Validation of Chemical and Isotopic Geothermometers from Low Temperature Deep Fluids of Northern Switzerland

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ABSTRACT
During more than 30 years, chemical and isotopic geothermometers have been extensively used to calculate and estimate the temperature of geothermal reservoirs in various geological, petrographical and thermal conditions. In this evaluation, chemical analyses of deep boreholes from the Molasse Basin and the Tabular Jura in Northern Switzerland were used to estimate reservoir temperatures with geothermometers, and results were compared to measured temperatures at depth. The presence of thermal waters in subhorizontal formations with a temperature range of 12-112°C, is associated with various geological and petrographical settings (sedimentary, crystalline rocks).

Composition of geothermal fluids depends on various and sometimes competing processes, such as full or partial chemical equilibrium, mixing with shallow groundwater or trapped seawater, dissolution of evaporite, ionic exchange with clays, or residence time in the reservoir. These processes are constraining for the application of geothermometers. Moreover, some of them have a limited temperature range of application cannot be used in some petrologic environments. Thus, a range of possible reservoir temperatures is calculated depending on several assumptions and compared to measured temperature. Application of chemical and isotopic geothermometers, using several calibrations proposed in the literature, is discussed in this specific context.

1. INTRODUCTION
Many different chemical and isotopic reactions might be used as geochemical thermometers or geothermometers to estimate reservoir temperature (Fournier, 1981). Geothermometers constitute one of the most important geochemical tool for the exploration and development of geothermal resources, and also during exploitation when monitoring the response of geothermal reservoirs to the production load (D'Amore and Arnorsson, 2000). They were developed from the mid-1960’s to the mid-1980’s and the most important ones are the silica (quartz and chalcedony), Na/K, Na-K-Ca. Others that have been developed are based on Na/Li, Li/Mg, K/Mg, Ca/Mg, Na/Ca, K/Ca ratios and Na-K-Mg relationships. Moreover, the geothermometer using the fractionation of oxygen isotopes between water and dissolved sulphate was tested. Gas and other isotope geothermometers were not employed in this paper, and therefore were not discussed.

Interpretation of results of these computations requires consideration of the geological and hydrogeological settings, and petrographical properties as well as complete chemical analyses of the sampled deep fluid (Fournier, 1981). Solute geothermometers are based on temperature-dependent mineral-fluid equilibria and their successful application relies on five basic assumptions (Fournier, 1977; Nicholson, 1993):

1) The concentration of the elements or species to be used in the geothermometer is controlled only by a temperature-dependent mineral-fluid reaction.
2) There is an abundance of the minerals and/or dissolved species in the rock-fluid system for the reaction to occur readily.
3) The reaction attains equilibrium in the reservoir or aquifer.
4) There is rapid flow to the surface with no re-equilibration after the fluid leaves the reservoir, ie. no near-surface reactions. In this paper, this condition does not occur because the studied deep fluids are subjected to lateral flows or are trapped in subhorizontal formations. Moreover, the deep fluids come from boreholes and not springs.
5) There is no mixing or dilution of the deep fluid (this assumption can be circumvented if the extent of dilution/mixing can be evaluated).

In this paper, the main objective consists to test the applicability of geothermometers in low temperature deep aquifers (200-2000 m) from Northern Switzerland with known reservoir temperature from borehole measurements (12-112°C). This paper will emphasize that different geothermometers can be applied in different geological setting and temperature ranges. Concerned aquifers are described in the first section and are located in the Molasse Basin and the Tabular Jura of the Northern Switzerland.

2. GEOLOGICAL SETTING
In total, 62 water analyses from deep boreholes in 16 geothermal sites were used to study the application of geothermometers. Their position on the simplified Swiss tectonic map can be subdivided into two areas (Figure 1). Some sites are located in the tectonic unit named Molasse Basin or Plateau whereas others are situated close to the Rhine River between the northeastern part of the Jura range in Switzerland and the Black Forest in Germany. This large area is characterized by a high geothermal gradient and a significant heat flow anomaly which can exceed 150 mW/m² (Rybach et al., 1987). For this reason, this area was regarded since decades as a zone of geothermal interest, and other boreholes exist but were not selected due to the absence of water analyses. Moreover, sites with ascending thermal springs located in the folded Jura between the Tabular Jura and the Molasse Basin were not taken into account. Indeed, the study of the application of geothermometers requires selecting sites where reservoir
depth is known, what is often difficult to identify for sites with ascending thermal fluids.

Geologically, Switzerland can be divided into three main parts: 12.5% of its surface lies in the Jura, 30.5% in the Molasse Basin and 57% in the External and Pennine Alps (Figure 1). The Jura can be also subdivided into two domains: the folded and the tabular Jura. The folded Jura extends from Geneva to Basel and consists of a succession of SW-NE folded chains, whereas the tabular Jura located at the south of the Rhine Valley contains subhorizontal formations which are slightly affected by tectonic events. In detail, the Tabular Jura consists of subhorizontal Mesozoic and Cenozoic cover rocks affected by Oligocene faulting overlapping a complex Hercynian basement (granite, gneiss) which outcrops in Germany (Back Forest). This sedimentary cover consists of an alternation of karstified limestones considered as aquifers and marls. At the bottom of the sedimentary cover, sandstones, quartzites and conglomerates are also present and can contain groundwater. Borehole investigations for geothermal prospection highlighted potential geothermal reservoirs from the Cretaceous to the Carboniferous. For the Jurassic formations, the Malm (upper) and Dogger (middle) karstified limestones with a variable thickness in the range of 200-500 m are separated by the Oxfordian marl.

The Triassic formations are unconformable with respect to the Permian and Carboniferous layers. They contain a greater variety of rocks than the Jurassic such as evaporite in the Keuper and Muschelkalk (Upper and Middle Triassic respectively), dolomite in the Muschelkalk and sandstone in the Buntsandstein (Lower Triassic). These rocks are considered as aquifers in addition to limestones which are also present, in particular in the Muschelkalk. Concerning the Permian and Carboniferous sediments, they are detrital deposits in old grabens inside the Hercynian basement. They are locally present in particular in a WSW-ENE band passing by Riniken and Weiach. In these two sites, boreholes crossed an alternation of sandstone, quartzite and silt with a thickness exceeding 1000 meters. More in the south (Schafisheim), the Buntsandstein sandstone of limited thickness directly overlies the Hercynian basement.

Figure 1: Map showing major structural units of Northern Switzerland and location of selected deep boreholes. Geological cross sections through Central and Northern Switzerland (A) and through Tabular and Folded Jura (B) (modified from Person et al., 1991).
On the southern part of the extremity of the Jura range, Cenozoic and Mesozoic formations are covered by Tertiary sediments of which the thickness increases towards the south and the Alps Mountains (Figure 1). This zone named Molasse Basin or Plateau has a hilly landscape, studded with lakes and with a few large plains. The Tertiary deposits, which stratigraphically overlie the Cenozoic and Mesozoic formations that are found in the tabular Jura, consist of three units: Lower Marine Molasse, Lower Freshwater Molasse and Upper Marine Molasse (Trümpy, 1980). Groundwater flow is often absent in the Lower Freshwater Molasse; it is therefore regarded as an aquiclude. Groundwater flow through the Upper Marine Molasse sandstone is common but dependent on local conditions. The geological formations of the Muschelkalk, Dogger and Malm beneath the Tertiary deposits represent the most important aquifers, and can contain great quantities of hot water in permeable fractures (Balderer, 1990).

Selected boreholes crossed the described aquifers at different depths due to the weak dip of layers towards the south. Some of boreholes reached the basement and samples and measurements were carried out on water inflows. The measured temperatures at depth at different sampling elevations highlight a geothermal gradient in the range 30-40°C/km from an average temperature at the surface fixed at 10°C (Figure 2). This result was already highlighted by Rybach (1992) in the study of the geothermal potential of the Swiss Molasse Basin. Some samples can be locally subjected to the rise of deep fluids from fractures or to mixing process with shallow groundwater due to their position beyond the gradient 30-40°C/km. The highest temperature at depth was measured at 112°C in the crystalline basement for the 2.3 km deep borehole at Weiach.

![Figure 2: Plot of sampling elevation vs. measured temperature at depth for the studied deep fluids in boreholes. Deep fluids were subdivided into different symbols showing their geological setting. Two temperature gradient lines were added from an annual average air temperature around 10°C at the surface.](image)

3. WATER CHEMISTRY

Many reports and publications concern the chemistry of geothermal fluids in formations of the sedimentary cover and its crystalline basement below. Chemical data of selected sites are given in Table 1 and are interesting from a geothermal point of view, because their temperature, mineralization and geological setting give information on potential geothermal reservoir. Their position on the Piper diagram (Figure 3) in relation to their geological formations indicates that different geochemical types of geothermal fluids occur. The geochemical type is defined by the most important cations and anions. Moreover, the Total Dissolved Solids (TDS) of waters tends to increase with depth, and a difference of TDS is visible between waters in the crystalline basement and waters from sedimentary formations which have higher TDS (Figure 4). In the following subsections, the different types of geothermal fluids are described in terms of geochemistry.

3.1. Ca-SO$_4$ waters

Two selected sites at Leuggern and Weiach have a Ca-SO$_4$ type water with a TDS of 1.1 and 3.3 g/L respectively. Measured temperatures for this type are 13 and 50°C. This water was met in the fractured Muschelkalk limestone and is influenced by the dissolution of sulphate minerals (mainly gypsum and anhydrite) contained in the Triassic sediments. Gypsum and anhydrite are quickly dissolved and therefore, the Ca-SO$_4$ fingerprint is easily acquired by shallow or deep groundwaters upon interaction with these rocks. This lithotype is also found in the Jura range and the Alps due to the occurrence of Triassic rocks, which are often found in thrust faults and are locally present at shallow depth.

3.2. Na-HCO$_3$ waters

Sampled Na-HCO$_3$ waters were often met in the selected boreholes and have a TDS lower than 1.4 g/L except for the mineralized waters of the Rheinfelden well (TDS = 4.2 g/L). Measured temperatures for this type are in the range 20-66°C, and this water mainly circulates in crystalline rocks. Their mineralization is relatively weak compared to other water types which are up to 1 g/L (Figure 4). The sodium concentration of Na-HCO$_3$ waters is related to reactions with feldspars in crystalline rocks. In the Tertiary deposits of the Molasse Basin, Na-HCO$_3$ waters were pumped in the Lower Marine Molasse with temperature and TDS close to 29°C and 1 g/L respectively (Berlingen and Zürich). Two other Na-HCO$_3$ waters were respectively sampled in the Jurassic (20°C, 0.9 g/L) and Triassic (22°C, 0.6 g/L) formations of the tabular Jura at Lottstetten and Siblingen.

3.3. Na-SO$_4$ waters

Five selected waters in the basement at Kaisten, Leuggern and Weiach have a Na-SO$_4$ type water and a TDS in the
range 1-1.4 g/L except for one mineralized water (TDS = 4.9 g/L). These waters circulate in crystalline rocks, their sulphate concentration is due to the dissolution of sulphide minerals or anhydrite veins and their sodium comes mainly from reactions with feldspars. Four Na-SO\textsubscript{4} waters were analyzed in the Muschelkalk, Buntsandstein and Permian-Carboniferous formations with higher mineralization reaching 15 g/L, strongly influenced by the dissolution of Triassic evaporite.

![Figure 4: Sampling elevation vs. Total Dissolved Solids](image)

3.4. Na-Cl waters
Thermal Na-Cl waters have generally a high mineralization (TDS > 1 g/L) with concentrations sometimes exceeding 10 g/L, as in Weiach (97 g/L) or Reinach (44 g/L). Measured temperatures at depth for 29 sampled Na-Cl waters from 10 sites are in the range 16-112°C for any geological formations and any depth. The origin of this fingerprint is twofold. It could be due to the mixing of old, deep, strongly mineralized seawater and fresh water at different depths as observed in the crystalline basement and the Tertiary deposits (Chloride/Bromide molar ratio lower than the ocean line in Figure 5). Stober and Bucher (1999) studied deep groundwaters in the crystalline basement of the Black Forest region which is directly located in the north of the tabular Jura. They concluded that saline thermal waters used in spas have their origin in 3-4 km deep crystalline reservoirs and have developed their composition by mixing of surface freshwater with saltwater (of ultimately marine origin), and by water-rock reactions with an increasing mineral dissolution due to the presence of CO\textsubscript{2}. Concerning thermal waters in the sedimentary cover below the Tertiary rocks, dissolution of halite deposits, locally present in the Triassic formations, generates high Na-Cl contents in water with Chloride/Bromide molar ratio up to the ocean line (Figure 5).

![Figure 5: Sampling elevation vs. Chloride/Bromide molar ratio](image)

4. WATER GEOTHERMOMETERS
A series of geothermometers based on a temperature-dependent fluid-mineral equilibrium and an assemblage of minerals has been applied to deep groundwaters contained in subhorizontal formations of Northern Switzerland. Equations of geothermometers were represented on plots by curves and their variations with temperature could be compared to the measured temperature at depth for sampled waters. Measured temperature refers to the aquifer temperature from which the sample was taken, directly measured during the sampling campaign or estimated from the geothermal gradient in the borehole. Temperatures illustrated in this paper are as representative as possible of the average temperature of the sampled aquifer. The approach based on the comparison on measured/calculated temperature is useful to evaluate the applicability of geothermometers for low temperature. To clarify the discussion about the applicability of the geothermometers, this chapter is divided into sections referring to a specific geothermometer.

4.1 Silica geothermometers
The silica phases present in geothermal fluids are quartz, chalcedony and amorphous silica (D’Amore and Arnorsson, 2000). The total dissolved silica in selected waters and measured temperature at depth were plotted and curves representing equations of geothermometers were added (Figure 6). The dispersion of points indicates that geothermal fluids are often strongly affected by mixing processes with either shallow groundwaters containing low silica concentrations or trapped seawater. Therefore, the silica content of the discharged mixed water is usually below the reservoir concentration, and silica temperatures are therefore underestimated. Various petrographical properties of rocks met at depth are also at the origin of under-balanced dissolved silica concentrations analysed in geothermal fluids.

A general tendency to the increase of dissolved silica with temperature is observed, which follows the curves D of the two geothermometers using chalcedony (Fournier, 1977 and Arnorsson et al., 1983). For reservoir temperatures lower than 120-160°C, conditions present in the studied region, chalcedony has a higher solubility than quartz and controls silica concentrations in solutions (Arnorsson, 1975; Nicholson, 1993). Fournier (1981 and 1977) specifies that below 100°C, geothermal fluids may remain supersaturated with respect to quartz for years, and therefore the quartz
geothermometer works best in the temperature range 150-225°C.

Figure 6: Dissolved silica vs. measured temperature at depth of deep fluids in Northern Switzerland. Curves correspond to selected silica geothermometers. A: amorphous silica; B: cristobalite β; C: cristobalite α (A to C: Fournier, 1977); D: chalcedony (Fournier, 1977 and Arnorsson et al., 1983); E: quartz (Arnorsson et al., 1983); F: quartz (Fournier, 1977; Truesdell, 1976; Fournier and Potter, 1982 and Verma and Santoyo, 1997).

4.2 Na-K geothermometer
The Na-K geothermometer was initially developed to locate the major upflow in high enthalpy geothermal systems, because a general decrease in Na/K ratios of geothermal fluids with increasing temperatures was observed (D’Amore and Arnorsson, 2000). This geothermometer is related to the variation of sodium and potassium in thermal waters due to ion exchange of these elements between co-existing alkali feldspars (Nicholson, 1993). Na-K equations are adapted for reservoir temperatures in the range 180-350°C (Ellis, 1979), but are limited at lower temperatures, notably less than 120°C (Nicholson, 1993) as illustrated in Figure 7.

Ion exchange between feldspars is limited for groundwaters of the sedimentary formations covering the basement because rocks are carbonates, evaporites or detrital deposits. The source of sodium and potassium comes from other minerals such as clays, seawater and precipitated minerals from seawater evaporation. Consequently, these two elements are not controlled by the feldspar ion-exchange reaction, and associated points on the plot in Figure 7 representing Na/K vs. measured temperature at depth are widely dispersed. Concerning selected data in the crystalline basement, values of Na/K ratios are better correlated with a general tendency to the decrease of Na/K ratios with temperature and thus depth.

Figure 7: Log (Na/K) vs. measured temperature at depth of deep fluids in Northern Switzerland (see legend of symbols in Figure 6). Curves correspond to Na-K geothermometers. A: Truesdell, 1976; B: Arnorsson et al., 1983; C: Nieva and Nieva, 1987; D: Fournier, 1979; E: Verma and Santoyo, 1997; F: Arnorsson et al., 1998; G: Giggenbach, 1988.

4.3 Na-K-Ca geothermometer
The Na-K-Ca geothermometer, developed by Fournier and Truesdell (1973), does not give high and misleading results for cold and slightly thermal, non-equilibrated waters (D’Amore and Arnorsson, 2000), compared to the Na/K geothermometer which generally gives very high calculated temperatures for low enthalpy systems when geothermal fluids have high calcium contents (Nicholson, 1993). The Na-K-Ca geothermometer is also based on ion-exchange reactions between feldspars. As discussed above, the source of sodium, potassium and calcium in studied groundwaters comes from other geochemical processes, and they are not controlled by the feldspar ion-exchange reaction, and as observed for the Na/K geothermometer, estimated temperatures systematically over-estimate measured temperatures at depth (Figure 8).

Falsely high temperatures were estimated by the Na-K-Ca geothermometer, as shown in Figure 8, when applied to low-temperature reservoirs (< 120°C) relatively rich in magnesium. The geothermometer using magnesium correction developed by Fournier and Potter (1979) was applied to the studied groundwaters. Due to specific conditions described in the formulas of Fournier and Potter (1979), only some fluids were subjected to the magnesium correction (Figure 9). The reason is related to various magnesium concentrations in geothermal fluids, lower than 1 mg/L generally for waters in the crystalline basement and mostly up to 10 mg/L for carbonated aquifers containing dolomite (especially for the Triassic formations).
Figure 8: Computed temperature with Na-K-Ca geothermometer of Fournier and Truesdell (1973) vs. measured temperature at depth of deep fluids in Northern Switzerland (see legend of symbols in Figure 6).

Figure 9: Computed temperature with Na-K-Ca geothermometer using magnesium correction of Fournier and Potter (1979) vs. measured temperature at depth of deep fluids in Northern Switzerland (see legend of symbols in Figure 6).

4.4 Na-K-Mg geothermometer

Selected data of geothermal fluids in Northern Switzerland were plotted in the ternary diagram of Giggenbach (1988) to estimate reservoir temperature and to recognize groundwaters which have attained equilibrium with the host lithologies (Figure 10). Corresponding groundwaters plot below the full equilibrium curve which determines variations of the Na/K geothermometry equation of Giggenbach (1988). Therefore, these groundwaters are not suitable for Na/K geothermometry as shown previously. Points representing groundwaters are shifted towards the magnesium vertex indicating that waters are partially equilibrated or mixed. Dilution and mixing coupled to water-rock interactions in studied heterogeneous geological formations are processes limiting the application of these types of ionic solute geothermometers.

4.5 Other cation geothermometers

4.5.1 K-Mg geothermometer

Two K-Mg geothermometers of Giggenbach (1988) and Fournier (1991) were applied to studied geothermal fluids to test their applicability. Data plotted in Figure 11 illustrate a trend to the increase of the K/Mg ratios with measured temperature at depth, but separated from curves which over-estimate temperature. Initially, the K-Mg geothermometer was developed in the same way as the Na-K geothermometer. D’Amore and Arnorsson (2000) explain that progressive interaction between water and rock towards equilibrium changes Na/K ratios towards equilibrium with feldspars, and similarly, magnesium concentrations decrease because magnesium is incorporated into precipitating minerals such as smectite and chlorite. These processes cause K/Mg ratios to increase strongly. The K-Mg geothermometer was first applied to waters from a low-enthalpy reservoir which had not attained equilibrium with alkali feldspars (Nicholson, 1993), as for the studied geothermal fluids which are partially equilibrated or mixed waters (Figure 10). However, data plotted in Figure 11 indicate that the K-Mg geothermometer is not appropriate because it over-estimates temperature. By considering only geothermal fluids in formations of the sedimentary cover which consist of carbonate, evaporite and detrital deposits, the K-Mg geothermometers cannot be applied. Indeed, these formations are poor in feldspars implying another origin for these elements such as dolomite dissolution, leaching of seawater brines, etc. Data plotted for sedimentary groundwaters are widely dispersed in Figure 11.
4.5.2 Mg-Li geothermometer

The Mg-Li geothermometer was developed in the same way as the K-Mg geothermometer, resting on exchange reactions with magnesium, for waters from a low-enthalpy reservoir which had not attained equilibrium with alkali feldspars (Nicholson, 1993). Thereby, these processes cause Mg/Li ratios to decrease strongly, and conversely for K/Mg. The two equations of Kharaka et al. (1985) and Kharaka and Mariner (1989) were tested on the studied geothermal fluids but they strongly over-estimate temperature, especially for waters in the crystalline basement (Figure 12). Data plotted in Figure 12 show a general trend to the decrease of the Mg/Li ratios with measured temperature at depth. This tendency is better organized for crystalline thermal waters. Data plotted for sedimentary groundwaters are widely dispersed due to the occurrences of dilution and mixing processes and water-rock interactions which are more pronounced in sedimentary formations.

4.5.3 Na-Li geothermometer

The Na-Li geothermometer was initially developed by Fouillac and Michard (1981) from a statistic study about groundwaters in granitic and volcanic domains. Two other Na-Li geothermometers are documented in Kharaka et al. (1982) and Verma and Santoyo (1997) and were tested on the studied waters. These two other equations are relatively distant because they result from empirical calibration, based on data in selected geothermal fields. Data plotted in Figure 13 highlight two distinct features. The first relates to geothermal fluids in sedimentary formations where data are widely dispersed (Figure 13). Some geothermal fluids have high Na/Li ratios because sodium is enriched by the dissolution of halite and the leaching of trapped seawater. Frequently, waters in deep carbonate aquifers have low lithium contents (< 1 mg/L) which can also explain the strong ratios. The second concerns groundwaters in crystalline rocks which have generally lower Na/Li ratios due to higher lithium concentrations (> 1 mg/L). Moreover, Na/Li ratios remain relatively stable around 2.5 whatever the measured temperature at depth. The Na/Li geothermometer appears to be sensitive to the total dissolved solids of the water at depth, locally controlled by contributions of Na-Cl, and the rock type.
concentrations up to 1 mg/L, and thus, Ca/Mg ratios tend to decrease compared to crystalline waters poor in magnesium (< 1 mg/L). Data plotted of selected waters in Figure 15 show differences due to their geological setting. Points for the sedimentary cover are clearly closer to the Ca-Mg geothermometer than points representing crystalline waters.

Figure 15: Log (Ca/Mg) vs. measured temperature at depth of deep fluids in Northern Switzerland (see legend of symbols in Figure 10). Curve A corresponds to Ca-Mg geothermometer of Marini et al. (1986).

4.6 Oxygen isotope geothermometer

The sulphate oxygen isotope geothermometer is based upon the experimental work of Lloyd (1968), who measured the fractionation of $^{18}$O and $^{16}$O between SO$_4^{2-}$ and water at 350°C, as well as the work of Mizutani and Rafter (1969) who measured the $^{16}$O and $^{18}$O between water and HSO$_4$ at 100 to 200°C (Fournier, 1981). Only the geothermometer of Mizutani and Rafter was applied to studied geothermal fluids (Figure 16).

In the case of geothermal fluids of northern Switzerland, various isotopic signatures of $^{18}$O in water and sulphate are observed due to water-rock interactions and chemical processes in different geological domains. As observed for the Paris Basin in France (Fouillac et al., 1990), the sulphate in studied groundwaters has different origins: dissolution of evaporite (gypsum and anhydrite), oxidation of sedimentary sulphides in rocks and leaching of trapped seawater. For each case, isotopic values of $^{18}$O in sulphate can be strongly different. Moreover, $^{18}$O values of marine evaporite sulphate minerals vary with their geologic age due to changes in the isotopic composition of oceanic sulphate with time (Pearson et al., 1991). Concerning $^{18}$O of water, a great difference in values can be caused by mixing processes with shallow groundwater or trapped seawater. All these processes in studied geothermal fluids induce that the oxygen isotope geothermometer is often not suitable. Data plotted in Figure 16 indicate that this geothermometer has the tendency to over-estimate temperature, especially for crystalline waters.

Figure 16: Computed temperature with oxygen isotope geothermometer of Mizutani and Rafter (1969) vs. measured temperature at depth of deep fluids in Northern Switzerland (see legend of symbols in Figure 10).

6. SYNTHESIS

Chemical and isotopic geothermometers were applied on chemical data and measured temperature at depth of geothermal fluids in boreholes from northern Switzerland, in the range of 12-112°C and considered as low-temperature geothermal systems. For each type of geothermometer, the method used was to plot measured temperature at depth with the corresponding geotemperature curves. Thereby, the accuracy and applicability of various geothermometers can be evaluated in these low-temperature geothermal systems.

For instance, there is some uncertainty in the interpretation of dissolved silica concentration in geothermal fluids
because the solid phase controlling dissolved silica is often unknown (quartz or chalcedony in general), mixing processes with shallow groundwaters and trapped seawater occur and water-rock interactions are difficult to identify. Consequently, the application of silica geothermometers often gives underestimated values even if the chalcedony geothermometer was shown to be the most accurate of these.

Cationic geothermometers using ratios between lithium, sodium, potassium, magnesium and calcium were also tested and obtained results largely overestimate the measured temperature at depth. Application of these geothermometers is more suitable for high-enthalpy systems (>150°C), containing groundwaters reaching equilibrium with feldspars and clay minerals. This assumption is fundamental for the use of the majority of cationic geothermometers, what is not verified for studied geothermal fluids, subjected to various chemical processes. Finally, the oxygen isotope geothermometer based on 18O of water and sulphate did not give useful results, especially for crystalline thermal waters. The isotopic signature of 18O in particular in sulphate depends of a lot on different origins from various geological domains. In conclusion, chemical and isotopic geothermometers can be applied in low temperature geothermal systems (< 100°C) with a much greater cautiousness than in high temperature systems (>150°C). Indeed, chemical reactions or isotopic fractionation may not reach equilibrium in low temperature reservoirs during the underground transit time of the deep fluids. Mixing of various types of fluids in heterogeneous rocks composition does not favour a complete equilibrium. However, detailed rock and fluid geochemistry in a given geothermal exploration zone can alleviate the uncertainties in the use of geothermometers.

REFERENCES


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| Site name   | X-Coord | Y-Coord | Elevation (a.m.s.l.) | Sampling elevation (a.m.s.l.) | Borehole depth (m) | Formation         | Formation age | Meas. Temp. (°C) | TDS (mg/l) | pH | Li | Na | K | Mg | Ca | Sr | F | Cl | SO4 | HCO3 | SiO2 | Ionic balance (%) | ‰ of 18O H2O | ‰ of 18O SO4 | Ref. |
|------------|---------|---------|----------------------|-------------------------------|-------------------|-------------------|----------------|----------------|------------|----|----|----|----|----|----|----|----|----|----|----|-----------------|----------------|----------------|-----|
| Berlingen  | 720142  | 281378  | 406.9                | -9                            | 416               | Molasse           | Tertiary      | 29             | 8.5        | 0.05 | 298 | 1.80 | 1.20 | 2.6  | 0.37 | 3.6 | 48.0 | 161 | 13.1 | -13.10          | -10.8          | 13.0          | 1    |
| Bernenstor | 660049  | 257455  | 343.7                | 103                           | 241               | Limestone         | Triassic       | 25             | 6.9        |     | 1446 | 50   | 258 | 990  | 8.3  |     |     |     |     |     |     | 4433            | 1900           | 43.2          | 2    |
| Boettstein  | 659340  | 268556  | 347.5                | 185                           | 1326              | Limestone         | Muschelkalk    | 21             | 6345       | 6.9  | 2.9  | 1100 | 83   | 199 | 612  | 11.0 | 2.6  | 1302 | 0.92 | 2624 | 388 | 20.3 | -11.16          | 13.70          | 3             |
| Boettstein  | 36      |         |                      |                               |                   | Borehole depth    | (m)             |                |             |     |     |     |     |     |     |     |     |     |     |     |     |                 |                |               |      |
| Boettstein  | 32      |         |                      |                               |                   | Limestone         | Buntsandstein  | 27             | 1977       | 8.6  | 1.60 | 662  | 16.9 | 2.3  | 20.1 | 0.97 | 12.1 | 638  | 0.78 | 287  | 319  | 18.4 | -10.08          | 3.83           | 3             |
| Boettstein  | -51     |         |                      |                               |                   | Granite           | Hercynian       | 29.5           | 1028       | 8.1  | 2.02 | 356  | 8.5  | 0.30 | 9.6  | 0.40 | 12.4 | 121  | 0.83 | 308  | 342  | 19.0 | 0.0            | -10.05         | 1.16          | 3    |
| Boettstein  | -270    |         |                      |                               |                   | Granite           | Hercynian       | 38             | 1098       | 7.9  | 1.45 | 378  | 9.8  | 0.20 | 11.8 | 0.34 | 12.0 | 124  | 1.00 | 340  | 372  | 28.3 | 1.3            | -10.04         | -0.15         | 3    |
| Boettstein  | -273    |         |                      |                               |                   | Granite           | Hercynian       | 38             | 1095       | 8.0  | 2.5  | 364  | 10.8 | 0.30 | 11.8 | 0.57 | 12.4 | 131  | 0.88 | 333  | 387  | 29.6 | -2.8            | -10.01         | -1.32         | 3    |
| Boettstein  | -444    |         |                      |                               |                   | Granite           | Hercynian       | 43             | 1302       | 8.3  | 1.35 | 395  | 8.3  | 0.20 | 8.5  | 0.09 | 12.9 | 142  | 1.20 | 339  | 372  | 22.5 | 0.6            | -9.96          | -0.58         | 2    |
| Boettstein  | -978    |         |                      |                               |                   | Granite           | Hercynian       | 60             | 13210      | 7.0   |     | 4037 | 4.5  |     |     |     |     |     |     |     |     |     |     | 1610            |                |               | 4    |
| Eglishaun  | 680800  | 270000  | 380                  | 140                           | 240               | Molasse           | Tertiary       | 16             | 2467       | 7.8  | 0.25 | 843  | 4.2  | 10.6 | 19.8 | 1.00 | 1.40 | 952  | 0.06 | 320  | 296  | 8.9  | 0.3            | -9.89          | 4             |
| Eglisau    | 680820  | 269865  | 381.8                | 122                           | 260               | Molasse           | Tertiary       | 16             | 2643       | 8.4  | 0.35 | 925  | 4.5  | 12.0 | 23.6 | 0.90 | 1.50 | 1260 | 0.59 | 144  | 250  | 8.8  | 0.1            | -9.41          | 14.7          | 4    |
| Kaisten    | 644641  | 265624  | 320.4                | 206                           | 1306              | Limestone         | Buntsandstein  | 17             | 6821       | 7.0   | 6.8  | 1780 | 37.6 | 56   | 445  | 12.6 | 2.4  | 2025 | 4.8  | 2083 | 366  | 8.9  | 0.1            | -9.03          | 14.7          | 3    |
| Leuggern   | 657634  | 271208  | 358.8                | -284                          | 1689              | Limestone         | Muschelkalk    | 13.3           | 1146       | 7.5   | 0.14 | 31.6 | 7.5  | 71   | 180  | 3.2  | 2.2  | 34.3 | 0.08 | 537  | 263  | 15.7 | -0.3            | -9.96          | 13.43         | 3    |
| Leuggern   | 141     |         |                      |                               |                   | Limestone         | Triassic       | 19.4           | 1858       | 8.8  | 0.83 | 608  | 9.1  | 3.7  | 17.7 | 0.71 | 10.0 | 486  | 0.85 | 445  | 268  | 7.8  | 0.2            | -10.39         | 8.63          | 3    |
| Lottstetten| 657634  | 271208  | 358.8                | -284                          | 1689              | Limestone         | Jurassic       | 20.4           | 1146       | 7.5   | 0.14 | 31.6 | 7.5  | 71   | 180  | 3.2  | 2.2  | 34.3 | 0.08 | 537  | 263  | 15.7 | -0.3            | -9.96          | 13.43         | 3    |
| Rheinfelden| 626750  | 266680  | 300                  | -300                          | 600               | Granite           | Hercynian      | 26.9           | 4180       | 6.5   |     | 856  | 35.0 | 45.6 | 260  | 4.5  |     |     |     |     |     |     | 556            | 950           | 49.7          | -2.4 |
| Reinach    | 612525  | 262126  | 305                  | -1488                         | 1793              | Limestone         | Triassic       | 77.6           | 44001      | 5.6  | 6.7  | 14200 | 270 | 580  | 1400 | 12.1 | 11.0 | 23650 | 19.0 | 3100 | 696  | 7.5  | 0.0            | -8.70          | 6             |

Sonney and Vuataz
### Table 1: Location, geology, chemistry and oxygen isotopic data of geothermal fluids from deep boreholes in northern Switzerland.

<table>
<thead>
<tr>
<th>Site name</th>
<th>X-Coord</th>
<th>Y-Coord</th>
<th>Elevation (a.m.s.l.)</th>
<th>Sampling elevation (a.m.s.l.)</th>
<th>Borehole depth (m)</th>
<th>Formation</th>
<th>Formation age</th>
<th>Meas. Temp. (°C)</th>
<th>TDS (mg/L)</th>
<th>pH</th>
<th>Li</th>
<th>Na</th>
<th>K</th>
<th>Mg</th>
<th>Ca</th>
<th>Sr</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>SO4</th>
<th>HCO3</th>
<th>SiO2</th>
<th>Ionic balance (%)</th>
<th>18O H2O (‰)</th>
<th>18O SO4 (‰)</th>
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