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Use of Cl/Br Ratio to Decipher the Origin of Dissolved Mineral Components in Deep Fluids from the Alps Range and Neighbouring Areas

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ABSTRACT

Cl/Br ratios were studied in deep groundwaters to decipher the origin of dissolved mineral components from the Alps and neighbouring areas. Cl/Br molar ratio represents a good marker to define if the salinity comes from seawater or residual brines (655 and lower) or from dissolution of halite or halite-rich gypsum, often present in the Triassic formations (upper than the seawater ratio). It can be an interesting tool for projects dealing with exploration and production of geothermal fluids. Results of this study showed the presence of trapped seawater in formations of the large basins from the Quaternary to the basement, resulting from infiltration during different marine intrusion periods. This method also showed the presence of brines in crystalline aquifers. Some of these waters discharge along subvertical faults and are diluted to various degrees by different types of meteoric waters. In some cases, this method raises new questions about the true geological origin of deep circulations.

1. INTRODUCTION

Some hydrothermal systems in the Alps range and neighbouring areas from various geological settings display high chloride contents reaching 190 g/L. The origin of the dissolved mineral components from deep fluids is still controversial after decades of chemical and isotopic investigations. To help interpreting the high chloride concentrations in thermal waters of the Alps range, the Cl/Br ratio is studied and employed as a natural tracer. Assuming Cl^- and Br^- as conservative elements in solution, the molar Cl/Br ratio is close to 655 for the seawater (mass ratio around 290), is lower for residual brines and is greater in waters dissolving halite mineral (Alcalá and Custodio, 2008; Davis et al., 1998; Davis et al., 2001; Fontes and Matray, 1993; Herrmann, 1972; Kloppmann et al., 2001; McCaffrey et al., 1987). Moreover, other chemical processes can provide saline groundwaters as it was shown for the Carnmenellis granite in England from hydrolysis of plagioclase and biotite (Edmunds et al., 1984). Chloride deriving from atmospheric and waste sources (Alcalá and Custodio, 2008) can be neglected compared to the leaching of brines and the dissolution of halite for deep fluids in the Alps range having Cl^->10% of the Total Dissolved Solids (TDS).

Several studies in the world highlight the use of the Cl/Br ratio to decipher the origin of the salinity in groundwaters from the dissolution of halite or the leaching of residual brines. A study on the applicability of the Cl/Br ratio was presented by Alcalá and Custodio (2008) for groundwaters in Spain and Portugal. They concluded that the leaching and dissolution of natural halite and gypsum-rich formations containing some halite may yield Cl/Br ratios between 1000 and several thousands, although the leaching of potassium halides near salt mines produces Cl/Br ratios below the seawater ratio.

Other examples were presented in Europe from deep groundwaters in sedimentary basins such as the Northern German Basin (Kloppmann et al., 2001) and the Paris Basin in France (Fontes and Matray, 1993). For the German Basin in the vicinity of a Permian salt dome (diapir of Gorleben-Rambow), all Na-Cl type salt waters are significantly depleted in bromide, with Cl/Br exceeding 1000 and situated in the typical domain of halite dissolution. Concerning deep groundwaters of the Paris Basin, three aquifers in the Dogger (Middle Jurassic), Rhaetian and Keuper formations (Upper Triassic) were crossed by boreholes, and contain waters with high chloride contents. The use of the Cl/Br ratio allowed defining two types of brines. The Dogger and Keuper ratios are lower than the seawater ratio, whereas the Rhaetian ratio is greater. Fontes and Matray (1993) concluded that the Dogger and Keuper salt waters are related to a primary brine, and the Rhaetian salt waters result from the mixing of brines of different origins (primary and secondary). The secondary brine was formed by salt dissolution. All of the saline solutions, especially those from the Dogger aquifer, are diluted by meteoric waters which had not modified their Cl/Br ratio.

As regards to studies in the crystalline basement, fluid inclusions in the Stripa granite in Sweden influence on the groundwater chemistry (Nordstrom et al., 1989). Indeed, the leaching of residual brines by meteoric waters was proposed as a hypothesis for the origin of major solutes (Na>Ca-Cl) in the deep groundwaters, due to Cl/Br measurements around 100.

In the Alps range, no publication is available about the use of Cl/Br in thermal waters. Recently, an unpublished report presenting the hydrothermal system of Saint-Gervais-les-Bains in the French Alps describes mixing processes between thermal components and shallow groundwaters. Although emerging from evaporitic formations (Permian-Trias), the deepest thermal component rich in chloride (1 g/L) has Cl/Br lower than for seawater. In this geothermal site, cold springs from evaporites are poor in chloride (20 mg/L), suggesting that the thermal component flows in the crystalline basement leaching residual brines below the Permian-Trias formations.

Out of Europe, several examples illustrate the use of Cl/Br ratio in natural groundwater systems. A study on the potable waters from Alberta in Canada and Kansas and Arizona in the United States carried out by Davis et al. (1998) gave results of mass ratios between 50-150 for atmospheric precipitation and upper than 1000 for waters affected by dissolution of halite. Later, Davis et al. (2001) were interested by other groundwaters in the United States. They concluded for Alexander Springs in Florida about the presence of seawater trapped in the aquifer due to Cl/Br measured ratios similar to seawater. They also measured high Cl/Br ratio in the Big Spring in Iowa from the dissolution of road salt or agricultural chemicals.

Another study based on the use of Cl/Br ratios was conducted for groundwaters from the Michigan and Alberta Basins, and their saline solutions were compared to deep waters in Precambrian crystalline rocks of the Canadian Shield (Kelly et al., 1986). Results showed that formation waters of the Alberta Basin have Cl/Br ratios consistently higher than those of the Michigan Basin waters and of the Precambrian minewaters (mass ratio around 100). For the Precambrian crystalline rocks, these brines have remarkably similar Cl/Br ratios, even if they are geographically dispersed and present in various geological settings (Kelly et al., 1986). More recently, a study of Cl/Br ratios in groundwaters in the Riverine Province of the southeast Murray Basin allows defining differences in groundwater recharge and flow path. Cartwright et al. (2006) showed that Cl/Br ratios correlate with differences in recharge and groundwater salinity. The variation in Cl/Br ratios was interpreted as due to small differences in the volume of windblown halite that the groundwater has dissolved during recharge.

All these studies emphasize the use of Cl/Br ratio to decipher the origin of saline solutions from various geographical and geological settings such as sedimentary basins or crystalline basements. Firstly, the natural variations of chloride and bromide contents in the seawater and its products during evaporation phases will be discussed in this paper. Then, the location of hydrothermal systems in the Alps range and neighbouring areas will be presented, and the geology of the Alps will be summarized. Lastly, different types of maps showing chloride contents, Cl/TDS and Cl/Br ratios will be presented and coupled to the geological setting to discuss about the origin of the dissolved mineral components from deep fluids.

2. CL/BR RATIO OF EVAPORATED SEAWATER

The most significant difference between bromide and chloride is the difference of natural abundances, and small changes in the total mass of bromide in fluids or solids will give rise to large variations of Cl/Br ratios (Davis et al., 1998). The molar and mass Cl/Br ratios for the seawater are around 655 and 290 respectively (Alcalá and Custodio, 2008). With the evaporation of seawater, geochemical equilibria are modified leading to precipitation and deposition of successive minerals (McCaffrey et al., 1987). Seawater is less saturated with respect to Na-Cl compared to carbonates and sulphates, therefore the precipitation of halite occurs later compared to the calcite and gypsum. In the seawater, the least concentrated salts are epsomite ($MgSO_4.7H_2O$), sylvite (KCl), carnallite ($KMgCl_3.6H_2O$) and bischofite ($MgCl_2.6H_2O$) which crystallize tardily (McCaffrey et al., 1987). Differences would exist in evaporitic series due to incomplete evaporitic cycles and geochemical unbalances in solutions. Indeed, the presence of sylvite is exceptional and occurs in shallow basins.

Progressively during evaporation, Cl/Br ratio in the residual seawater remains stable during the precipitation of calcite and gypsum (figure 1). It starts to decrease when halite precipitates at about 6.2 mol/L of Na-Cl concentration. Precipitated halite is poor in bromide, especially in the early phases, since bromide is not easily included in the crystalline network (Alcalá and Custodio, 2008). Therefore, the molar Cl/Br ratio in halite increases and can reach 40’000 (Herrmann, 1972) and the molar ratio in the residual seawater or brine decreases continuously until values around 70-100 reaching the bischofite stage (Fontes and Matray, 1993; McCaffrey et al., 1987).

Evaporites in the Alps range are found in the Permian-Triassic formations and locally in some Tertiary layers. They result from the deposition of minerals during the evaporation of seawater, and mainly contain carbonates and sulphates. The occurrence of halite in evaporites is uncertain because halite quite seldom outcropping, but it seems to be locally present in limited areas. Evaporites in the Alps range can be met everywhere and are often found in thrust faults which drain deep fluids towards the surface. They are fractured and sometimes karstified what gives them high hydraulic conductivities being able to generate deep flow systems.

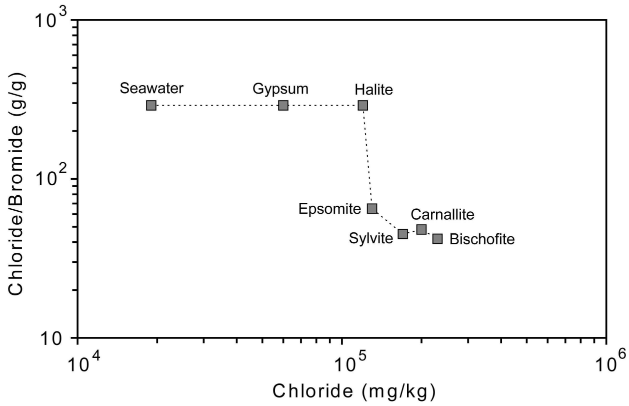

Figure 1: Cl/Br vs. Cl plot for residual brines formed during the successive phases of seawater evaporation (modified from Fontes and Matray, 1993)

3. THE FIELD AREA

A total of 223 geothermal sites with deep fluids from springs and boreholes were selected and gathered in table 1. Their location is presented in the geographical map of the Alps range which extends from France to Austria (figure 2). Concentration of sites is related either to the availability of data from the literature, or to the presence of high geothermal gradients and significant heat flow anomalies as for the northern part of Switzerland (> 150 mW/m^2, Rybach et al., 1987), a local zone in the Po Basin and the western part of Slovenia (> 100 mW/m^2, Hurtig et al., 1991).

In Switzerland, data of 66 geothermal sites were documented from BDFGeotherm database (Sonney and Vuataz, 2008), and completed adding bromide concentrations from various literature such as PhD theses, published papers, books and technical reports (table 1). Concerning Austria and Germany, data come from the study of mineral and thermal waters in Central Europe (Carlé, 1975) and the Atlas of Geothermal Resources in Europe (Hunter and Haenel, 2002). For France, data were documented from several PhD theses, whereas for Italy and Slovenia they are generally listed in published papers and in the Atlas previously quoted.

4. GEOLOGY OF THE ALPS

This section, based on the publication by Schmid et al. (2004), summarizes the geological and tectonic overall architecture of the Alps range. The European Alps are located in the south-central Europe and record the closure of ocean basins located in the Mediterranean region during convergence of the African and European plates. Oceanic and continental paleogeographical domains were intensively deformed and arranged in a non-cylindrical form during the tectonic events from the Cretaceous, and were affected by different ages of metamorphic events (Tertiary in the western Alps, Cretaceous in the Austroalpine units of the eastern Alps). The map presented in plate 1 represents a simplified overview of the major tectonic units (Schmid et al., 2004). From the NW to the SE, the main tectonic domains including units consist of the Northern Alpine foreland and Helvetic nappes, the Sub-Penninic nappes, the Penninic nappes, the Austroalpine nappes and the Southern Alps.

4.1. Northern Alpine foreland and Helvetic nappes

This domain also named European margin is located in the northern and western part of the Alps. It consists of external crystalline massifs and their sedimentary covers which extend towards the north below the Tertiary Molasse, and Helvetic cover nappes. This domain was affected by Miocene thick-skinned thrust propagation leading to the formation of external massifs and the Chaînes Subalpines (southern part of the unit 39 in plate 1), followed by thin skinned deformation during Late Miocene to Pliocene (Jura Mountains, northern part of the unit 39). The Molasse Basin (unit 2) is well developed in Switzerland and in the south of Germany, and forms foreland hills studded with lakes and large plains. The Tertiary formations stratigraphically overlie the Cenozoic and Mesozoic formations and consist of alternation of marine and continental deposits. The Oligocene flysch unit is found on top of the Helvetic nappes and thrust onto the Molasse Basin. In Eastern Austria, the molasse foreland is narrower and shallower as compared to Switzerland and its sedimentary fill is dominated by deeper water clastics.

The external massifs of the western Alps and their sedimentary cover were strongly affected by Neogene thick-skinned thrusting. By contrast, the eastern Alps are devoid of external massifs. Concerning Helvetic and Ultrahelvetic nappes (unit 36), they are also part of the European margin and are present in the Swiss and western Austrian Alps.

4.2. Sub-Penninic nappes (distal European margin)

The Sub-Penninic nappes refer to pre-Mesozoic basement onto which sediments were deposited in distal parts of the European upper crust. These nappes (units 33 to 35), predominantly consist of Variscan basement, and occasionally, the Mesozoic cover was not detached. The Sub-Penninic basement nappes, which were detached from their deeper crustal underpinnings during subduction are presently exposed in Lepontine dome (central part of the Alps between Zürich and Milano in plate 1), as well as in the Tauern window (central part of the Alps between München and Trieste).

4.3 Penninic nappes

The Penninic nappes can be divided into three main subdomains from the distal European margin (NW) to the Apulian margin (SE). The northwestern subdomain represents the Lower Penninic nappes which consist of two units (31 and 32) considered as derived from the Valais Ocean. Formations predominantly consist of rather monotonous calcareous shales and sandstones with mostly the absence of pre-Mesozoic crystalline basement. Only parts of these sediments were deposited on ophiolitic rocks which can be locally found.

The second subdomain refers to the Middle Penninic nappes or Briançonnais terrane and is located more in the southeastern. It includes four units (27 to 30) such as the sedimentary cover of Middle Penninic basement nappes, the same basement nappes, the detached cover nappes and the Permo-Carboniferous sediments (Zone Houillère) with their Mesozoic cover (Briançonnais). These tectonic units derived from a micro-continent zone between the Valais and the Piedmont-Liguria Oceans. Rocks of the Piedmont-Liguria Ocean represent the third subdomain located directly adjacent to the Apulian margin. These rocks are ophiolites and calcareous shales named Schistes Lustrés of the Upper Penninic nappes (unit 26) which dominate in the western Alps between France and Italy.

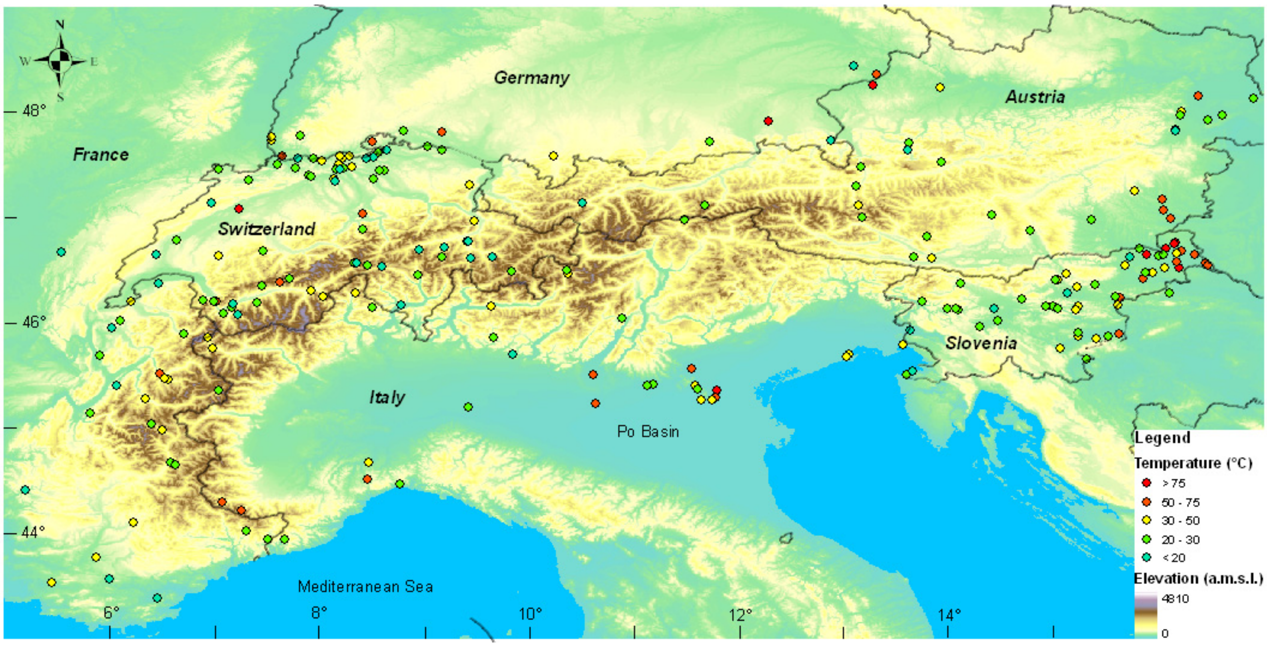

Figure 2: Locations of hydrothermal sites in the Alps range and neighbouring areas.

4.4 Austroalpine nappes

As for the Penninic nappes, the Austroalpine nappes can be divided into three subdomains which are the Lower Austroalpine nappes, the Upper Austroalpine basement nappes and the Northern calcareous Alps and Grauwackenzone (Upper Austroalpine). These subdomains are mainly present in the eastern Alps except for the nappes derived from Margna-Sesia fragment (unit 25) between Switzerland and Italy.

The Margna-Sesia fragment belongs to the Lower Austroalpine nappes, and small fragments of the Apulian margin rifted off Apulia during the opening of the Piedmont-Liguria Ocean and were later incorporated into the accretionary wedge along the active northern and western margin of Apulia.

To the north of the Periadriatic Line, line delimiting the Southern Alps and the Austroalpine nappes, remnants of the southern margin of the Piedmont-Liguria Ocean are only preserved in the form of basement and cover slices and form the Austroalpine nappes (units 15 to 25). Most of them are completely detached from their deeper crustal underpinnings. Around the Tauern window, the Austroalpine nappes overlie the Penninic units.

4.5 Southern Alps

South of the Periadriatic Line, the Southern Alps refer to the Apulian Plate denoting all continental domains located south of the Piedmont-Liguria Ocean (units 11 to 14). From the Periadriatic Line to the south, formations of the lower crust (Ivrea zone), the upper crustal basement, the post-Variscan volcanic and sedimentary cover and the Adriatic micro-plate occur. The most important unit of the Southern Alps is represented by the post-Variscan volcanic and sedimentary cover with thick Mesozoic series (unit 13).

4.6 Various units

Various units in the Alps are also described in the tectonic map of Schmid et al. (2004). They are granitic intrusions along the Periadriatic Line (unit 5), post tectonic Tertiary covers (units 3 and 4) and finally the Plio-Pleistocene deposits of the Po Plain in Italy and the Pannonian Basin in Slovenia. Moreover, the northern part of the Dinarides Mountains was also taken into account in this study because data could be collected in this area. The most important unit of this domain refers to the External Dinarides whose Mesozoic formations occur.

5 DEEP FLOW SYSTEMS IN THE ALPS AND WATER CHEMISTRY

Deep flow systems in the Alps can be encountered in all major geological and tectonic units. Geothermal aquifers may be formed by fractured (granite, gneiss), karstified (limestone) or porous rocks (sandstone, fluvio-alluvial deposits). The location and limits of the aquifers are not easily definable at this studied scale, and are highly dependent on local tectonic features (Sonney and Vuataz, 2008). In the Alps Mountains, deep flow systems reaching 1 to 4 km depth mostly occur along contact between units due to the presence of thrusts and subvertical faults having higher hydraulic conductivities. These fractures support the rise of deep fluids along the glacial and alluvial valleys, and complex mixing processes with shallow groundwaters occur (Vuataz, 1997). The emergence of thermal waters can differ from one site to another: in some cases, only one large thermal spring occurs whereas in other cases, more than 10 thermal springs with different chemical composition and temperature discharge. Concerning neighbouring areas such as Tertiary and Quaternary basins, geothermal fluids can be found in deep and subhorizontal permeable formations with low flow velocity (trapped fluids).

The chemical characteristics of the Alpine thermal waters are as diverse as the rocks which compose the crystalline massifs, the sedimentary and metamorphic nappes (table 1). Geochemistry of thermal waters can be subdivided into several types according to the distribution of major dissolved chemical species. From Vuataz (1997), three principal groups presented below are classified according to the main reservoir rock of the thermal water. In turn, they form many subgroups, due to the complex flow paths, water rock interactions and mixing processes.

- Sedimentary rocks including Tertiary and Quaternary basins (except evaporites): Ca-HCO_3, Ca-Mg-HCO_3, Na-HCO_3, Na-Cl, etc.

- Evaporitic rocks: Ca-HCO_3-SO_4, Ca-SO_4, Ca-Na-SO_4-Cl, Na-Ca-Cl-SO_4, Na-Cl, etc.

- Crystalline rocks (granite, gneiss): Na-HCO_3, Na-HCO_3-SO_4, Na-SO_4, Na-SO_4-Cl, Na-Cl, etc.

6. RELATION CHLORIDE, CHLORIDE/TDS AND CL/BR RATIOS AND GEOLOGY

Compiled data of chloride, bromide and TDS (Total Dissolved Solids) from deep fluids in the Alps range and neighbouring areas have been subdivided according to their geological setting and plotted to discuss about the origin of the dissolved mineral components (figure 3). In an overall view, high chloride contents (> 100 mg/L) can be found in any types of geological formations as well as in sedimentary layers and in crystalline rocks. Chloride concentrations in thermal waters are mainly lower than 1 g/L but sometimes they can reach the seawater content (about 19 g/L), and in 5 cases they exceed seawater with 3 waters above 140 g/L (Bad Ischl and Bad Richenhall in Austria, Rheinfelden in Switzerland). Only Bad Ischl is really a thermal water (28°C).

Beyond 1 g/L of chloride, there is a correlation with TDS. The points are on a line going to seawater, what shows that TDS is controlled by Na-Cl derived from the seawater and its products. This process can also be observed in the chloride/TDS vs. chloride plot where a significant increase of chloride/TDS values occurs, reaching 0.6 for the most mineralized thermal waters (> 2 g/L of chloride).

Deep fluids with chloride content in the range 0-2 g/L are more dispersed and are located above the seawater line, because chloride does not represent the dominant anion compared to other anions as sulphate and bicarbonate. In this range, chemical characteristics of the Alpine thermal waters are diverse.

Concerning the Cl/Br vs. chloride plot from an overall view, the points are largely scattered. Values of Cl/Br ratio can exceed 1000 or be lower than 300 for deep fluids with various chloride contents. In detail, these values can be explained for each geological domain from the Tertiary deposits to the crystalline basement.

6.1. Tertiary and Quaternary basins

Deep fluids in Tertiary and Quaternary basins mainly concern the Molasse Basin, the Pannonian Basin and the Po Plain in Italy respectively in Switzerland, Slovenia and

Italy. These areas are considered as neighbouring areas of the Alps, and their subhorizontal Tertiary and Quaternary formations at different depths can contain thermal fluids mainly of Na-HCO_3 and Na-Cl types (figure 4). Measured chloride concentrations in deep fluids are in the range 0.001-14 g/L. Five deep fluids having high chloride contents (4-14 g/L) show Cl/Br ratios close to seawater. Therefore, it can be assumed that they are related to trapped seawater in the Molasse Basin as well as in the Pannonian Basin. For the Po Plain, it was not possible to apply the Cl/Br method because bromide analyses were not found in the literature. However, previous studies led on the deep fluids in the Po Plain showed the relation between highly saline waters and seawater intrusions (Conti et al., 2000). In this area, the Po Valley brines represent the level of the Quaternary aquifer inside a thick clay-sands sequence, and geochemistry indicates that these are marine waters, evaporated to the stage of gypsum precipitation and trapped at the bottom of the basin in the late Messinian. Conti et al. (200) specify that these Na-Cl brines are subjected to mixing processes with shallow groundwaters laterally recharged from the Alpine chain.

Five selected waters with chloride contents in the range 0.5-5 g/L have Cl/Br ratios greater than 1000 which tends to indicate the dissolution of halite from Tertiary evaporites.

Deep fluids having lower chloride contents (< 0.5 g/L) are mainly Na-HCO_3 waters. In some locations of the Pannonian Basin, deep fluids are strongly affected by the rise of CO_2 which gives high HCO_3 concentrations up to 8 g/L in the Pannonian Basin (Lapanje, 2006). Most deep fluids having lower chloride contents also have low TDS with various Cl/Br which allow assuming the influence of surface conditions (Alcalá and Custodio, 2008).

6.2. Cretaceous and Jurassic aquifers

The Cretaceous and Jurassic thermal aquifers are mostly associated to deep flow systems in fractured limestone reservoirs with Ca-HCO_3 waters. These aquifers are often located in the sedimentary external Alps of Switzerland and France, and in the Slovenian Southern Alps. Waters are characterized by low chloride contents with a large range of Cl/Br ratios which can be lower than 300 or above 1000. Due to the very low bromide concentrations in these Ca-HCO_3 aquifers (in particular for the Jurassic) and potential analytical errors, strong differences of the Cl/Br ratio can be generated. The application of the Cl/Br method for these Ca-HCO3 aquifers does not give useful results. It seems that they are subjected to surface conditions and mixing processes with shallow groundwaters.

Cretaceous and Jurassic aquifers underlying the Tertiary and Quaternary basins contain deep fluids with various geochemical types. Na-Cl waters are often present with chloride concentration up to 7 g/L. Various Cl/Br ratios are observed for the highest saline waters. Some points in the Cl/Br vs. chloride plot are close to the Cl/Br seawater value or slightly lower, and two points have Cl/Br ratios significantly greater than seawater (> 1000). Certainly, the majority of deep saline fluids in Cretaceous and Jurassic aquifers located in sedimentary basins are influenced by trapped seawater as it was assumed for waters in the Tertiary and Quaternary formations.

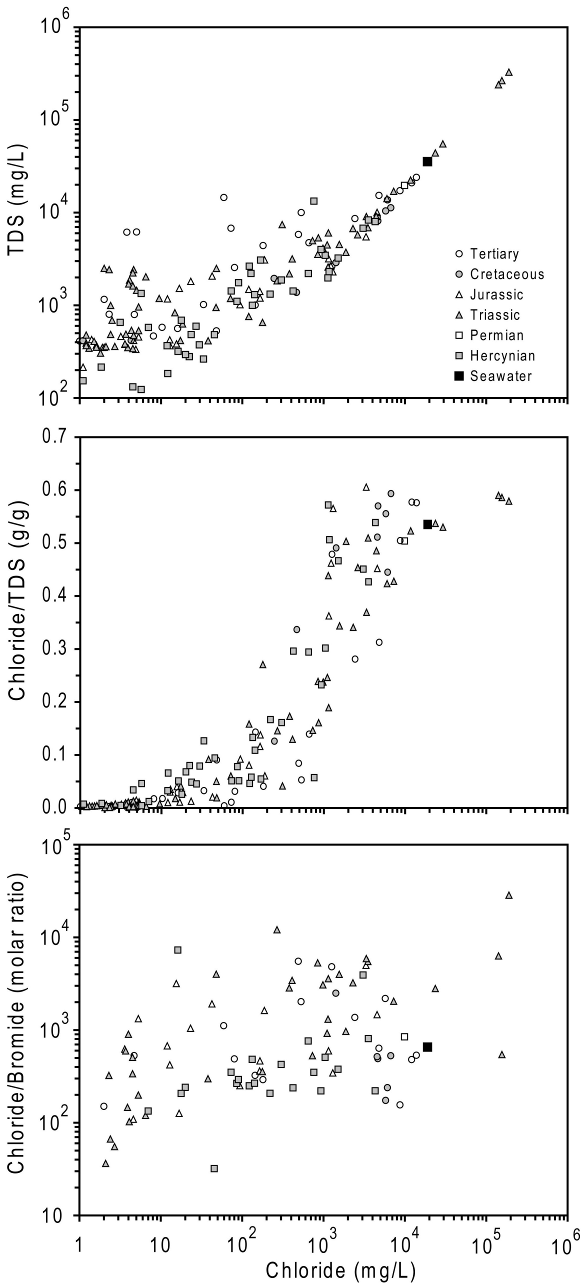

Figure 3: TDS, Chloride/TDS and Cl/Br ratios vs. chloride for the deep fluids in the Alps and neighbouring areas. All data are listed in table 1.

6.3. Triassic aquifers

Selected sites with deep fluids in Triassic aquifers are quite important and are located in all geological domains from the external Alps to the Southern Alps. The Triassic formations are often present in thrusts bordering the geological units such as nappes, and their higher hydraulic conductivities (fractured limestone and evaporite) facilitate the rise of deep fluids. Three dominated chemical types are observed in waters: Ca-HCO_3 in limestone, Ca-SO_4 and Na-Cl in evaporites (figure 4). In evaporitic aquifers, waters can have strong chloride contents, sometimes above seawater, or very low chloride (< 20 mg/L), while having TDS generally upper than 1 g/L. This difference depends on initial conditions of evaporite deposition and the stage of seawater evaporation which can reach or not the halite precipitation.

Concerning the relation between chloride, Cl/Br and geological setting for the Triassic aquifers, four categories of deep fluids can be highlighted. The first group gathers the Ca-HCO_3 and Ca-SO_4 waters with low chloride concentrations (< 10 mg/L) which respectively circulate in limestone and evaporite. These waters are often rich in magnesium showing the presence of dolomite in the Triassic formations of the Alps, and even two Mg-HCO_3 thermal waters were found (figure 4). The Cl/Br ratios of these waters vary between 30 and 1000. As for the Cretaceous and Jurassic limestone reservoirs, the application of the Cl/Br method does not give useful results.

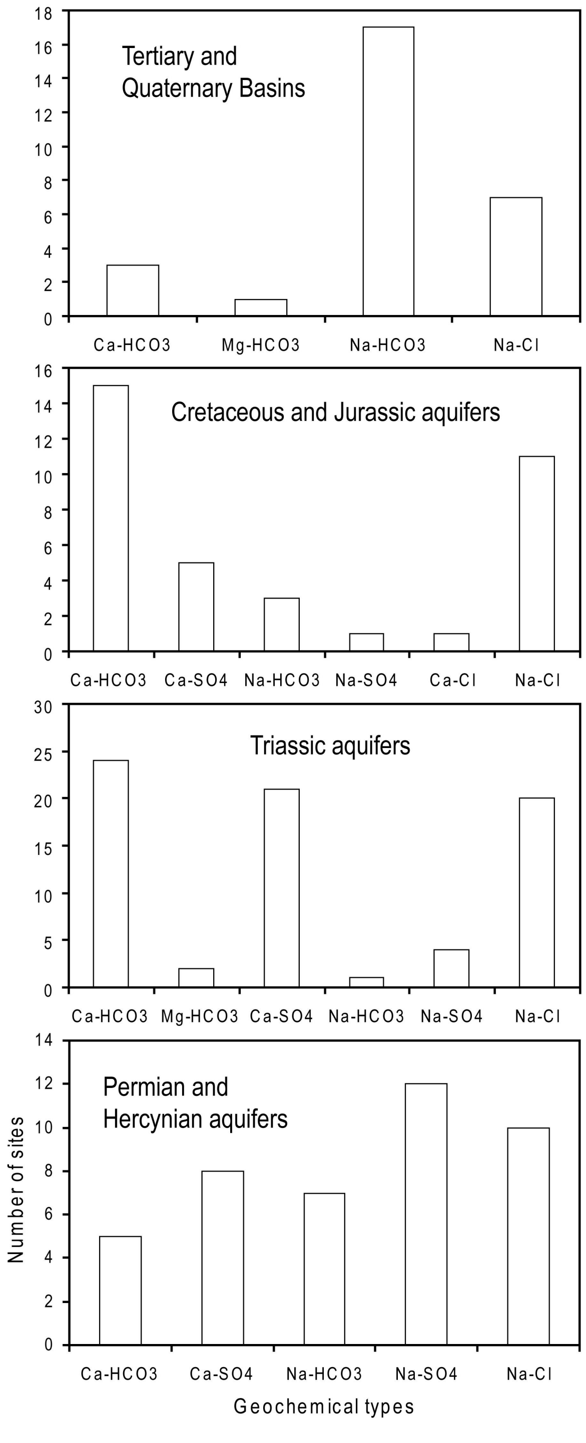

Figure 4: Histograms of geochemical types for deep fluids in various geological settings in the Alps and neighbouring areas.

The second group refers to deep fluids between 10-500 mg/L of chloride. The Cl/Br ratios are also variable in the range 200-12000. For some sites with Cl/Br ratio greater than 1000, the dissolution of halite controls the chloride concentrations. The third group with waters in the range 0.5-7 g/L of chloride includes the Na-SO_4, Na>Ca-Cl>SO_4 and Na-Cl geochemical types. Their mineralization in evaporites is controlled by the dissolution of halite (Cl/Br > 2000), but for two cases, the Cl/Br ratios is around 1000 (Bellingen in Germany and Baden in Switzerland), and one site is close to the seawater (Combioula in Switzerland). For these three sites with deep waters emerging from Triassic evaporites, the influence of seawater is possible. Finally, four sites have chloride contents greater than seawater. The Reinach fluid in Switzerland (77.6°C and Cl = 23.6 g/L) is controlled by the dissolution of halite (Cl/Br = 2800). The same process applies to coldest and hyper saline water of Rheinfelden in Switzerland (11°C, Cl = 190 g/L and Cl/Br = 28500) and of Bad-Richenhall in Austria (13°C, Cl = 141.5 g/L and Cl/Br = 6300). For the thermal water at Bad-Ischl in Austria (28.3°C and Cl = 156 g/L) the Cl/Br ratio is around 550 and close to seawater.

6.4. Permian and Hercynian aquifers

The Permian and Hercynian thermal aquifers are located in several zones. In the western Alps, they refer to the external crystalline massifs from which thermal discharges at the low elevation of these crystalline massifs are witnesses of deep flow systems (Arthaud and Dazy, 1989; Perello et al., 2001). Moreover, deep fluids in Permian and Hercynian aquifers are also present in the Penninic and Austroalpine Alps. Finally, deep crystalline aquifers are known below the sedimentary cover from the Molasse Basin in Switzerland.

Chloride concentrations in deep fluids are in the range 0.001-4.3 g/L and are homogeneously distributed in this interval. The Cl/Br vs. chloride plot shows correlation of the points from low values of Cl/Br and chloride (respectively in the range of 100-200 and lower than 10 mg/L) to seawater. It seems that for these crystalline aquifers, meteoric waters having low Cl/Br ratios would leach with various degrees seawater brines contained in the basement. Deep flow systems in the crystalline aquifers would mobilize brines at depth before uprising as mentioned by Arthaud and Dazy (1987) for the external crystalline massifs in the French Alps.

6.5. Relation temperature, Cl/Br ratios and geology

Compiled data of Cl/Br ratios and temperature from deep fluids in the Alps range and neighbouring areas have been subdivided according to their geological setting and plotted (figure 5). In an overall view, different values of temperature in deep fluids (15-90°C) can be found in any types of geological formations as well as in sedimentary layers and in crystalline rocks. This can be explained by the fact that these different types of geological formations can be met at different depths due to the effects of tectonic events in the Alps. However, the hottest deep fluids (> 50°C) are often related to boreholes in Tertiary and Quaternary basins located at the periphery of the Alps. Inside the Alps range, deep flow systems generate thermal resurgences of which temperatures are concentrated in the interval 15-50°C.

Concerning the Cl/Br vs. temperature plot from an overall view or while regarding for each geological domains, the points are largely scattered. Values of Cl/Br ratio can exceed 1000 or be lower than 300 for deep fluids with various temperatures and therefore, there is no distinct correlation. In detail, this process can be explained by the presence in the Alps of various geological formations at different depths which contain deep fluids with various Cl/Br ratios from the dissolution of halite or the leaching of seawater brines. The great chemical diversity of deep fluids in any formations at different depths does not give useful results at the Alps scale, but locally tendencies can appear.

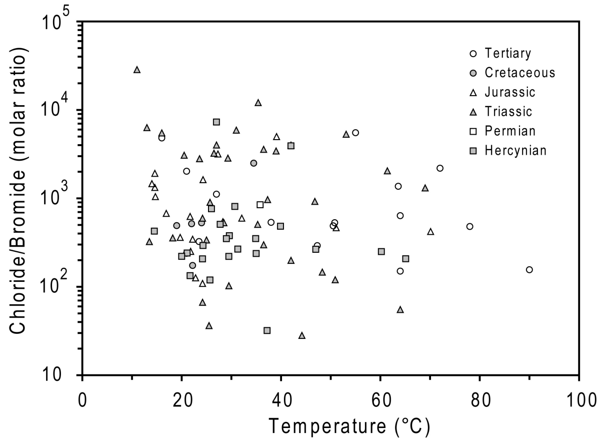

Figure 5: Cl/Br ratios vs. temperature for the deep fluids in the Alps and neighbouring areas. All data are listed in table 1.

7. DISCUSSION

The applicability of the Cl/Br ratio was tested for deep fluids in the Alps range and neighbouring areas to decipher the origin of the dissolved mineral components. This method allows defining three main processes leading to high chloride concentrations in deep fluids. The dissolution of halite mostly controls the chloride in the Triassic aquifers (Cl/Br > 1000). The presence of trapped seawater was assumed in aquifers from large basins including formations from the Quaternary to the basement (Cl/Br close to seawater). Finally, deep fluids in the Hercynian basement can be related to leaching with various degrees of brines by meteoric waters (Cl/Br lower than seawater).

The Cl/Br ratio method is not often used for all hydrogeological problems, partly due to the lack of data for bromide most often in shallow groundwater studies. Where possible, accurate bromide analyses should systematically accompany chloride analyses during groundwater investigations. But the difficulty in measuring usually low bromide contents in natural water limits the application of use of Cl/Br method. Higher bromide contents are usually met in deep aquifers, where the question arises about the origin of dissolved salts.

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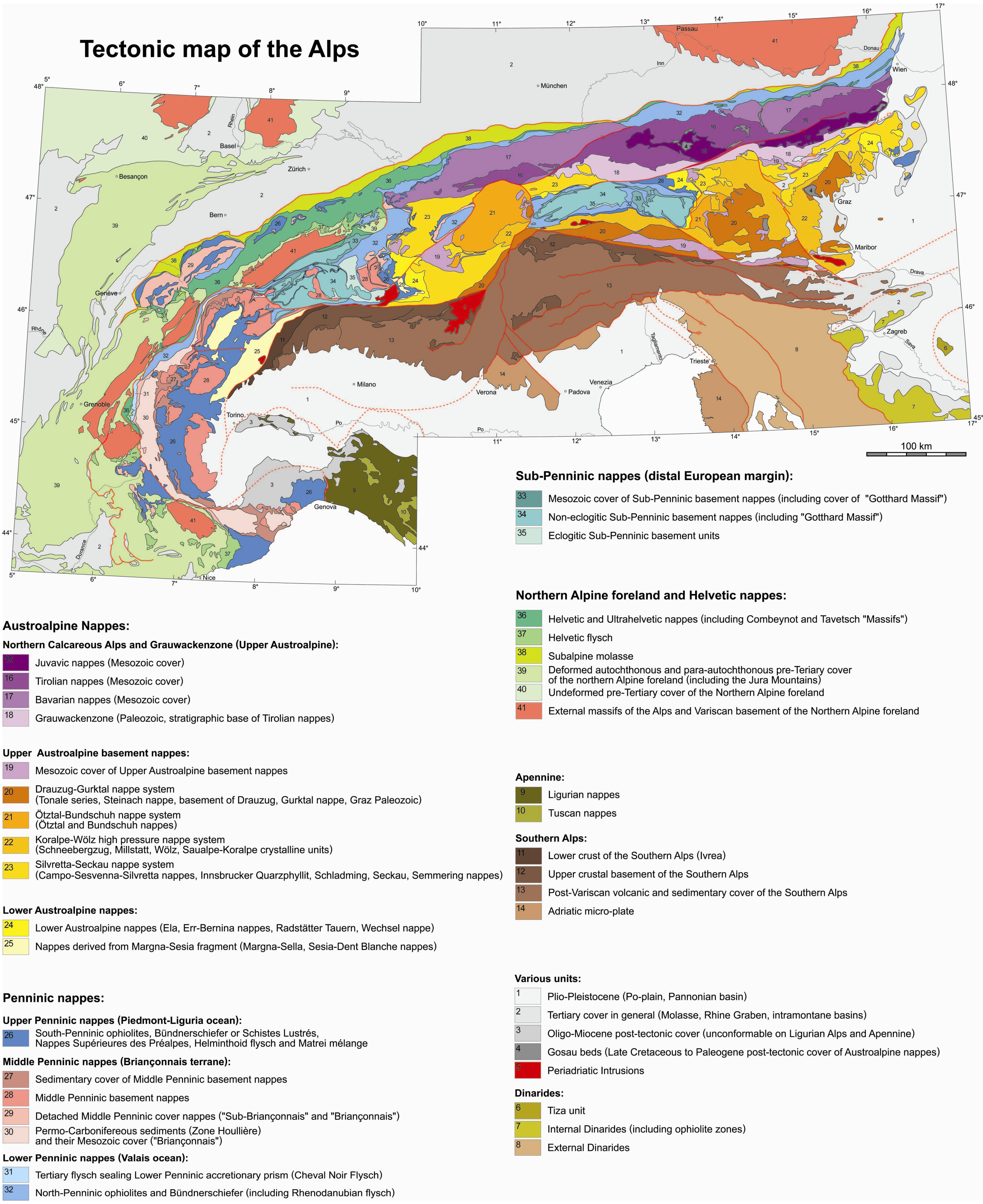

Plate 1: Tectonic map of the Alps range (Schmid et al., 2004).

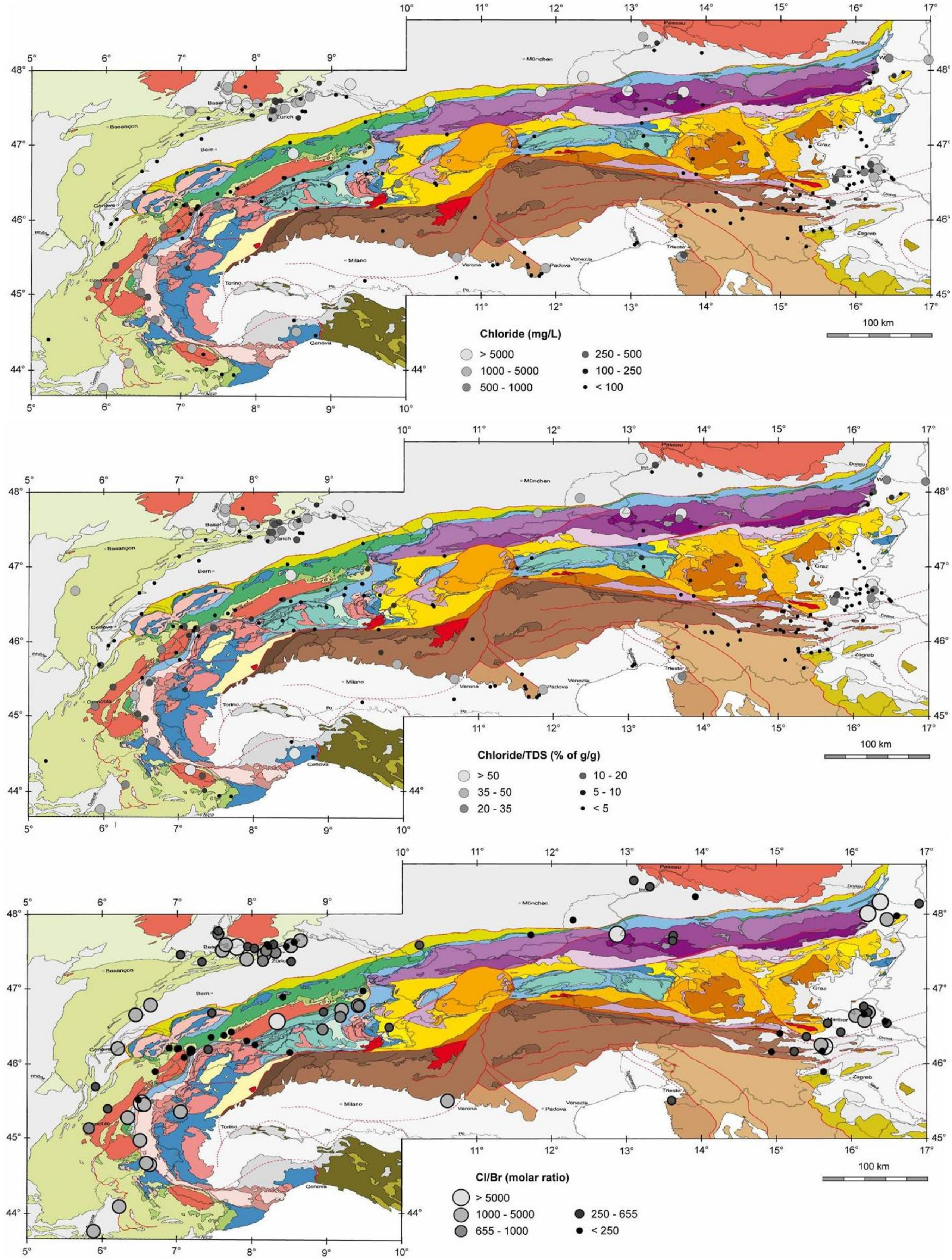

Plate 2: Maps of chloride contents, Chloride/TDS and Cl/Br ratios for the deep fluids in the Alps. Due to the lower density of the Cl/Br points, symbols are shown larger.

Table 1: Location, geology and chemistry of deep fluids in the Alps range and neighbouring areas.

N°	*Site name*	*Country*	*Latitude (dec.deg.)*	*Longitude (dec.deg.)*	*Reservoir formation*	*Age of the reservoir formation*	*Geochemical type*	*Temp. (°C)*	*Cl (mg/L)*	*Br (mg/L)*	*Cl/Br (Molar)*	*TDS (mg/L)*	*Ref.*
1	Bad Fischau	Austria	47.8328	16.1669	Dolomite	Triassic	Ca-HCO3	21	17.3			417	a
2	Bad Fischau-Brunn	Austria	47.8244	16.1600	Limestone	Triassic	Ca-HCO3	20					b
3	Bad Gastein	Austria	47.1181	13.1422	Orthogneiss	Hercynian	Na-SO4	46	29.6			375	a
4	Bad Goisern	Austria	47.6408	13.6169	Dolomitic-Limestone	Triassic	Na-Cl	18.2	177.2	1.12	357	654	a
5	Bad Ischl	Austria	47.7117	13.6239	Schists	Triassic	Na-Cl	28.3	155800	645	544	265779	a
6	Bad Reichenhall	Austria	47.7278	12.8783	Dolomitic limestone	Triassic	Na-Cl	13	141500	50.6	6303	239776	a
7	Bad Vöslau	Austria	47.9675	16.2117	Dolomite	Triassic	Ca-HCO3	23	18.4			630	a
8	Baden bei Wien	Austria	48.0064	16.2200	Evaporite	Triassic	Ca-SO4	35.4	268	0.05	12081	1839	a
9	Bleiberg	Austria	46.6278	13.6719	Limestone	Triassic	Ca-HCO3	27.4	1.3			344	a
10	Deutsch-Altenburg	Austria	48.1381	16.9061	Gneiss	Hercynian	NaCl	27.75	1046	4.64	508	3464	a
11	Einöd	Austria	47.0228	14.4142	Schistous Limestone	Mesozoic	Ca-HCO3	23	81.1			2880	a
12	Fürstenfeld	Austria	47.0733	16.0539			Na-Cl	75					b
13	Geinberg	Austria	48.2644	13.2861			HCO3	96					b
14	Grins	Austria	47.1422	10.5178	Evaporite	Triassic	Ca-SO4	17.6	2			2507	a
15	Häring	Austria	47.2494	15.7725	Limestone	Permian-Triassic	Ca-SO4	38.8				2296	a
16	Hintertux	Austria	47.1153	11.6825	Limestone	Mesozoïc	Ca-HCO3	22.5	5.8			212	a
17	Kleinkirchheim	Austria	46.8161	13.7983	Dolomitic Schists	Hercynian	Ca-HCO3	24	1.84			215	a
18	Leithaprodersdorf	Austria	47.9261	16.4728	Schists	Jurassic	Ca-SO4	24.3	187.6	0.26	1626	3092	a
19	Lend	Austria	47.2978	13.1189	Limestone	Hercynian	Ca-HCO3	23.4	11.9			366	a
20	Loipersdorf	Austria	46.9842	16.1164			HCO3	62					b
21	Mannersdorf	Austria	47.9739	16.6078	Schists	Jurassic	Ca-SO4	22.8	16.8	0.3	126	1523	a
22	Mitterndorf	Austria	47.5319	13.9331	Gypsum	Triassic	Ca-SO4	28.5	14.8			833	a
23	Schallerbach	Austria	48.2306	13.9183	Granite	Hercynian	Na-HCO3	37.2	45.4	3.2	32	482	a
24	Scharten	Austria	47.4792	13.1728	Sand - Conglomerate	Tertiary	Na-HCO3	21.6	8.06			466	a
25	Tauerntunnel	Austria	47.0028	13.1742	Orthogneiss	Hercynian	Ca-SO4	23.8	168			3076	a
26	Tobelbad	Austria	46.9803	15.3653	Sediments	Hercynian	Ca-HCO3	27.8	3.15			654	a
27	Villach	Austria	46.6078	13.8461	Limestone	Triassic	Ca-HCO3	31	4.33			538	a
28	Waltersdorf	Austria	47.1700	16.0328			HCO3	61					b
29	Weissenbach	Austria	46.8739	14.7767	Gneiss	Hercynian	Na-HCO3	25	128			2208	a
30	Wien-Oberlaa	Austria	48.1594	16.3856	Limestone	Triassic	Na-SO4	53.1	848	0.36	5309	3550	a
31	Aix-en-Provance	France	43.5250	5.4539	Limestone	Jurassic	Ca-HCO3	34.5	12.8			424	c
32	Aix-les-Bains	France	45.6894	5.9156	Limestone	Jurassic	Ca-HCO3	70.1	12.9	0.069	421	367	d
33	Allevard	France	45.3939	6.0750	Micaschists	Hercynian	Na-SO4	14.5	302	1.6	425	1874	c
34	Barjols	France	43.5575	6.0064		Triassic	Na-Cl	16	3510	1.44	5494	6885	c
35	Bonneval	France	45.3547	7.0472			Ca-SO4	27	123	0.16	1733	1420	c
36	Breil	France	43.9386	7.5136			Ca-SO4	30	17			961	c
37	Brides-les-Bains	France	45.4525	6.5664	Dolomitic limestone	Triassic	Na-SO4	36.5	1145	0.72	3584	6050	c
38	Condorcet	France	44.4072	5.2008	Evaporite	Triassic	Ca-SO4	17	4.6			2429	c
39	Digne-les-Bains	France	44.0911	6.2314	Evaporite	Triassic	Na-Cl	42	1560	0.88	3996	4537	c
40	Draguignan	France	43.3744	6.4647			Ca-Cl	15	553	0.24	5194	2228	c
41	Gréoux-les-Bains	France	43.7586	5.8853	Limestone	Cretaceous	Na-Cl	34.5	1418	1.28	2497	2888	c
42	Lautaret	France	45.0342	6.4050	Evaporite	Triassic	Na-SO4	24	861			5352	c
43	La Léchère	France	45.5158	6.4836	Micaschists	Hercynian	Ca-SO4	60.2	122	1.1	250	2642	e
44	Lons-le-Saunier	France	46.6742	5.5517	Evaporite	Triassic	Na-Cl	17.5	6005			14181	a
45	Le Monetier-les-Bains	France	44.9758	6.5078	Evaporite	Triassic	Ca-SO4	39	411	0.27	3431	3172	c
46	Mont-Blanc	France	45.8533	6.9394		Hercynian	Ca-SO4	34	5.7			124	f
47	Pont La Caille	France	46.0128	6.1117	Limestone	Cretaceous	Ca-HCO3	25	4.3			418	c
48	Réotier	France	44.6689	6.5917	Dolomitic limestone	Triassic	Na-Cl	20.5	982	0.72	3074	4130	c
49	Risoul	France	44.6489	6.6372	Dolomitic-limestone	Triassic	Na-Cl	26.5	2297	1.6	3236	6736	c
50	Roquebilière	France	44.0119	7.3064		Hercynian	Na-HCO3	29	22.3			279	c
51	La Rotonde	France	45.6875	5.9139	Limestone	Cretaceous	Ca-SO4	28	246			1951	c
52	St-Gervais-les-Bains	France	45.8931	6.7111	Micaschists	Hercynian	Na-SO4	29.5	930	9.5	221	4002	g
53	St-Jean-de-Maurienne	France	45.2767	6.3453	Micaschists	Hercynian	Na-Cl	42	3063	1.76	3923	6792	c
54	Salins-les-Thermes	France	45.4717	6.5283	Dolomitic-limestone	Triassic	Na-Cl	31.0	3354	1.28	5906	9080	c
55	Sallingy	France	45.9456	6.0347	Limestone	Cretaceous	Ca-HCO3	16.5	1.1			415	c
56	Thonon-les-Bains	France	46.3733	6.4783	Glacial deposits	Quaternary	Ca-HCO3	18	6			508	c
57	Uriage	France	45.1372	5.8247	Micaschists	Hercynian	Na-Cl	26	649	1.92	762	2205	c
58	Bad Wiesse	Germany	47.7181	11.7239	Sandstone	Cretaceous	Na-Cl	21	6105	57.6	239	13718	a
59	Bellingen	Germany	47.7333	7.5544	Limestone	Triassic	Na-Cl	37.3	1880	4.38	967	3735	a
60	Birnbach	Germany	48.4450	13.0961	Limestone	Cretaceous	Na-Cl	15-19	4646	21.3	492	8149	a
61	Buerchau	Germany	47.7739	7.8272	Granite	Hercynian	Ca-HCO3	20.5	4.5			132	a
62	Endorf	Germany	47.9172	12.2856	Sand	Tertiary	Na-Cl	35-90	8710	126	156	17254	a
63	Füssing	Germany	48.3592	13.3106	Limestone	Jurassic	Na-HCO3	51.1	165.2	0.8	465	1197	a
64	Lottstetten	Germany	47.6167	8.5667	Limestone	Jurassic	Na-HCO3	21.8	93.6	0.84	251	1016	a
65	Owingen	Germany	47.8108	9.1756	Dolomite	Triassic	Na-Cl	75	29260			55189	a
66	Saeckingen	Germany	47.5586	7.9467	Granite	Hercynian	Na-Cl	29.6	1509	9	378	3234	a
67	Singen	Germany	47.8258	8.8036	Limestone	Jurassic	Na-SO4	26	120			1486	a
68	Stein	Germany	47.5800	10.2383	Molasse	Tertiary	Na-Cl	38	13845	58.3	535	24025	a
69	Steinenstadt	Germany	47.7694	7.5553	Limestone	Jurassic	Na-Cl	32.1	1152	4.35	597	3177	a

N°	Site name	Country	Latitude (dec.deg.)	Longitude (dec.deg.)	Reservoir formation	Age of the reservoir formation	Geochemical type	Temp. (°C)	Cl (mg/L)	Br (mg/L)	Cl/Br (Molar)	TDS (mg/L)	Ref.
70	Abano	Italy	45.3581	11.7933	Evaporite	Triassic	Na-Cl	80.0	2620			5772	h
71	Acquasanta	Italy	44.4572	8.7697				21					b
72	Acqui	Italy	44.5086	8.4694	Gneiss	Hercynian	Na-Cl	68.0	1170			2310	i
73	Albettone	Italy	45.3683	11.6064	Carbonate	Mesozoic	Ca-SO4	24					b
74	Bormio	Italy	46.4675	10.3781	Evaporite	Triassic	Ca-SO4	41.7	9.5			1186	j
75	Brennerbad	Italy	46.9731	11.4886	Limestone		Ca-HCO3	21.6	10.3			452	a
76	Caldiero	Italy	45.4089	11.1939	Carbonate	Mesozoic	Ca-HCO3	27					b
77	Cinto Euganeo	Italy	45.2644	11.6442	Carbonate	Mesozoic	Ca-Cl	36					b
78	Comano	Italy	46.0347	10.8911			Ca-HCO3	27.0	1			267	a
79	Craveggia	Italy	46.1464	8.5081	Gneiss	Hercynian	Na-SO4	25.7	0.9	0.017	119	310	g
80	Latisana	Italy	45.7003	13.0544	Carbonate	Mesozoic	Na-HCO3	41					b
81	Masino	Italy	46.1600	9.6400	Gneiss	Hercynian	Na-SO4	37.9	23.5			483	j
82	Miradolo	Italy	45.1886	9.4214				21					b
83	Monfalcone	Italy	45.7917	13.5667	Carbonate	Mesozoic	Na-Cl	36					b
84	Monselice	Italy	45.2569	11.7489	Carbonate	Mesozoic	Na-Cl	32					b
85	Mossano	Italy	45.4028	11.5939	Carbonate	Mesozoic	Ca-SO4	34					b
86	Piedilago	Italy	46.2800	8.3528	Gneiss	Hercynian	Ca-SO4	42.7	5.7			1342	k
87	Pigna	Italy	43.9328	7.6747				28					b
88	Pré-Saint-Didier	Italy	45.7575	6.9867	Limestone	Triassic	Ca-HCO3	36.0	47.5			948	j
89	Rodigo	Italy	45.2289	10.6444				57					b
90	San Martino B.	Italy	45.3950	11.1292	Carbonate	Mesozoic	Ca-HCO3	29					b
91	San Michele al Terme	Italy	45.6733	13.0281	Carbonate	Mesozoic	Na-HCO3	49					b
92	San Pelegrino	Italy	45.8514	9.6628	Dolomite	Triassic	Ca-SO4	26.8	71.5			1185	a
93	Simplon	Italy	46.2508	8.0425	Evaporite	Triassic	Ca-SO4	44.2	0.2	0.016	28	1216	l
94	Sirmione	Italy	45.5003	10.6122	Evaporite	Triassic	Na-Cl	69.0	1135	1.95	1312	2588	a
95	Terme Arqua'Petrarca	Italy	45.2839	11.7831	Carbonate	Mesozoic	Na-Cl	72					b
96	Trescore	Italy	45.6950	9.8467	Chalk	Jurassic	Na-Cl	17.0	1228			2657	a
97	Valdidentro	Italy	46.4925	10.3600	Evaporite	Triassic	Ca-SO4	22					b
98	Valdieri	Italy	44.2064	7.2689	Gneiss	Hercynian	Na-SO4	60.5	33.3			263	m
99	Vicenza	Italy	45.5647	11.5511				65					b
100	Vinadio	Italy	44.2886	7.0767	Gneiss	Hercynian	Na-Cl	52.3	1130			1975	m
101	Visone	Italy	44.6622	8.4794			Na-Cl	33					b
102	Banovci	Slovenia	46.5728	16.1756	Sand - Sandstone	Tertiary	Na-Cl	63.6	2427	4	1368	8635	n
103	Benedikt	Slovenia	46.6433	15.8853	Dolomitic marble	Tertiary	Ca-HCO3	78	72.5			6788	n
104	Bled	Slovenia	46.3672	14.1128	Dolomite	Triassic	Ca-HCO3	21.7	2.5			691	n
105	Božakovo pri Metliki	Slovenia	45.6486	15.3128	Limestone	Jurassic	Ca-HCO3	20.9	1.4			427	n
106	Buseca vas	Slovenia	45.8700	15.5231	Dolomite	Triassic	Ca-HCO3	26-28	1.2	<0.1	>27	391	n
107	Čatež	Slovenia	45.8917	15.6314	Dolomite	Triassic	Ca-HCO3	64	2.7	0.11	55	360	n
108	Cerkno	Slovenia	46.1281	13.9928	Dolomitic limestone	Jurassic	Ca-HCO3	30	1.1			215	n
109	Curnovec	Slovenia	46.0200	14.4658	Dolomite	Triassic	Ca-HCO3	23					n
110	Dankovci	Slovenia	46.7636	16.1672	Conglomerate	Tertiary	Na-Cl	78	12113	56.9	480	20979	n
111	Dobrna	Slovenia	46.3392	15.2283	Limestone	Triassic	Ca-HCO3	35.5	4.6	<0.01	>1036	473	n
112	Dobrovnik	Slovenia	46.6514	16.3503	Sand - Sandstone	Tertiary	Na-HCO3	55.3	16	<0.02	>1803	563	n
113	Dolenjske Toplice	Slovenia	45.7583	15.0622	Carbonate	Jurassic	Ca-HCO3	33	1.9	<0.01	>428	351	n
114	Gabrnik	Slovenia	46.4803	15.9525	Carbonate	Tertiary	Ca-HCO3	<40					n
115	Hotavlje	Slovenia	46.1194	14.0922	Carbonate	Mesozoic	Ca-HCO3	21					n
116	Izola	Slovenia	45.5367	13.6600	Limestone	Cretaceous	Na-Cl	19.9	464			1378	n
117	Jakobski dol	Slovenia	46.6281	15.7350	Sandstone	Tertiary	Na-HCO3		660			4735	n
118	Janežovci	Slovenia	46.4703	15.8831	Sand	Tertiary	Na-HCO3	28	1			412	n
119	Janžev vrh	Slovenia	46.6308	16.0097	Sand	Tertiary	Mg-HCO3	25.4	3.8			6152	n
120	Jezero pri Družinski vasi	Slovenia	46.2817	16.1019	Dolomite	Triassic	Ca-HCO3	23.5	1.5			408	n
121	Klevevz	Slovenia	45.9067	15.2375	Dolomite	Triassic	Mg-HCO3	25.2	1.2			478	n
122	Kopačnica	Slovenia	46.1322	14.0761	Dolomite	Triassic	Mg-HCO3	24	0.6			267	n
123	Kostanjevica na Krki	Slovenia	45.8508	15.4128	Limestone	Jurassic	Ca-HCO3	35.4	1.6	<0.05	>72	372	n
124	Kotredež Toplice	Slovenia	46.1553	14.9986	Dolomite	Traissic	Ca-HCO3	27	18			694	n
125	Lajše pri Velenju	Slovenia	46.4039	15.0464	Limestone	Triassic	Ca-HCO3	48.3	3.9	0.06	147	350	n
126	Laško	Slovenia	46.1592	15.2372	Dolomite	Triassic	Ca-HCO3	35.3	4.5	0.02	507	341	n
127	Lendava	Slovenia	46.5650	16.4514	Sand	Tertiary	Na-HCO3	64	2	0.03	150	1159	n
128	Lendava - Petišovci	Slovenia	46.5389	16.4733	Sand	Tertiary	Na-HCO3	50.5	80.2	0.37	489	2559	n
129	Ljutomer	Slovenia	46.5183	16.1964	Brecciated dolomite	Triassic	Na-Cl	148	11735			22436	n
130	Lucija	Slovenia	45.5053	13.6022	Limestone	Cretaceous	Na-Cl	24	6700	28.6	528	11290	n
131	Maribor	Slovenia	46.5408	15.6814	Metamorphic rocks	Palaeozoic	Na-Cl	37.3	365	2	411	1128	n
132	Medijske Toplice	Slovenia	46.1567	14.9328	Dolomite - Sandstone	Triassic	Ca-HCO3	25.5	2.1	0.13	36	358	n
133	Mislinjska Dobrava	Slovenia	46.4686	15.1250	Dolomitic conglomerate	Tertiary	Na-HCO3	40.3	10.3	<0.05	>464	579	n
134	Moravci	Slovenia	46.6828	16.2267	Carbonate	Tertiary	Na-Cl	72	5735	5.9	2191		n
135	Moravci v Slovenskih G.	Slovenia	46.5150	16.0572	Sand	Tertiary	Na-HCO3	42.2	2.3	<0.1	>52	801	n
136	Moravske Toplice	Slovenia	46.6833	16.2208	Sandstone	Tertiary	Na-Cl	64	4800	17	636	15350	n
137	Murska Sobota	Slovenia	46.6594	16.1703	Sand	Tertiary	Na-HCO3	47.3	180	1.39	292	4413	n
138	Nova Gorica	Slovenia	45.9219	13.6372	Carbonate	Mesozoic	Na-HCO3	20					n
139	Pečarovci	Slovenia	46.7469	16.1514	Dolomite	Triassic	Na-HCO3	78	309			7433	n
140	Podčetrtek	Slovenia	46.1656	15.6103	Dolomite	Triassic	Ca-HCO3	42	5.3	0.06	199	533	n
141	Podgorje pri Apačah	Slovenia	46.7056	15.8178	Sandstone	Tertiary	Na-HCO3	23	33.3			1019	n
142	Podlog pri Zalcu	Slovenia	46.2761	15.1386	Carbonate	Mesozoic	Ca-HCO3	20					n
143	Podplat	Slovenia	46.2486	15.5947	Andesite	Tertiary	Na-HCO3	27	59.3	0.12	1114	14568	n
144	Portorož	Slovenia	45.5069	13.6033	Limestone	Cretaceous	Na-Cl	22	4559	19.9	516	8916	n
145	Ptuj	Slovenia	46.4228	15.8589	Sand	Tertiary	Na-HCO3	50.8	4.7	0.02	530	795	n
146	Radenci	Slovenia	46.6411	16.0550	Sand	Tertiary	Na-HCO3	21	530	0.59	2025	10018	n
147	Rimske Toplice	Slovenia	46.1203	15.2097	Dolomite	Triassic	Ca-HCO3	39.6	1.2			368	n
148	Rogaška Slatina	Slovenia	46.2289	15.6419	Andesite	Tertiary	Na-HCO3	55	490	0.2	5522	5811	n
149	Spodnje Pirniče	Slovenia	46.1328	14.4411	Dolomite	Triassic	Ca-HCO3	20.1	1.8			305	n
150	Strukovci	Slovenia	46.7036	16.0675	Carbonate	Tertiary	Na-HCO3	90	5	<0.01	>1127	6182	n
151	Šmarješke Toplice	Slovenia	45.8658	15.2428	Dolomite - Limestone	Triassic - Jurassic	Ca-HCO3	33.8	3.2	<0.01	>721	462	n
152	Topolšica	Slovenia	46.4044	15.0219	Dolomitic limestone	Triassic	Ca-HCO3	28	3.6	<0.01	>811	384	n
153	Trbovlje	Slovenia	46.1300	15.0400	Brecciated dolomite	Triassic	Ca-HCO3	30.2	2.4			485	n
154	Vaseno Snovik	Slovenia	46.2194	14.7044	Dolomite - Limestone	Triassic	Ca-HCO3	29.6	1.6			353	n
155	Vrhnika	Slovenia	45.9586	14.3019	Limestone - Dolomite	Jurassic	Ca-HCO3	23.8	2			352	n
156	Zatolmin	Slovenia	46.2017	13.7467	Carbonate	Mesozoic	Ca-HCO3	22					n
157	Zreče	Slovenia	46.3586	15.4028	Dolomite	Triassic	Ca-HCO3	24.2	3.7	0.014	596	488	n

N°	*Site name*	*Country*	*Latitude (dec.deg.)*	*Longitude (dec.deg.)*	*Reservoir formation*	*Age of the reservoir formation*	*Geochemical type*	*Temp. (°C)*	*Cl (mg/L)*	*Br (mg/L)*	*Cl/Br (Molar)*	*TDS (mg/L)*	*Ref.*
158	Acquarossa	Switzerland	46.4547	8.9430	Evaporite	Triassic	Ca-SO4	25	5.3	0.012	996	2620	o
159	Andeer	Switzerland	46.6129	9.4449	Evaporite	Triassic	Ca-SO4	18	4.5	<0.05	>203	2238	o
160	Bad-Ragaz	Switzerland	46.9693	9.4870	Limestone	Triassic	Ca-HCO3	36.5	38	0.287	298	415	g
161	Baden	Switzerland	47.4805	8.3139	Limestone	Triassic	Na-SO4	46.8	1106	2.7	923	4489	o
162	Bassersdorf	Switzerland	47.4442	8.6252	Molasse	Tertiary	Na-Cl	22.9					p
163	Benken	Switzerland	47.6449	8.6496	Limestone	Jurassic	Na-Cl	14	4550	7	1465	10065	q
164	Berguen	Switzerland	46.6185	9.6587		Triassic	Ca-SO4	17	5			1453	a
165	Berlingen	Switzerland	47.6720	9.0384	Molasse	Tertiary	Na-HCO3	29	48			530	q
166	Birmenstorf	Switzerland	47.4651	8.2351	Limestone	Triassic	Na-Cl	23.2	4433			9129	q
167	Boettstein	Switzerland	47.5650	8.2272	Granite	Hercynian	Na-HCO3	31.3	142	1.2	267	1303	q
168	Bovernier	Switzerland	46.0812	7.0987	Gneiss	Hercynian	Ca-HCO3	21.1	20	0.187	241	294	g
169	Brigerbad	Switzerland	46.3030	7.9310	Gneiss	Hercynian	Na-SO4	47	86	0.73	266	1103	g
170	Bulle	Switzerland	46.6300	7.0502	Molasse	Tertiary		36					q
171	Combioula	Switzerland	46.1874	7.4177	Evaporite	Triassic	Ca-SO4	28.5	730	3.11	529	4983	g
172	Courtemaiche	Switzerland	47.4546	7.0468	Limestone	Jurassic	Na-Cl	22.2	1300	8.5	345	2299	r
173	Delemont	Switzerland	47.3557	7.3336	Limestone	Jurassic	Ca-HCO3	21.7	3.6	0.013	624	379	d
174	Eglisau	Switzerland	47.5742	8.5221	Molasse	Tertiary	Na-Cl	16	1260	0.59	4814	2631	o
175	Epinassey	Switzerland	46.1957	7.0049	Gneiss	Hercynian	Ca-SO4	21.7	7	0.118	134	577	g
176	Furka	Switzerland	46.5416	8.4686	Granite	Hercynian	Na-HCO3	21.7	1.1			153	s
177	Gletsch	Switzerland	46.5627	8.3610	Gneiss	Hercynian	Na-SO4	18.6	12.1			184	q
178	Gotthard	Switzerland	46.5276	8.6002	Granite	Hercynian		18					q
179	Grimsel	Switzerland	46.5607	8.3372	Granite	Hercynian	Na-SO4	27	16.2	0.005	7303	318	t
180	Hauenstein	Switzerland	47.3965	7.9066	Limestone	Triassic	Ca-SO4	26.7	5.3			960	q
181	Hausen	Switzerland	47.4607	8.2057	Limestone	Triassic	Ca-HCO3	10.9	120			757	q
182	Hermrigen	Switzerland	47.0823	7.2434	Limestone	Triassic	Na-Cl	85					q
183	Itingen	Switzerland	47.4716	7.7825	Limestone	Triassic	Na-Cl	22					q
184	Kaisten	Switzerland	47.5398	8.0315	Granite	Hercynian	Na-SO4	34.9	73.1	0.47	351	1427	q
185	Kloten	Switzerland	47.4491	8.5856	Molasse	Tertiary		22.7					q
186	Kreuzlingen	Switzerland	47.6448	9.1775	Molasse	Tertiary		28.5					q
187	Lavey-les-Bains	Switzerland	46.1990	7.0251	Gneiss	Hercynian	Na-SO4	65.1	220	2.39	207	1319	u
188	Leuggern	Switzerland	47.5890	8.2048	Granite	Hercynian		35	422	4	238	1425	q
189	Leukerbad	Switzerland	46.3788	7.6300	Evaporite	Triassic	Ca-SO4	50.9	6.5	0.122	120	2031	g
190	Leytron	Switzerland	46.1826	7.1870	Evaporite	Triassic	Ca-SO4	24.2	2.4	0.081	67	997	g
191	Locarno	Switzerland	46.1652	8.7839				16					q
192	Loetschberg	Switzerland	46.4191	7.7235	Granite	Hercynian	Ca-SO4	24.2	17.8	0.194	207	690	g
193	Lostorf	Switzerland	47.3929	7.9330	Limestone	Triassic	Ca-SO4	27	48	0.027	4007	2502	o
194	Moiry	Switzerland	46.6488	6.4508	Limestone	Jurassic	Ca-HCO3	14.6	5.3	0.009	1327	456	d
195	Peiden	Switzerland	46.7167	9.2003	Schists	Jurassic	Ca-SO4	14.6	42.5	0.05	1916	2068	o
196	Rawyl	Switzerland	46.3506	7.4581	Limestone	Jurassic	Na-HCO3	24.2	4.6	0.095	109	418	g
197	Reinach	Switzerland	47.5098	7.6049	Limestone	Triassic	Na-Cl	77.6	23650	19	2806	44019	v
198	Rhaezuens	Switzerland	46.7729	9.4189	Schists	Jurassic	Ca-HCO3	14.7	23.2	0.05	1046	1813	o
199	Rheinfelden	Switzerland	47.5575	7.7994	Evaporite	Triassic	Na-Cl	11	190000	15	28551	327949	o
200	Riehen	Switzerland	47.5871	7.6495	Limestone	Triassic	Na-Cl	61.4	7270	8	2048	16986	v
201	Riniken	Switzerland	47.5054	8.1900	Breche	Permian/Carboniferous	Na-Cl	35.8	9900	26.4	845	19642	q
202	Rothenbrunnen	Switzerland	46.7698	9.4267	Schists	Jurassic	Ca-HCO3	16.9	12	0.04	676	1174	o
203	Saint-Moritz	Switzerland	46.4821	9.8345	Granite	Hercynian	Na-HCO3	29	760	4.9	350	13304	q
204	Saillon	Switzerland	46.1735	7.1883	Limestone	Jurassic	Ca-SO4	19.7	164	1.023	361	1412	g
205	Saxon	Switzerland	46.1450	7.1716	Gneiss	Hercynian	Ca-SO4	24.3	90	0.693	293	1753	g
206	Schafisheim	Switzerland	47.3695	8.1487	Granite	Hercynian	Na-Cl	30.7	3555	9.9	809	8329	q
207	Schinznach-Bad	Switzerland	47.4578	8.1646	Limestone	Triassic	Na-SO4	29.3	379	0.3	2848	2189	o
208	Seon	Switzerland	47.3446	8.1598	Molasse	Tertiary		19.5					q
209	Siblingen	Switzerland	47.7259	8.5061	Granite	Hercynian	Na-HCO3	57	27			595	q
210	Sonvilier	Switzerland	47.1388	6.9761	Limestone	Jurassic	Ca-HCO3	18.8	4.9			335	w
211	Tenigerbad	Switzerland	46.6875	8.9590	Limestone	Triassic	Ca-SO4	13.5	2.3	0.016	324	2428	o
212	Thonex	Switzerland	46.2018	6.2113	Limestone	Jurassic	Ca-Cl	39.1	3325	1.5	4996	5489	x
213	Val d'Illiez	Switzerland	46.2072	6.9009	Evaporite	Triassic	Ca-SO4	29.5	4.1	0.09	103	1871	g
214	Val de Bagnes	Switzerland	46.0752	7.2356	Evaporite	Triassic	Ca-SO4	17.4	0.8			950	q
215	Vals	Switzerland	46.6221	9.1806	Evaporite	Triassic	Ca-SO4	25.7	4	0.01	902	1702	o
216	Weggis	Switzerland	47.0330	8.4251	Molasse	Tertiary		73					q
217	Weiach	Switzerland	47.5638	8.4585	Gneiss	Hercynian	Na-Cl	20	4312	44	221	8003	q
218	Weissbad	Switzerland	47.3096	9.4329	Molasse	Tertiary		45					q
219	Weissenburg	Switzerland	46.6748	7.4665	Evaporite	Triassic	Ca-SO4	25	4.5	0.03	338	1619	o
220	Wellenberg	Switzerland	46.8878	8.4152	Limestone	Cretaceous	Na-Cl	22.2	5800	75	174	10440	q
221	Yverdon-les-Bains	Switzerland	46.7809	6.6489	Limestone	Jurassic	Ca-HCO3	27.3	15.5	0.011	3176	384	d
222	Zurich	Switzerland	47.3631	8.5261	Molasse	Tertiary	Na-HCO3	23.5	144	1	325	1006	o
223	Zurzach-Bad	Switzerland	47.5886	8.2891	Gneiss	Hercynian	Na-SO4	39.9	133	0.62	484	1000	o

References

a: Carlé, 1975; b: Hunter and Haenel, 2002; c: Grimaud, 1987; d: Muralt, 1999; e: Thiébaud, 2008; f: Dubois, 1991; g: Bianchetti, 1993; h: Norton and Panichi, 1978; i: Bortolami et al., 1983; j: Vuataz, 1982; k: Martinotti et al., 1999; l: Bianchetti et al., 1993; m: Perello et al., 2001; n: Lapanje, 2006; o: Högl, 1980; p: Sieber, 1996; q: Unpublished reports; r: Boem et al., 2006; s: Vuataz et al., 1993; t: Pfeifer et al., 1992; u: Sonney in preparation; v: Hauber, 1993; w: Rieben, 1999; x: Jenny et al., 1999.