Proceedings World Geothermal Congress 2015
Melbourne, Australia, 19-25 April 2015

# Chloride Boride Relationship in the Pannonian Basin Geothermal Systems

Gísli Guðmundsson

Mannvit, Urðarhvarf 6, 203 Kópavogur, ICELAND

gislig@mannvit.is

**Keywords:** Chloride, boron, boron absorption, Pannonian Basin


## ABSTRACT

The correlation between chloride and boron concentrations of geothermal waters from the Pannonian Basin is very good, in spite of relatively scattered data and the fact that the Cl/B ratio (mass) of the geothermal fluid has a very wide range from about 1 to 500. At temperatures less than 100 °C, boron is taken up by low-temperature alteration minerals. The relationship between chlorides and boron underlines the progressive rock dissolution of these species and the contribution from fossil NaCl-type water.


## 1. INTRODUCTION

The Pannonian Basin is a part of the Alpine–Carpathian mountain belt in Central Europe. It is surrounded by the Eastern Alps to the west, the Carpathians to the north and east and the Dinarides to the south. These mountain belts are the result of the Cenozoic continent–continent collision of Europe and Africa. The Pannonian Basin is a Neogene extensional basin that was filled by large deltaic systems originated from the surrounding mountain ranges. Several sub-basins separated by metamorphic core-complexes were formed (Tari et al., 1992). These sub-basins were filled with thick sediments of Miocene to Quaternary age. During the sedimentation, marine to brackish, syn-rift sediments were deposited. The hydrological extension of the Pannonian Basin is a large (100,000 km$^2$), non-uniform multi-layer flow system formed mainly during the late Tertiary and Quaternary periods (Varsány et al., 1997).

The pre-Tertiary basement rocks, overlain by the Miocene and Quaternary sediments, are mainly composed of crystalline Precambrian rocks and/or Mesozoic sediments. The basement rocks have undergone multiple and complicated tectonic events. Due to the crustal extension, crustal thinning occurred which resulted in relatively high geothermal gradient. The average geothermal gradient in Hungarian geothermal systems is about 50 °C/km (Tulinius et al., 2010), comparable to the value of about 30 °C for the bulk of the European continent. Consequently, hidden geothermal systems are well-known in the Pannonian Basin.

The chloride and boron concentration in geothermal waters of volcanic and sedimentary rocks varies by several orders of magnitude. Chloride concentration ranges from ~10 ppm to ~25,000 ppm (i.e. Mahon, 1970; Ellis and Mahon, 1977; Arnórsson et al., 1982; McKibben et al., 1987; Michard et al., 1989, Bernard et al., 2011) and for boron, the range is much narrow, from ~ 1 ppm to ~1,000 ppm B (i.e. Ellis and Sewell, 1963; Ellis and Mahon, 1966, 1977; Arnórsson et al., 1982; Shaw and Sturchio, 1992, Bernard et al., 2011).

The concentration of chloride and boron in rain and fresh ground water is generally much lower than in geothermal water, particularly in areas like the Pannonian Basin, where the coastal areas are not nearby.

The concentration of chloride and boron in volcanic rocks is normally low, but relatively high in sedimentary rocks and evaporates. However, volcanic rocks derived from subduction environments, like the basement within the Pannonian Basin, can have relatively high chloride and/or boron content. This might suggest deep circulation paths of geothermal fluids to interact with magmatic fluids. Nevertheless, the likely source of high chloride and boron content of geothermal fluid in the Pannonian Basin lies within relatively thick sedimentary cover. The concentration of chloride and boron in the host rock is an important parameter from the chloride boron relationship in geothermal fluid, but is beyond the scope of this paper.

The relatively high concentration of chlorides and boron, as well as other species in thermal water from the Pannonian Basin is unique in many ways. The area is landlocked, which rules out the influence from seawater in terms of the composition, yet the concentration has the same level with the seawater-dominated geothermal systems in Iceland for instance (e.g. Arnórsson et al., 1982). The source of the high concentration in the Pannonian Basin is fossil NaCl-type water (Varsányi et al., 1997).

Arnórsson and Andrésdóttir (1995) studied processes which controlled the distribution of chloride and boron in natural waters in Iceland. One of the main conclusions was that both chlorides and boron act essentially as incompatible elements at all temperatures in the natural water-volcanic rock environment in Iceland. The absence of clay minerals that tend to absorb boron in low temperature geothermal systems and high water/rock ratios was considered as the main reason for the incompatible nature of boron at low temperatures. Later, Aggarwal et al. (2000) concluded that there is evidence, which suggests some uptake of boron into secondary minerals in low temperature waters in Iceland.

The purpose of this work was to study the chloride-boride relationship in geothermal fluid from various geothermal systems within the Pannonian Basin. The geothermal systems which were studied are either low enthalpy geothermal systems, with temperatures less than 100 °C or medium high enthalpy systems with temperatures between 100 and about 180 °C.

## 2. CHLORIDE BORIDE RELATIONSHIP IN GEOTHERMAL FLUID

The chloride and boron content of geothermal water has been widely studied for various purposes. Chloride and boron content of geothermal fluids give indication of the origin of the fluid (i.e., White, 1957a, b) and allow to evaluate the degree of mixing between hot and cold water in the up-flow zones of geothermal systems. The species can also be used to assess other characteristics of geothermal systems (i.e. Ellis, 1970; White, 1970; Founier, 1977, 1979; Arnórsson, 1985; Janik et al., 1991).

The two species are useful for these purposes for several reasons. Their concentration range is wide providing characteristic Cl/B ratios for the individual geothermal reservoirs. Chloride and boron are also highly soluble in geothermal waters, and do not reach state of saturation in most geothermal systems. Therefore, their uptake into secondary minerals does not occur, especially at high temperatures (> 100°C) (Ellis and Mahon, 1964; Ellis and Mahon, 1967). At these temperatures both the species are called conservative elements. At lower temperatures (< 100°C), boron can be removed from solution by absorption onto clays and incorporation into secondary minerals, especially illite and mica (Harder, 1970; Keren and Mezuman 1981; Seyfried et al., 1984; Palmer et al., 1987). Furthermore, boron is readily removed from solution during a low temperature (< 100°C) basalt-seawater interaction (Seyfried et al., 1984). The concentration of chloride and boron in the source rocks controls the concentration of the elements in the geothermal fluid along with the temperature and concentration of the elements in the source (recharge) water.

Water-dominated hydrothermal systems have a strong positive correlation between chloride and boron with a wide range of Cl/B ratio, from 1 for Ngawha, New Zealand (weight ratio, i.e., Ellis and Mahon, 1977) to 1000 for Cerro-Prieto, Mexico (i.e., Truesdell et al., 1981).

The geochemistry of geothermal fluids observed in the Pannonian Basin has been extensively studied, both in closed applied studies as well as academic research (e.g. Varsányi et al., 1997). Based on dD and d$^{18}$O analyses, Varsányi and Kováca (2006) classify thermal water in the Basin into three end-members:

- a fossil NaCl-type water with a salinity similar to that of the former Lake Pannon,
- a paleometeoric $NaHCO_3$-type water that infiltrated during the last glacial, and
- a $NaHCO_3$ paleometeoric water that infiltrated during a warm period before the last glacial.

These end-members are mixed in various degrees and result in different geothermal water types, observed in various parts of the Basin. The degree of mixing with local rain water is not mentioned. This model was applied to the central part of the Pannonian Basin in Hungary, but it is unknown whether it can be applied to the entire Basin. However, throughout the Basin, chloride and boron rich geothermal water is commonly encountered at the base of geothermal systems.

## 3. DATA COLLECTION/DATA TREATMENT

The chemical data used for this study has been collected by Mannvit over the past seven years. The data is taken from various reports, all of which are open to the public. Extensive data is available for the entire area. For this study, only the data from 1985 and younger was selected. Most of the data originates from Hungary, which is not surprising since the bulk of the Pannonian Basin is within the Hungarian border. In this study, the data from countries within the Pannonian Basin other than Hungary are not as complete as the Hungarian record. All the data is based on analyses of thermal waters collected at well heads.

In this study, the data was not treated; the only requirement was that the charge balance as a percentage of the total ionic charge of the solution should be less than 5 %.

The pH value was measured in most samples, but it was not dealt with for this work, or for the speciation of chloride or boron. It was assumed that chloride was as $Cl^-$ and boron as $H_3BO_3$. This may or may not be true for boron at low temperature (Arnórsson and Andrésdóttir, 1995). However, the main aqueous species of boron are undissociated boric acid, $H_3BO_3$, and the borate anion $B(OH)_4^-$. The relative abundances of the boron species are sensitive to pH. At low pH, $H_3BO_3$ is the main species, but at high pH (> 8 – 9) $B(OH)_4^-$ dominates (Barth, 2000). The measured pH value for bulk of the studied samples was less than 8; hence the main species is found as $H_3BO_3$.

## 4. RESULTS

The temperature of the thermal water studied in this study ranges from just above ambient up to approximately 180 °C. The information on the temperature measurements is very limited in most records, but in most cases, if not all cases, the temperature is a discharge temperature.

The chloride content increases with increasing temperature. Figure 1 shows how the chloride content varies with temperature. The chloride content ranges from about 5 ppm up to about 25.000 ppm, but for bulk of the data 15.000 ppm is the maximum chloride content.

The response of boron with increasing temperature is shown in Figure 2. The data is much more scattered than is observed for chloride (see Figure 1), but the tendency of increased concentration with increased temperature is clear. The boron content has much lower range than chloride, from about 0.5 ppm to about 350 ppm.

It seems that both chloride and boron content is influenced by inflow and mixing of cold groundwater with the hotter water at low temperatures.

The chloride boron relationship is shown in Figure 3 in a log-log plot. The chloride-boron relationship in geothermal fluid of Pannonian Basin geothermal systems is such that the Cl/B ratio follows the ratio of seawater. However, for fixed boron content, the chloride concentration is considerably lower in the Pannonian Basin than the seawater. The chlorides and boron are well correlated on a single linear trend, although the data is considerably scattered.

## 5. DISCUSSIONS

In Figure 4, the chloride/boron ratio is plotted as a function of the chloride content. The Cl/B ratio has a wide range from about 1 up to about 500. Geothermal fluids from water-dominated geothermal systems have wide a range of Cl/B ratio, while common range is known as 10–100 (e.g. Ellis and Mahon, 1977). This underlines the wide range of Cl/B ratio for the geothermal fluids in the Pannonian basin.

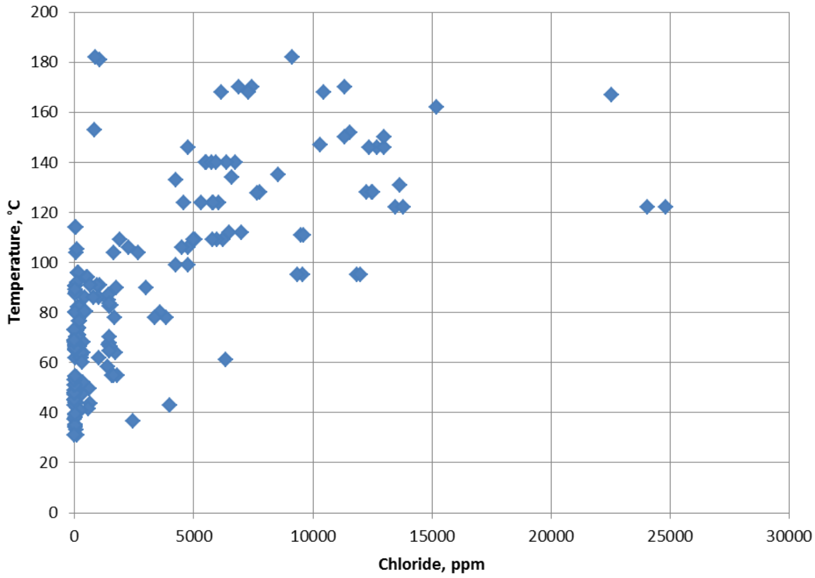


**Figure 1. The chloride content as a function of temperature in geothermal water from the Pannonian Basin.**

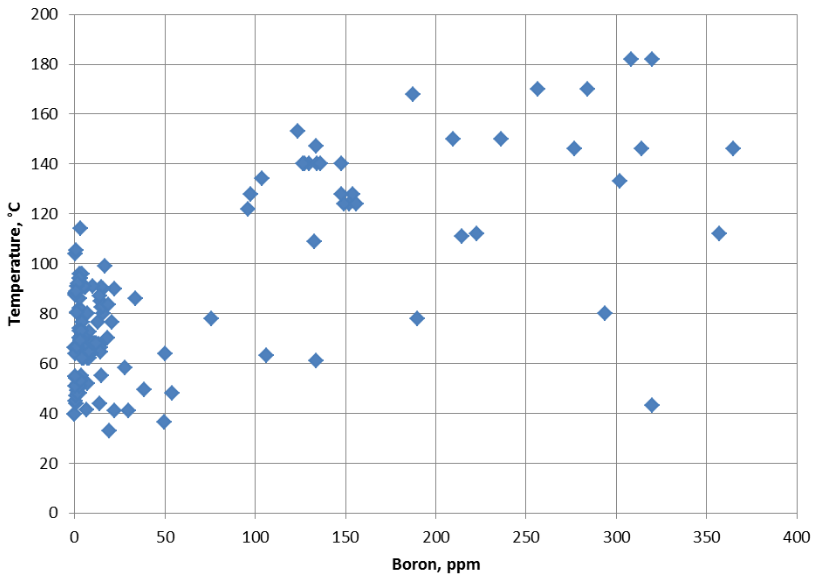


**Figure 2. The boron content as a function of temperature in geothermal water from Pannonian Basin.**

When the chloride/boron ratio is plotted as a function of the chloride content with a distinction between low temperature data (< 100 °C) and high temperature data (> 100 °C), the low temperature data has lower chloride concentration than the high temperature data, for a given Cl/B ratio, see Figure 4. In other words, the low temperature samples have higher Cl/B ratio than the high temperature samples. Geothermal fluid, which has evolved at temperatures above 100°C, has generally much higher boron content than fluids from less than 100°C systems. This suggests that boron in the Pannonian Basin geothermal systems acts as a reactive element in low-enthalpy geothermal systems as it precipitates from solution presumably having low temperature clay minerals. However, in medium enthalpy geothermal systems, boron behaves as an incompatible element.

Similar conclusion was reached for the thermal waters in western Turkey (Gemici and Tarcan, 2002). The lower Cl/B ratio of the higher temperature samples (> 100°C) in western Turkey is possibly (partially) caused by boron degassing from massive intrusives at depth. For the Pannonian Basin, this seems unlikely, but still cannot be ruled out.

The correlation between chlorides and boron underlines the progressive rock dissolution of these species, see Figure 3. Arnórsson and Andrésdóttir (1995) came to the conclusion that chlorides and boron are released from rock during water–rock interaction in approximately stoichiometric proportions for the high temperature waters. Since the concentration of chlorides and boron of the host rock was not studied in this work, it cannot be evaluated whether this is the case for the Pannonian Basin. Nevertheless, the source of chlorides and boron for geothermal fluids in the Pannonian Basin is interpreted as affected by progressive water-rock interaction with a contribution from fossil NaCl-type water. Mixing between two or more local aquifers is very likely to be a contributing/influencing factor, but the data does not allow for such studies. Contribution from magmatic fluids cannot be ruled out.

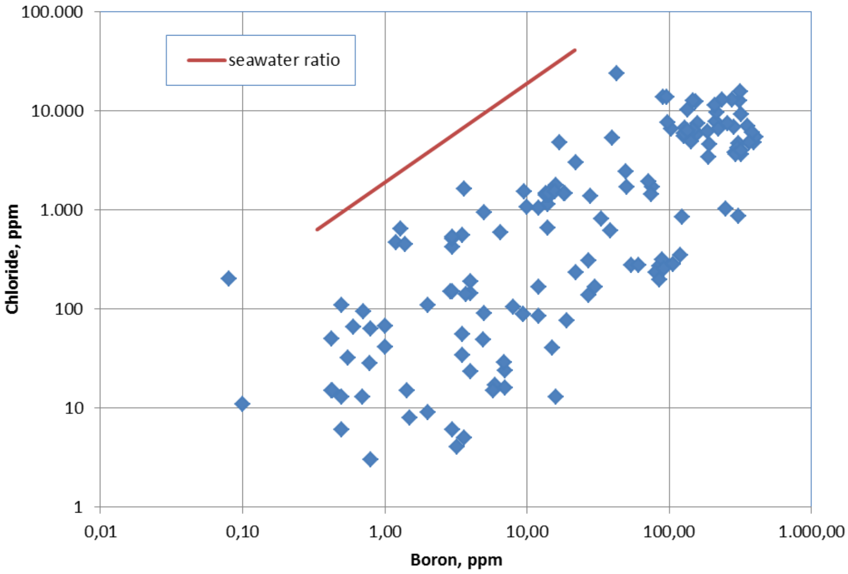


**Figure 3: The chloride–boron relationship in geothermal water from the Pannonian Basin, in a log-log scale. The solid line shows the Cl/B ratio in seawater.**

The correlation between $HCO_3$ and boron content is reasonably good, of both low and high temperature samples, which suggests that the concentration of boron in thermal waters are associated with the dissolution of carbonates. This is similar to what Gemici and Tarcan (2002) found in western Turkey. The Pannonian thermal water is relatively rich in carbonate and often associated with $CO_2$ gas phase, therefore it is necessary to understand the correlation between boron and carbonates in geothermal waters of the Pannonian Basin.

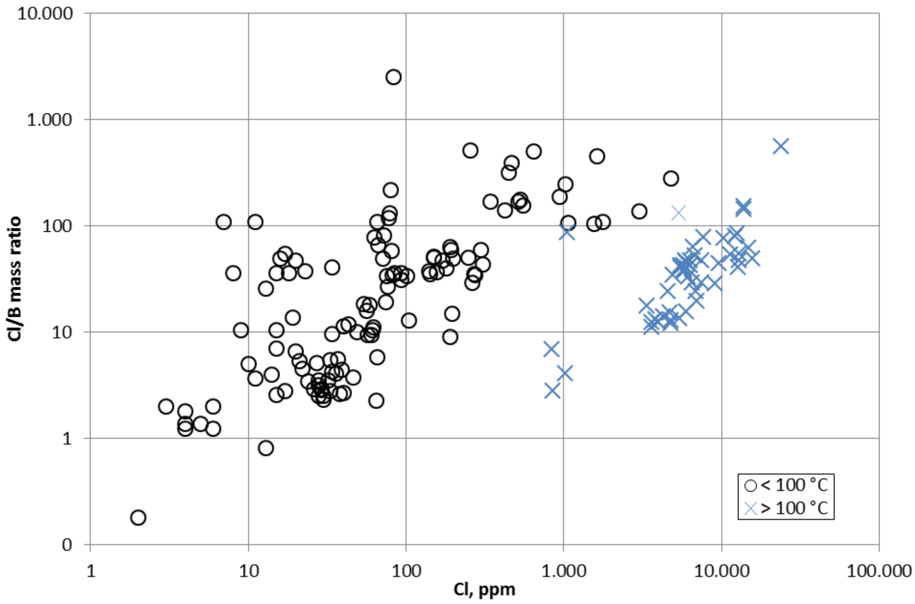


**Figure 4: The chloride/boron ratio vs chloride content in geothermal water from the Pannonian Basin in a log-log plot. Open circles show data for temperature less than 100 °C and crosses show the data for temperatures higher than 100 °C.**

## 5. CONCLUSIONS

The chloride and boron concentrations of geothermal waters from the Pannonian Basin increase with increasing water temperatures. Furthermore, the correlation between the two species is very good, although the data is scattered. This is particularly evident for the chlorides in thermal areas where temperature is higher than 100°C. However, the correlation for the low temperature waters is not good because of mixing with ground waters during the up flow to the surface. Additionally, at low temperature, boron is taken up by alteration minerals, causing the Cl/B to be relatively higher at low temperatures.

The correlation between chlorides and boron highlights the progressive rock dissolution of these species and contribution from fossil NaCl-type water.

The Cl/B ratio (mass) of geothermal fluid from the Pannonian Basin has a very wide range changing from about 1 to about 500, which covers almost the entire world range of 1 to 1000.

This study is based on publically available open source data, which did not allow for detailed study on each area, or for mixing between different aquifers within one group of wells. In order to understand the nature of chloride-boron relationship and to take full benefits from geothermal data, this needs to be carried out.

**ACKNOWLEDGEMENTS**

Enikö Mérész and László Ádám are thanked for collecting the data in Hungary.

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