are also characterized by high ^{3}He/^{4}He values >20 R$_A$. These trends are thought to indicate a deep mantle source of volatiles within some off-rift areas in Iceland, whereas other areas are characterized by insignificant deep gas input but are dominated by shallow fluid-rock processes.

4. CONCLUSIONS

The isotope systematics of volatile elements in thermal fluids in Iceland were studied. The fluids are dominated by water (usually >99mol%), have wide temperature range (<10 to >440°C) and variable salinity (Cl concentration of <10 to >20,000 ppm). Previous studies spanning over half a century have revealed a large range of values for volatile isotopes. Based on available data it can be concluded that the thermal fluids in Iceland originate from meteoric and/or seawater whereas other volatile elements have variable and sometimes mixed sources including degassing of mantle-derived melts contributing to He and CO$_2$, water-rock interaction contributing to CO$_2$, SO$_4$, Cl and B. The large range of many non-reactive volatile isotope ratios, such as δ^{37}Cl and ^{3}He/^{4}He, are considered to indicate heterogeneity of the mantle and derived melts beneath Iceland. In contrast, the large range of many reactive isotope elements, such as CO$_2$ and SO$_4$, are heavily affected by processes occurring within the geothermal systems, including fluid-rock interaction, and isotopic fractionation between secondary minerals and the aqueous and vapor species. Variations due to these geothermal processes may exceed any differences observed among various sources highlighting the importance and effects of chemical reactions on the isotope systematics of reactive elements.

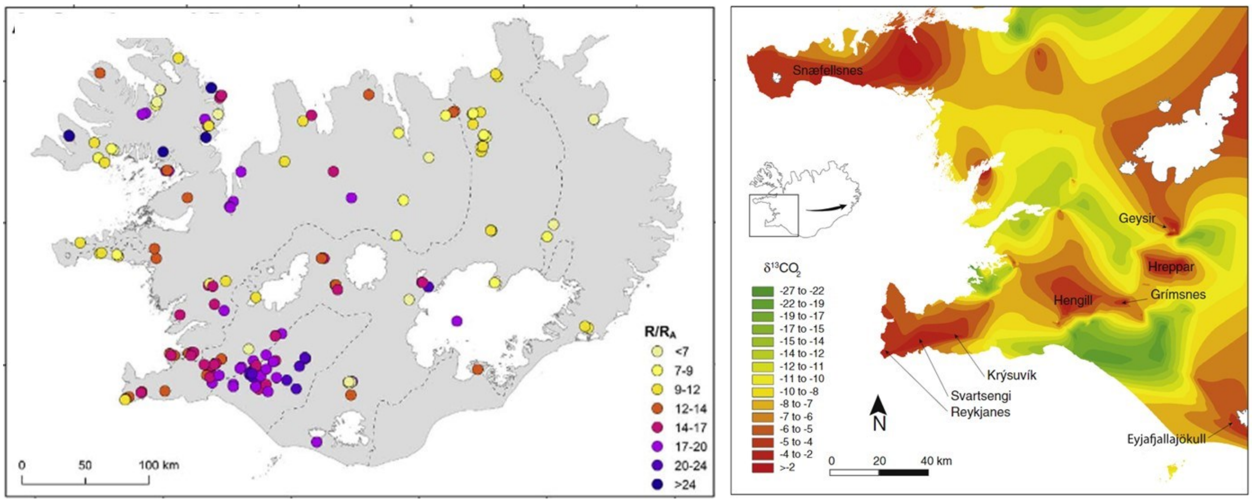

Figure 4: Distribution of helium isotope ratios in thermal fluids in Iceland as well as corresponding $\delta^{13}C$-CO_2 isotope ratios in western and southern Iceland. As observed, clear signals of high and local He isotope values are observed at NW-Iceland and S-Iceland the latter also showing mantle $\delta^{13}C$ values of > -5 ‰. Based on Stefánsson et al. (2017) and Harðardóttir et al. (2018).

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