

Geochemical Characterization of Thermal Water from Central Vietnam and Borgarfjörður, West-Iceland

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ABSTRACT

The geochemistry of low-temperature geothermal water in Central Vietnam and Borgarfjörður (West-Iceland) was studied. Twenty samples of geothermal water were collected in Central Vietnam and twelve samples in Borgarfjörður in the summer of 2018. The water temperature, pH, DIC and H₂S concentrations were measured on site and major elemental composition analysed using ICP-OES and IC at the University of Iceland. Stable isotopes of hydrogen and oxygen (δD and $\delta^{18}O$) were also determined at the University of Iceland, by IRMS. The surface temperatures of the geothermal waters in Vietnam were 42- 96°C and in Borgarfjörður they were 40-98°C.

The stable water isotope ratios, Cl and B concentrations were used to assess the water origin, mixing and water-rock interaction. Based on the results of this analysis it was concluded that geothermal waters in Vietnam and Borgarfjörður are of meteoric origin affected by rock leaching and mixing with non-thermal water and with possible seawater or salt evaporates in the case of geothermal water in Vietnam.

The SiO₂ concentrations of the geothermal fluids in Vietnam and Borgarfjörður were 38-138 ppm and 54-178 ppm, respectively. Using these concentrations and assuming equilibrium with chalcedony the reservoir geothermal temperatures in Vietnam and Borgarfjörður were found to be as high as ~120°C and ~135°, respectively. The geographical projection of the major elemental concentrations and geothermometer temperatures revealed three geothermal anomalies in Vietnam: Le Thuy, Quang Binh; Mo Duc, Quang Ngai; Hoi Van, Quang Binh and the highest temperatures at Hægindi in Borgarfjörður.

1. INTRODUCTION

Low-temperature geothermal activity is widespread worldwide and associated with variable geological settings (e.g., Arnórsson, 1995; Hawkins, 2016; Lund and Boyd, 2016; Reyes, 2015). The heat source of most low-temperature geothermal systems is the surrounding warm rocks and commonly they are associated with active tectonics and permeable rock formations (e.g., Arnórsson, 1995). Low-temperature geothermal systems have been classified based on temperatures being less than 150°C at 1000 m depth (Böðvarsson, 1961; Fridleifsson, 1979).

Among the key questions arising when discussing utilization and low-temperature geothermal resources and their nature is the origin of the water itself. Stable isotopes and conservative elements have been applied to address these questions in the past. The pioneering work by Craig (1961, 1963), Friedman et al. (1964) and Árnason (1976, 1977) led to extensive work on stable water isotopes of cold and geothermal waters and precipitation. The relationship between δD and $\delta^{18}O$ values for most low-temperature water closely follows the global meteoric water line (GMWL) suggesting meteoric sources and sometimes also seawater. In most cases, the δD and $\delta^{18}O$ ratios of the geothermal water resemble those of a local meteoric source but sometimes they differ suggesting water transport, for example from high to low ground or water originating from when climate conditions in the area were different (Árnason, 1977; Arnórsson and Andrésdóttir, 1995). Conservative elements like B, Cl and SO₄ have also been applied to trace water sources and mixing of two or more water types as well as water-rock interaction (Arnórsson and Andrésdóttir, 1995; Gunnarsson-Robin et al., 2017). In precipitation, their concentrations are usually low, and upon water-rock interaction and mixing with for example seawater, their relative ratios show changes that can, in turn, be used to quantify the various sources of elements.

Water-rock interaction has been considered one of the major processes affecting low-temperature geothermal water composition. Based on inspections of temperature related equilibria between the waters and the geothermal minerals observed in the systems it has been concluded that a close approach to mineral-water equilibria is often attained, which in turn controls the solute concentrations in the water (e.g., D'Amore and Arnórsson, 2000). Such mineral-water equilibria have been applied in order to estimate subsurface water temperatures based on single or multi ion concentration relations, i.e. makes the theoretical background for geothermal geothermometry (e.g., D'Amore and Arnórsson, 2000).

The aim of the current study was to use the chemical and isotope composition of low-temperature geothermal water in central Vietnam and Borgarfjörður (west-Iceland) to investigate the origin of the water, assess mixing between two or more water sources and quantify water-rock interaction including the application of solute geothermometry for estimation of the reservoir temperatures.

2. STUDY AREAS

This study focuses on central Vietnam but a low temperature geothermal field in Borgarfjörður in western Iceland is used for comparison. In Vietnam, the study area is located in the central part of Vietnam extending from Ha Tinh to Khanh Hoa provinces.

The area has undergone many geological events since the Palaeozoic to form the land. The bedrocks mainly consist of sedimentary units such as limestone, sandstone, siltstone and felsic and mafic volcanism of different ages. There are some metamorphic and magma intrusion masses in between.

Most of the main faults in central Vietnam are in a NW-SE direction such as the Nao Ray and Bach Ma faults. They play a very important role in the division of geological structures. There are also fault zones running in the NE-SW, N-S or even E-W directions. These faults intersect with the main faults and formed the pull-apart basins, which were filled by Cenozoic sediment. Hot springs are mostly located along the fault zones or pull-apart basins.

Most of the hot springs had been explored since the last century. After that, several geothermal studies have been explored with the aim of investigating and estimating the geothermal potential in the country (Koenig, 1981; Vo et al., 1998, VIGMR, 1995; 1998). Geochemical and geophysical methods were applied to determine the temperature of the reservoirs and their potential for heating and other possible utilization. Two reservoirs were considered to have a higher potential than others including Le Thuy and Mo Duc. The chemical composition of the low-temperature geothermal waters was characterized by neutral to alkaline pH values and low to moderate Cl concentrations (VIGMR, 1995; 1998).

In Borgarfjörður, Iceland, the area is among the largest low-temperature fields in Iceland (Georgsson et al., 1984). It is located adjacent to the Reykjanes-Langjökull axial rift zone and is commonly divided into five thermal systems based on the resistivity and the chemical composition of the thermal water (Jóhannesson et al., 1980; Gunnlaugsson, 1980).

The basement of the Borgarfjörður area consists mainly of Late Tertiary basaltic lava flows. The region is divided into two fault systems based on the origins and character of the faults (Jóhannesson, 1980). The first one runs NE-SW like the fissure swarms of the active rift zone, which have been derived from the crustal tension inside the rift zone. The second one is faults formed by lateral shear forces in different directions, located in the Snæfellsnes Fracture Zone.

The geothermal geochemistry of low-temperature waters in Borgarfjörður has been previously studied in some detail (e.g., Gunnlaugsson, 1980; Arnórsson and Ólafsson, 1986; Kristmannsdóttir et al., 2005). Several projects have entailed geochemical studies of the geothermal fields in Borgarfjörður. Based on these studies, the waters are known to be of meteoric origin, with alkaline pH values and low Cl concentrations (<50 ppm). Based on geothermometer temperature estimations, reservoir temperatures may be as high as ~150°C in the area.

3. METHODS

In Central Vietnam 20 samples and in Borgarfjörður 12 samples of cold and low-temperature geothermal water were collected (32 samples in total). Samples were collected from both hot springs and non-thermal water according to standard methods (e.g., Arnórsson et al., 2006). The components analysed for were pH, DIC, H₂S, B, Si, F, Cl, Br, SO₄, Al, Ca, Fe, K, Mg, Na, δD and δ¹⁸O: these were analysed at the University of Iceland.

The processing of the data involved two steps: (1) estimation of fluid origin and mixing using conservative element behaviour and isotope ratios in water; (2) calculation of reservoir fluid composition and estimation of reservoir temperature;

Geothermal fluid origin and fluid mixing were assessed using stable water isotopes (δD and δ¹⁸O) and B and Cl concentration relations. For these calculations, the Cl concentration in precipitation was assumed to be 1-10 ppm (Sigurdsson and Einarsson, 1988). For basalts in Iceland, the Cl and B concentrations were taken to be 170 ppm and 1.2 ppm, respectively (Arnórsson and Andrésdóttir, 1995). The corresponding Cl and B concentrations for basalts, sandstone and carbonates in Vietnam were taken to be 60 ppm and 5 ppm, 10 ppm and 35 ppm, and 150 ppm and 20 ppm, respectively (Turekian and Wedepohl, 1961).

The calculations of reservoir temperatures, reservoir fluid composition, aqueous speciation and mineral saturation indices were carried out using the WATCH program (Arnórsson et al., 1982; Bjarnason, 2010). For these calculations, the quartz (Fournier and Potter, 1982), chalcedony (Fournier, 1977) and Na/K (Arnórsson et al., 1983) geothermometers were applied.

4. RESULTS

4.1 Chemical composition of waters from Vietnam

The measured surface temperatures of geothermal water in central Vietnam ranged between 42-96°C and the pH ranged between 6.24-9.29 (measured in the field after cooling). There were indications that H₂S was present in many samples from Vietnam but technical problems prevented it from being determined. The concentrations of SiO₂ were 38-138 ppm, B were 0.03-3.5 ppm and Cl concentrations were variable ranging from 3.36 to 2999 ppm with most waters sampled displaying low Cl concentrations except for Phu Vang, Mo Duc, and Tu Son thermal waters. Dissolved inorganic carbon concentrations were also elevated in some thermal fluids for example up to 277 ppm in Cam Tuyen and 866 ppm in Phu Vang. The δ¹⁸O and δD ratios were -8.92 to -5.84‰ and -57.56 to -32.64‰, respectively.

Based on the major elemental composition and geographical location (Figure 1), the water samples were divided into four groups: (1) ground water, (2) highland geothermal water, (3) lowland geothermal water and (4) coastal geothermal water (Fig. 2A). The coastal geothermal waters displayed high Cl and SO₄ concentration and most lowland geothermal waters were high in DIC concentration. Most of the samples were elevated in Na concentrations.

4.2 Chemical composition of waters from Borgarfjörður

The temperature of geothermal waters sampled in Borgarfjörður (Iceland) was 40-98°C and the pH measured in the field at ambient temperature was 6.24-9.29. The concentrations of SiO₂ were 54-178 ppm, those of B were 0.20-0.43 ppm and the Cl concentrations were 23.4-103 ppm. The DIC concentrations displayed a narrow concentration range of 23.2 to 44.3 ppm. The δ¹⁸O and δD ratios ranged between -12.05 to -9.32‰ and -88.76 to -68.37‰, respectively.

Based on the major constituent composition and geographical location of the waters (Figure 1), five groups were distinguished for the Borgarfjörður area: non-thermal water, Húsafell water, Runnar water, Laugarholt water, and 30–40 ppm Cl water (Fig. 2B). In all cases, the waters were relatively dilute, with DIC, SO_4 and Cl all being important anions and Na being the dominant cation.

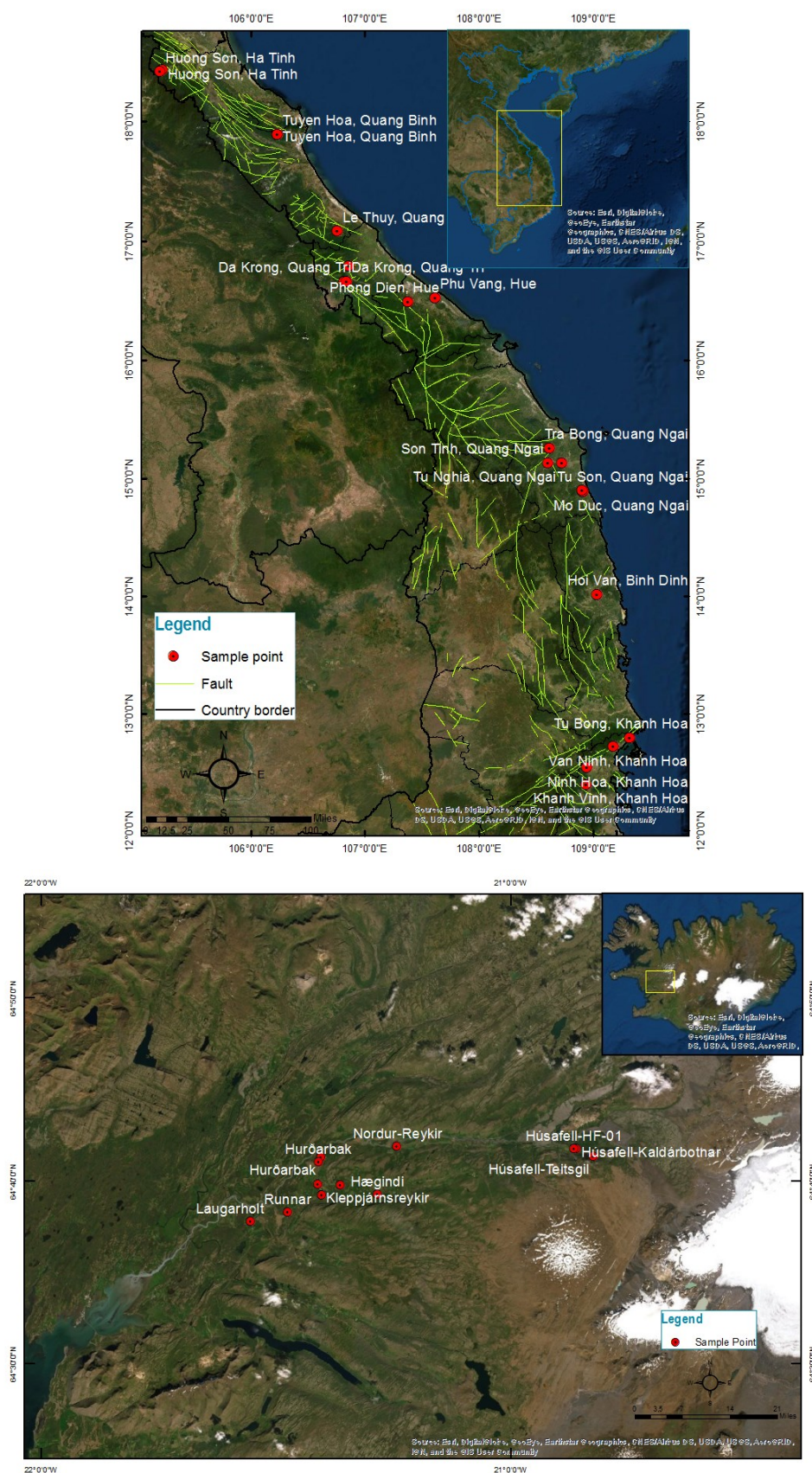


Figure 1: Sample locations at Borgarfjörður Iceland and Central Vietnam

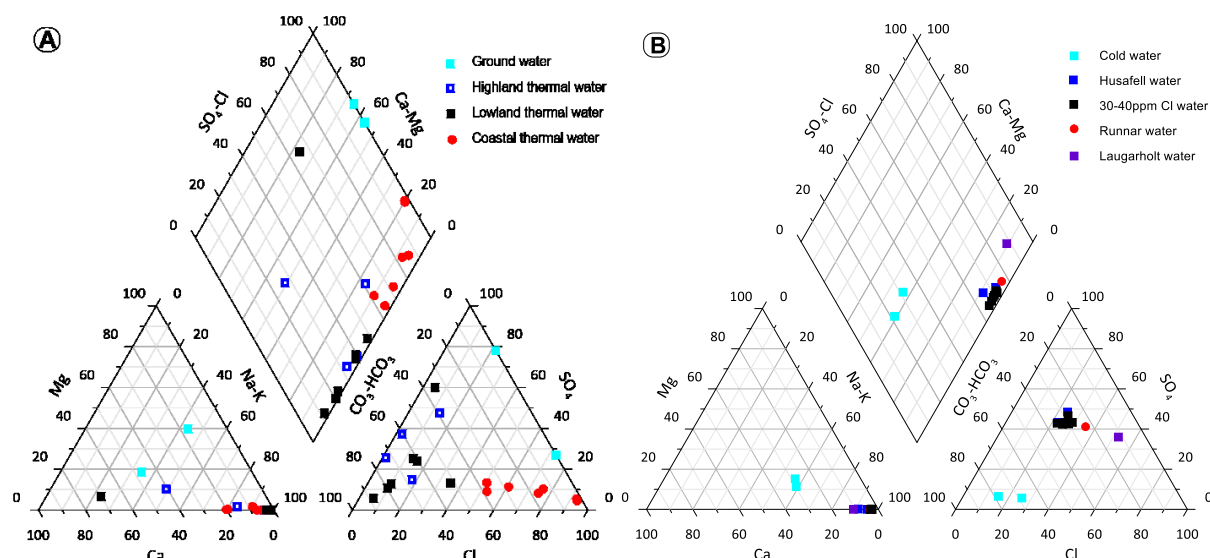


Figure 2: The chemical composition of non-thermal and geothermal waters in Central Vietnam (A) and Borgarfjörður Iceland (B) shown on a Piper diagrams

5. DISCUSSION

5.1 Water origin traced by δD and $\delta^{18}\text{O}$

Isotope ratios in water (δD and $\delta^{18}\text{O}$) are commonly applied to trace the origin of geothermal water (Craig, 1963; Árnason, 1976; Stefánsson 2017). The relationship between δD and $\delta^{18}\text{O}$ values for most low-temperature geothermal water closely follows the global meteoric water line (GMWL) suggesting meteoric sources and sometimes seawater (e.g., Árnason, 1976). In many cases, the δD and $\delta^{18}\text{O}$ ratios of the geothermal water resemble a local meteoric source but sometimes they differ suggesting water transport (for example from high to low ground or water originating from when climate conditions in the area were different).

In the Vietnam samples, the δD and $\delta^{18}\text{O}$ ratios ranged between -57.56 to -32.64‰ and -8.92 to -5.84‰ , respectively, whereas the corresponding values at Borgarfjörður Iceland were -88.76 to -68.37‰ and -12.05 to -9.45‰ , respectively. The δD of local precipitation in Vietnam was taken from the Atlas of Isotope Hydrology – Asia and the Pacific (IAEA, 2008) with values between -44 and -31.6‰ for two stations, both of which are located in the lowlands. The δD of precipitation in Borgarfjörður Iceland was taken from Árnason (1976), with values ranging from -82 to -62‰ for the region.

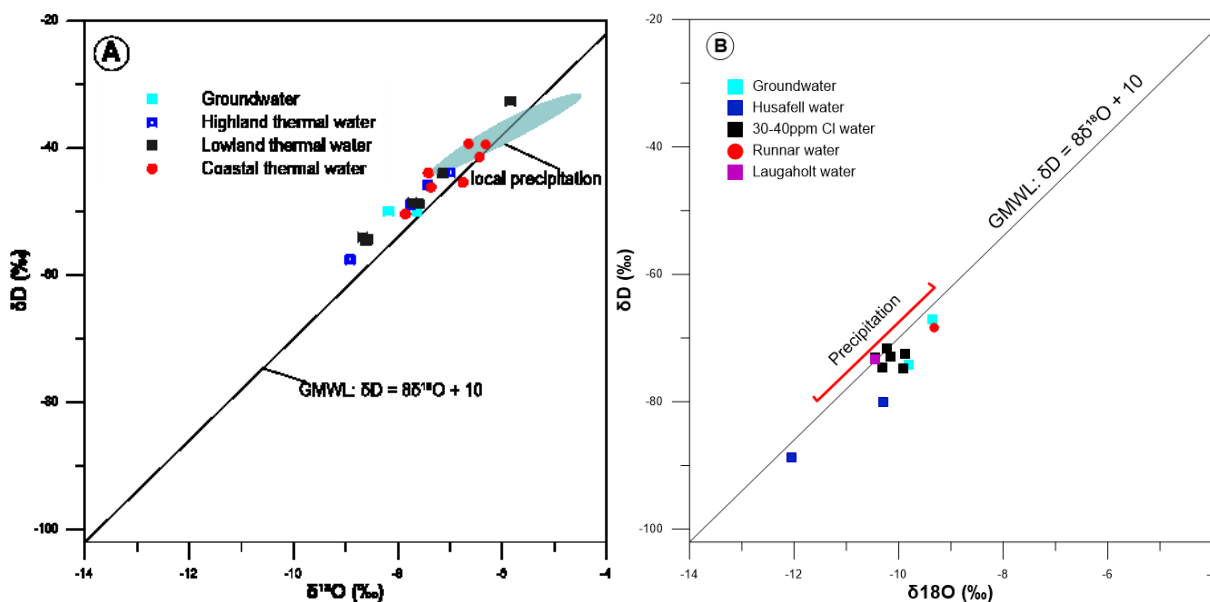


Figure 3: The relationship between δD and $\delta^{18}\text{O}$ in waters in Vietnam (A) and Borgarfjörður (B). Also shown is the range of values for local precipitation and the global meteoric water line (GMWL)

As seen in Figure 3, the δD and $\delta^{18}\text{O}$ of geothermal waters in Vietnam and Borgarfjörður closely follow the global meteoric water line indicating meteoric sources. The values for δD and $\delta^{18}\text{O}$ in Vietnam cover a wide range and show that the geothermal waters are likely from different reservoirs. The Vietnam thermal samples are generally more isotopically depleted than the reported precipitation

in the lowlands, which suggests that the hot springs may be recharged by rain that fell in the highlands. The δD and $\delta^{18}O$ values in Borgarfjörður are more tightly clustered indicating a similar and local source. All the water samples with 30–40 ppm Cl and waters at Laugarholt formed one group in terms of isotope ratios. In contrast, waters at Runnar displayed higher values and waters at Húsafell displayed lower values. According to Árnason (1976) the origin of geothermal water in Borgarfjörður is traced to the glacier ice melt and local precipitation with a general groundwater flow from the east towards the west. The higher δD values at Runnar and lower values at Húsafell are in good agreement with the geographical distribution of deuterium in local groundwater and precipitation. The geothermal waters are generally more depleted than non-thermal waters sampled near-by.

5.2 Water origin, mixing and progressive water-rock interaction

The Cl and B components of geothermal water have been used to gain information on the origin of the geothermal water and assess possible mixing of two or more water components of different composition (Arnórsson and Andrésdóttir, 1995; Stefánsson et al., 2017). Chloride and B are considered to be conservative in geothermal systems and are not incorporated into secondary minerals upon water-rock interaction. Non-thermal waters generally have low Cl and B concentrations, between <0.001 ppm and a few ppm and <1 ppb to several tens of ppb, respectively (e.g., Arnórsson and Andrésdóttir, 1995). In contrast, seawater has high Cl and B concentrations of 19400 ppm and 4.45 ppm respectively (Bruland, 1983). Upon water-rock interaction, Cl and B are dissolved from the primary rocks and volcanic glasses, the rock typically having a different Cl/B ratio than the meteoric and seawater sources. It follows, that Cl and B may be ideal to trace water origin (meteoric or seawater) and progressive rock leaching. It can further be used to assess mixing between two or more water sources given that their Cl/B ratios and concentrations are different.

The relationship of the Cl and B concentrations in the geothermal waters in Vietnam and Borgarfjörður are shown in Figure 4. The values for precipitation are also shown as well as the seawater ratio and trends corresponding to progressive rock leaching.

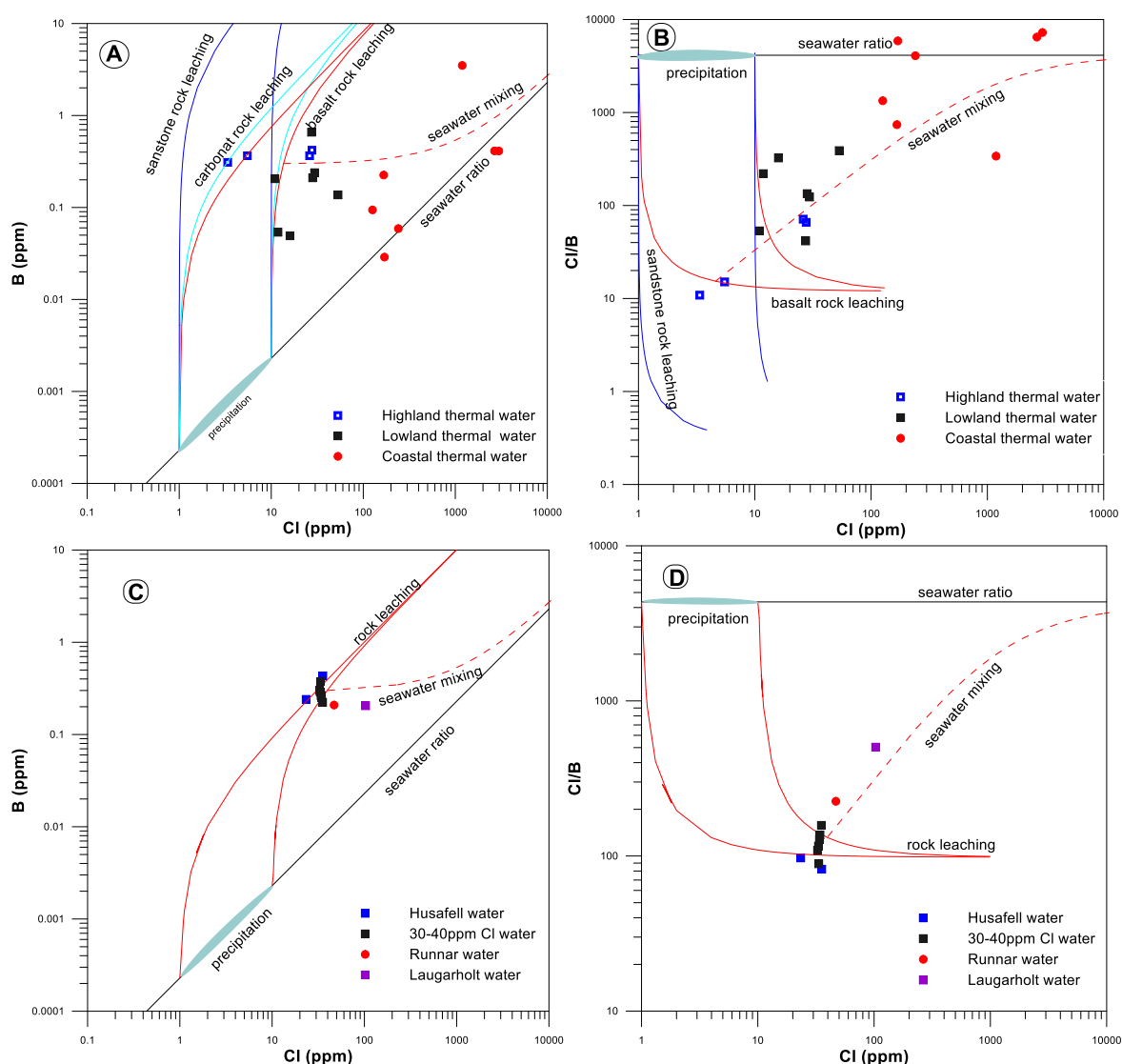


Figure 4: The relationship between Cl and B (A, C) and Cl/B and Cl (B, D) for geothermal waters in Borgarfjörður (C, D) and Central Vietnam (A, B). The Cl/B ratio of seawater was taken from Bruland (1983) and the corresponding rock ratios were taken from Arnórsson and Andrésdóttir (1995) and Turekian and Wedepohl (1961). The Cl concentration of local precipitation for both areas was assumed to be 1–10 ppm but may vary to greater degree: the limitation of assessing the exact value is the lack of data on precipitation chemical composition (in the Vietnam data)

Most of the waters in Borgarfjörður were observed to be enriched in B relative to the local meteoric water and have approached the Cl/B ratio of basaltic rock. The geothermal waters in Runnar and Laugarholt were enriched in Cl relative to B and the Cl/B basalt ratio thus raised. Mixing with old seawater or interaction with rocks having different Cl/B ratios could explain these discrepancies. Inspection of the relationship between δD and Cl/B ratio reveals the waters to be of modern and meteoric origin supporting the latter explanation. Moreover, the two samples from Húsafell displayed different δD values from deep well water having lower δD compared to the surface spring water sample. These findings suggest a slightly different water source depending on depth possibly suggesting a deep groundwater flow from Langjökull towards the west and more local meteoric water at shallow depths or there might be a mixture of the deep geothermal water (as the sample from the HF-well) and cold groundwater in the surface (Húsafell spring sample).

The relationship between Cl and B for the geothermal waters in Vietnam is shown in Figure 4 together with the corresponding values for precipitation and seawater and rock ratios. As the geothermal waters in Vietnam were located in systems of variable host rock composition (basalts, sandstone and carbonates) several trends upon rock leaching are shown. As observed, the geothermal waters in the highland areas indicate a meteoric origin affected by progressive water-rock interaction whereas waters in coastal and lowland areas indicate seawater mixing. However, an inspection of the relationship between δD and Cl/B (Figure 5) suggests that the source of the salts is not in all cases directly seawater input but rather meteoric water affected by dissolution of salt deposits of seawater origin or having similar Cl/B ratio as seawater, possibly indicative of old evaporites.

From the δD , $\delta^{18}O$, Cl and B relationships it can be concluded that all these low-temperature geothermal waters are predominantly of meteoric origin that have later been modified by progressive water-rock interaction. In Borgarfjörður, most of geothermal waters are from a similar reservoir with the exception of waters in Húsafell whereas the geothermal waters in Vietnam differ with respect to their geographical location.

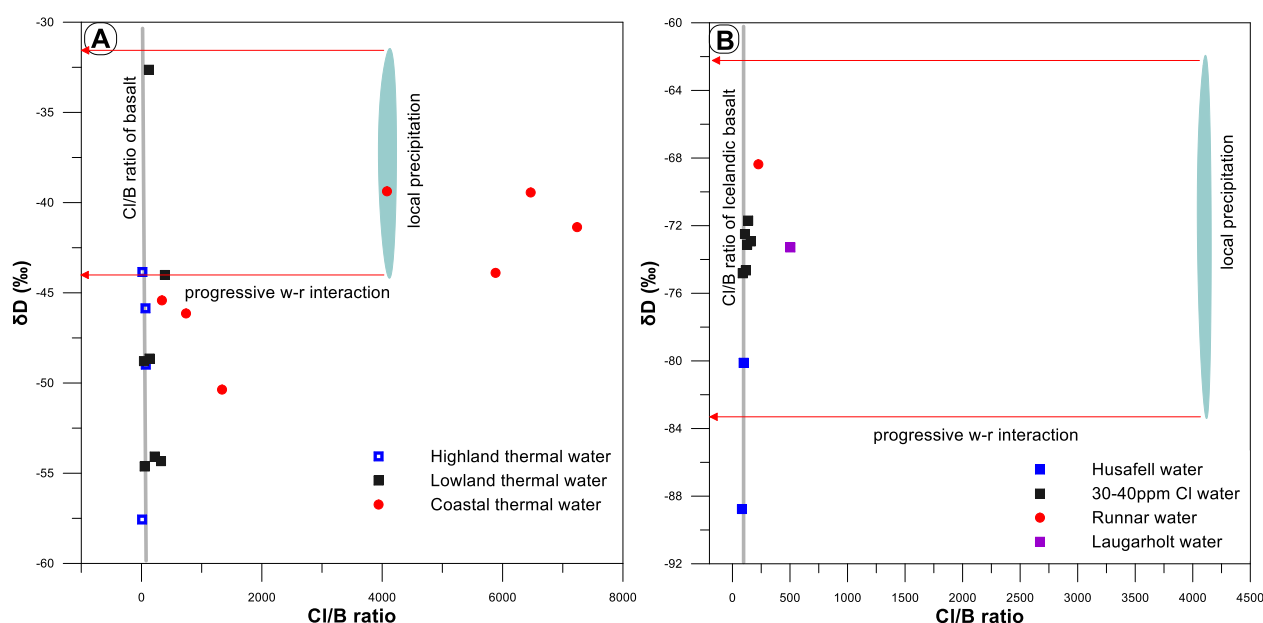


Figure 5: The relationship between δD and Cl/B in geothermal water from Vietnam (A) and Borgarfjörður Iceland (B). The Cl/B ratio of the various rock types were taken from Turekian and Wedepohl (1961) and Arnórsson and Andrésdóttir, 1995 and the seawater composition is taken from Bruland (1983)

5.3 Temperature of reservoir

Geothermometers have been applied to estimate geothermal reservoir temperatures at depth (e.g., Fournier and Truesdell, 1973; Fournier and Potter, 1979, 1982; Arnórsson et al., 1983; Giggenbach, 1988). For this study, the geothermometer temperatures were calculated for individual samples based on the quartz (Fournier and Potter, 1982), chalcedony (Fournier, 1977) and Na/K (Arnórsson et al., 1983) geothermometers. The calculations were conducted with the aid of the WATCH program (Arnórsson et al., 1982; Bjarnason, 2010). The results are reported in Table 1. Some discrepancy is observed between the different geothermometers. As expected, the quartz geothermometer always gives higher temperatures than the chalcedony geothermometer. The Na/K geothermometer falls below both silica geothermometers for all but one of the Icelandic samples, but it is more scattered around the silica geothermometry values for the Vietnamese samples; sometimes the highest and sometimes on the low end.

The silica geothermometers are expected to equilibrate faster than the Na/K geothermometer, as they are based on a precipitation-dissolution reaction whereas the Na/K geothermometer is based on a slower ion-exchange reaction. On the other hand, the Na/K geothermometer is less sensitive to boiling and dilution effects as it is based on an activity ratio and not the activity of a single species. Arnórsson (1983) has shown that waters sampled from geothermal drillholes in Iceland are generally at equilibrium with chalcedony at temperatures up to about 180°C, but in equilibrium with quartz at higher temperatures. For these reasons we suggest that the chalcedony geothermometer provides the most credible estimate of reservoir temperatures in the current study.

Table 1: The results of geothermometers for geothermal reservoir water in Vietnam and Borgarfjörður

Sample	Location	Water type	Surf. Temp °C	Quartz °C	Chalcedony °C	Na/K °C
<i>Vietnam</i>						
LV1	Huong Son	Na-HCO ₃	78	122	94	118
LV3	Tuyen Hoa	Na-HCO ₃	62	113	84	175
LV4	Le Thuy	Na-HCO ₃	96	147	121	158
LV5	Cam Tuyen	Na-HCO ₃	42	90	58	94
LV6	Da Krong	Na-HCO ₃	55	113	83	83
LV7	Da Krong	Na-HCO ₃	56	118	89	141
LV8	Phong Dien	Ca-SO ₄	64	109	80	241
LV9	Phu Vang	Na-Cl	50	75	43	142
LV10	Khanh Vinh	Na-HCO ₃	44	101	70	76
LV11	Ninh Hoa	Na-HCO ₃	66	106	76	87
LV12	Van Ninh	Na-Cl	66	109	79	93
LV13	Tu Bong	Na-Cl	75	125	97	109
LV14	Hoi Van	Na-Cl	79	139	112	136
LV15	Mo Duc	Na-Cl	80	139	112	136
LV16	Tu Son	Na-Cl	53	145	119	154
LV17	Tu Nghia	Na-Cl	80	126	98	114
LV18	Son Tinh	Na-HCO ₃	68	129	102	103
LV19	Tra Bong	Na-HCO ₃	64	100	69	93
<i>Iceland</i>						
L001	Húsafell-Teitsgil	Na-Cl	40	96	65	67
L003	Húsafell-HF-01	Na-Cl	76	115	86	68
L004	Nordur-Reykir	Na-Cl	91	142	116	95
L005	Hægindi	Na-HCO ₃	98	160	136	123
L006	Laugavellir	Na-HCO ₃	92	148	123	102
L007	Deildartunguhver	Na-Cl	97	141	115	94
L008	Kleppjársreykir	Na-Cl	89	139	112	94
L009	Runnar	Na-Cl	56	127	99	81
L010	Hurðarbak	Na-Cl	98	145	119	94
L012	Laugarholt	Na-Cl	77	138	111	83

6. CONCLUSION

The geochemistry of low-temperature geothermal water in Central Vietnam and Borgarfjörður (W-Iceland) was studied. Twenty samples of geothermal water were collected in Central Vietnam and twelve samples in Borgarfjörður in the summer of 2018. The water temperature, pH, DIC and H₂S concentrations were determined on site and major elemental composition analysed using ICP-OES and IC at the University of Iceland. The surface temperatures of the geothermal waters in Vietnam were 42- 96°C and in Borgarfjörður they were 40-98°C.

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