Hydrochemistry and isotope hydrology of thermal springs in the Alps

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Abstract

Thermal springs in orogenic belts are the most visible signs of heat transfer from the crust to the surface and may provide a significant amount of heat transport in orogenic belts. However, because of the complex geological structure in mountain belts, the sources and pathways of hydrothermal systems in orogenic belts are not entirely understood. I aim to quantify these by collecting and analysing information on hydrochemistry and isotopic data for around 175 springs in the Alps in a thermal springs database. With this database I calculated (i) the mean elevation of the recharge area of the springs by comparing stable isotopes $\delta^2 H$ and $\delta^{18}O$ of springs to isotopic data in precipitation from the Global Network of Isotopes in Precipitation (GNIP), (ii) the groundwater age from tritium concentrations, (iii) the maximum fluid temperature and maximum circulation depth of spring water by using the silica geothermometer. This information will provide a better understanding of the dynamics of thermal springs, in particular the origin and the pathways of fluid flow. I found out that the lowest isotopic values are usually in higher elevations, corresponding to the elevation effect. Existing geographical deviations are caused by rain shadow and different origins of rain masses. The linear correlation between δ^2 H and δ^{18} O in spring water, according to the Global Meteoric Water Line, indicates a meteoric origin of all spring water in the Alps. The tritium concentrations in spring water show that 35 out of 60 springs have young groundwater. The silica geothermometer provide information on the maximum temperature of spring water, which is complicated by the mixing of deep and shallow groundwater sources. The maximum fluid temperature as recorded by the silica geothermometer ranges from 11 °C to 128°C, with a median of 61 °C. This corresponds to a circulation depth of 34 m to 3934 m, with a median of 1692 m.

Zusammenfassung

Thermale Quellen in Gebirgen sind die sichtbarsten Zeichen von Wärmetransport von der Kruste zur Oberfläche. Womöglich transportieren sie eine signifikante Menge an Wärme in Gebirgen. Aufgrund der komplexen geologischen Struktur von Gebirgen sind sowohl Herkunft als auch Fließwege von thermalen System Bestandteil der aktuellen Forschung.

Ziel dieser Arbeit ist eine Quantifizierung von etwa 175 thermalen Quellen in den Alpen. Die Datengrundlage bildet eine neu erstellte Datenbank mit hydrochemischen und isotopischen Parametern. Ausgehend von dieser Datenbank wurden folgende Punkte bearbeitet: (i) die Ermittlung der durchschnittlichen Höhe des Einzugsgebietes der Quellen, durch den Vergleich der stabilen Isotope δ^2 H und δ^{18} O in Quellwasser mit Isotopendaten aus Niederschlagswasser, (ii) das Grundwasseralter aus den Konzentrationen von Tritium und (iii) die Berechnung der maximalen Fluidtemperatur und Zirkulationstiefe von Quellwasser, basierend auf dem Quarz Geothermometer. Diese Informationen können ein besseres Verständnis über die Dynamik von thermalen Quellen liefern, insbesondere über die Herkunft und die Fließwege des Fluides. Die Verteilung der Isotopenwerte entspricht dem Höheneffekt. Bestehende geographische Abweichungen der isotopischen Zusammensetzung werden durch Regenschatten und den unterschiedlichen Ursprung von Regenmassen verursacht. Die lineare Korrelation zwischen δ^2 H und δ^{18} O in Quellwasser entspricht der Globalen Meteorischen Wasser Linie und zeigt einen meteorischen Ursprung für die Quellen in den Alpen. Junges Grundwasser konnte in 35 von 60 Quellen anhand der Tritium Konzentration nachgewiesen werden. Durch die Vermischung von flachen und tiefen Grundwassertypen wird das Ergebnis des Quarz Geothermometers beeinflusst. Die durch das Quarz Geothermometer aufgezeichnete maximale Fluidtemperatur reicht von 11 °C bis 128 °C, mit einem Median von 61 °C. Dies entspricht einer Zirkulationstiefe von 34 m bis 3934 m, mit einem Median von 1692 m.

1 Introduction

Thermal springs in the European Alps are the most visible source of fluid flow and heat transport from the subsurface. Thermal springs are widespread in the European Alps and are used by humans since ancient times (Volpi et al. 2017). However, the dynamics of fluid flow are not entirely understood. The European Alps are a continental hydrothermal system without a magmatic heat source. The thermal system consists of three components: a fluid, a heat source and a thermal pathway (Dzikowski et al. 2016). The fluid flow in orogenic belts is mainly topography driven by hydraulic gradients resulting from high elevation recharge areas and low elevation discharge areas (Diamond et al. 2018). During the flow through permeable rocks and faults, the water gets heated up by the surrounding hot bedrock and chemical reactions with the rocks affect the water composition (Diamond et al. 2018). The elevation difference between recharge and discharge area is high enough to heat the fluid (Dzikowski et al. 2016; Taillefer et al. 2018). The high permeability of fault zones can connect shallow and deep groundwater reservoirs and allows a quick rise of water to the surface (Bense et al. 2013; Taillefer et al. 2018). Spring water preserves the traces of the reactions the fluid has experienced in a unique hydrochemical and isotopic composition.

There are several studies in the European Alps about the estimation of the elevation of the recharge area by using the stable isotopes δ^2 H and δ^{18} O in alpine spring water and precipitation. These studies focus on specific areas in Switzerland (Pearson et al. 1991; Kozel and Schotterer 2003; Sonney and Vuataz 2009; Schotterer 2010; Diamond et al. 2018), Austria (Liebminger et al. 2006; Krainer et al. 2007), Italy (Peña Reyes et al. 2015; Giustini et al. 2016; Volpi et al. 2017; Sappa et al. 2018) and Slovenia (Kanduč et al. 2012).

The radioactive hydrogen isotope tritium was used to estimate the age and the distribution of young groundwater (Schlosser et al. 1988; Blavoux et al. 2013).

The interaction between rock and water provides us with information about the hydrochemistry and the maximum heating of the water. To quantify the maximum temperature of the fluid the quartz geothermometer has experienced wide application (Fournier 1977, 1981; Verma and Santoyo 1997; Verma 2000; Verma et al. 2008).

To gain a better understanding of the pathways of fluid flow the circulation depth of spring water can be calculated from the estimated maximum fluid temperature by the quartz geothermometer and the local thermal gradient (Ferguson et al. 2009).

In this thesis I focus on two main objectives: The origin of spring water and the pathways of the fluid in the subsurface. This study is the first one to address these two objectives for the entire alpine orogen. Based on a newly created thermal spring data base (Luijendijk et al.), the origin of spring water is determined with the stable isotopes $\delta^2 H$ and $\delta^{18}O$ and the radioactive tritium in alpine spring water and precipitation. The pathways of fluid flow are studied by comparing the results from the quartz geothermometer and the hydrochemistry of alpine springs.

1.1 Study area

The study area of this work encompasses the entire mountain range of the European Alps and parts of the foreland basin. As seen in Figure 1, the study area includes the countries Austria, France, Germany, Italy, Slovenia and Switzerland. The European Alps are an interesting study area because of its complex geology, high topography and meteorological boundary between the Atlantic Ocean and the Mediterranean Sea.



Figure 1: Overview of the study area in the Alps. The orange area represents the study area. The study area includes the countries Germany, Switzerland, Austria, Slovenia, Italy and France.

1.2 Geology of the Alps

The Alps were formed by the collision and subduction of Mesozoic ocean basins, continental margins and continental fragments during two mountain building events in the Jurassic and Triassic (Froitzheim et al. 2008). The Alps have an arc shaped form and extend from the Vienna Basin in the east to the Ligurian Sea in the west. The length of the Alps is around 1000 km and

the width ranges between 100 and 250 km. The Alps are build up by 4 tectonically different subdivision: the Helvetic, Penninic, Austro Alpine and South Alpine unit (Froitzheim et al. 2008). The Helvetic unit is build up by the Mesozoic European shelf, while the Penninic unit mostly consists of ocean crust from the Vailais Ocean, the Brianconnais Terrane and the Piemont-Liguaria Ocean (Froitzheim et al. 2008). The Austro Alpine and the Southern Alpine units are build up by the Apulian continental margin (Froitzheim et al. 2008). The Southern Alpine has almost experienced no metamorphic overprint, while the Austro Alpine, the Helvetic and the Penninic units are partly metamorphosed (Froitzheim et al. 2008). The area of the Southern Alps are sharply separated from the other units by east-west orientated valleys, which are the morphological expression of the Tertiary Periadriatic Fault (Froitzheim et al. 2008).

2 Methods

2.1 Data collection

This master thesis is based on a thermal spring database with information from springs, boreholes, wells and tunnels in the Alps. For each entry I collected information about location, elevation, water temperature, flow rate, hydrochemistry and isotopic data if available. The sample points for the database were taken from published literature and online databases from federal bureaus of different countries. Each spring is assigned to a certain host rock lithology from the global lithological map database GLiM (Hartmann and Moosdorf 2012).

My target is to better understand thermal springs and therefore I use, besides natural springs, data from boreholes and wells that are not deeper than 100 m. In the following, data from boreholes and wells under 100 m are also referred to as springs. Overall there are 546 springs. Of these 546 springs, 131 springs have δ^2 H data, 145 springs have δ^{18} O data, 61 springs have tritium data and 175 springs have SiO₂ data (Table 1).

	$\delta^2 H$	δ ¹⁸ Ο	Tritium	SiO ₂
Number of springs	131	145	61	175

Table 1: Number of springs with data about the respective parameters $\delta^2 H$, $\delta^{18}O$, Tritium and SiO₂.

To understand the behaviour of stable isotopes in spring water it is crucial to look at the origin of spring water. The isotope signal in spring water may be strongly related to the isotope signal in precipitation. The Global Network of Isotopes in Precipitation (GNIP) is a worldwide database from the International Atomic Energy Agency (IAEA). The 25 GNIP stations in the Alps that I, used for this study, provide a good monitoring network of isotopes in precipitation (IAEA/WMO, 2019). An overview of the used GNIP stations with the location is given in Figure 2. There are 14 stations in Switzerland, 1 in Slovenia, 6 in Austria, 1 in Germany and 3 in France. The operational time of the stations varies. Some stations started in 1960 and are still running today, while other stations just operated for three years. The GNIP provide long time and monthly data series of δ^{18} O, δ^{2} H, tritium, temperature and precipitation measurements from precipitation (IAEA/WMO 2019). The long-time data series are presented as yearly means calculated by the arithmetic and weighted annual averages (IAEA 1992). Not all stations have data on all parameters.



Figure 2: Overview of the Alps with the GNIP stations in Switzerland, Slovenia, Austria, France and Germany and the respective elevation (m) at each station.

2.2 Stable isotopes in precipitation

The stable isotopes ¹⁸O and ²H are ideal tracers for different processes in the water cycle (Schotterer 2010). They provide us with information about the elevation of the recharge area, mixing between groundwater from different sources and local origin of groundwater (Dansgaard 1964; Etcheverry and Vennemann 2009). The fundamental process that controls the behaviour of different isotopes is the isotopic fractionation. During phase transitions, for example evaporation, heavier isotopes preferably remain in the liquid phase resulting in a depletion of heavier isotopes in the gas phase in comparison to the liquid phase (Etcheverry and Vennemann 2009). There are various effects causing regional and temporal variations on ¹⁸O

and ²H of precipitation (Mook 2001). These effects are caused by temperature, elevation, seasonal changes, amount, latitude and geographical position (Dansgaard 1964; Gat et al. 2001; Mook 2001; Etcheverry and Vennemann 2009). It is expensive to measure the absolute content of ¹⁸O or ²H in water. An easier way is to measure the relative difference between the sample and a standard (Dansgaard 1964). The relative difference is usually given in the δ notation in per mille, which is defined as:

$$\delta(\%_0) = \frac{R_{sample} - R_{standard}}{R_{standard}} \cdot 10^3$$
(1)

where R is the isotope ratio between the heavy and the light isotope of an element, for example ${}^{18}\text{O}/{}^{16}\text{O}$. For water the most common used standards are the older Standard Mean Ocean Water (SMOW) or the newer Vienna Standard Mean Ocean Water (VSMOW), which is an artificial mixed water standard with the same isotopic composition as the SMOW (Etcheverry and Vennemann 2009). In case of a positive δ value the sample is enriched in heavy isotopes, while for a negative δ value the sample is depleted in heavy isotopes relative to the standard (Gat et al. 1981). There is a worldwide observed linear correlation between δ^{18} O and δ^{2} H in precipitation, which is shown in the following empirical equation after Craig (1961):

$$\delta^2 H = 8 \cdot \delta^{18} 0 + 10 \% 0 \tag{2}$$

where the slope of 8 expresses the ratio of equilibrium fractionations for hydrogen and oxygen during rain condensation and 10 $\%_0$ is the deuterium excess (Mook 2001). This linear correlation is called the Global Meteoric Water Line (GMWL). There can be variations from the GMWL caused by geographical and climatic effects (Etcheverry and Vennemann 2009). Therefore it is useful to create a Local Meteoric Water Line (LMWL) for the study area, to clarify these variations (Etcheverry and Vennemann 2009). I created Local Meteoric Water Lines for Switzerland, Austria, France and Italy based on δ^{18} O and δ^{2} H in spring water.

2.3 Stable isotopes in springs

Because of the dependence of the stable isotopic composition on temperature and elevation, the stable isotopes can be used to estimate the mean elevation of the recharge area. The mean elevation of the recharge area can be determined by the comparison of isotopic data from precipitation and springs (Giustini et al. 2016). It is possible to estimate the mean elevation of

the recharge area by using a regression analyses for water samples from springs or precipitation where the recharge area is known (Pearson et al. 1991). The exact recharge area for every spring in the Alps from the database cannot be identified without studying every spring in detail. Therefore, I tried to estimate the mean elevation of the recharge area by using the stable isotopic composition in precipitation from the GNIP stations. I chose the GNIP stations Buchs and Pontresina as endmembers. I made a regression fit between the two stations and calculated the recharge area for all springs that are between the two GNIP stations or 20 km around one station.

2.4 Tritium

Tritium is the only radioactive isotope of hydrogen with a half-life of 12.32 years (Lucas and Unterweger 2000). Tritium is measured in Tritium Units (TU). Tritium Units express the radioactive activity of the sample in dependence of the mass and time (Etcheverry and Vennemann 2009). Natural tritium is produced in the upper atmosphere, while most tritium is produced in atmospheric nuclear tests (Schlosser et al. 1988). The natural tritium concentration in the atmosphere is between 10 -20 TU. Due to nuclear tests in the 1950s and 1960s the concentration increased up to 6000 TU (Blavoux et al. 2013). Since the end of atmospheric nuclear tests in rain are at the same magnitude as the natural background contents (Schotterer 2010; Blavoux et al. 2013).

2.5 Silica geothermometer

A simple and fast way to calculate the maximum temperature a groundwater was exposed to is the silica based geothermometer (Fournier 1981). The silica geothermometers is an empirical equation derived from the relation between water temperature and silica solubility, calibrated by temperature and SiO₂ data from boreholes (Fournier and Potter 1982; Verma and Santoyo 1997; Verma et al. 2008). There are several empirical equations (3-9), which are listed in (Table 2). The different equations are developed for different temperature ranges and for no expected steam loss or maximum steam loss (Verma et al. 2008).

I used these equations to calculate the maximum fluid temperature for each spring with SiO_2 data. From the former calculations, except the equation Verma-Santoyo 2, I calculated the mean maximum fluid temperature for each spring as an average from all calculations. I cut off negative temperatures, which are caused by SiO_2 concentrations under 3 mg/l.

Table 2: Different geothermometers for the calculation of the maximum fluid temperature from SiO₂ in spring water (modified after Verma et al. (2008). After Verma et al. (2008) the geothermometer Quartz (Verma-Santoyo 1) can be used for temperatures between 20 - 210 °C, Quartz (Verma-Santoyo 2) for temperatures between 210 - 330 °C and all geothermometers by Fournier for temperatures between 0 - 250 °C. (Fournier 1) can be used for no steam loss and (Fournier 2) for maximum steam loss.

Geothermometer	Equation to obtain temperatures (°C)	Equation
Quartz (Fournier-1)	[1309/(5.19 - log S)] - 273.15	(3)
Quartz (Fournier-2)	[1522/(5.75 - log S)] - 273.15	(4)
Quartz (Fournier-Potter)	$-42.198(\pm 1.345) + 0.28831(\pm 0.01337)\text{S} - 3.6686 \cdot$	(5)
	$10^{-4} (\pm 3.152 \cdot 10^{-5}) S^2 + 3.1665 \cdot 10^{-7} (\pm 2.421 \cdot 10^{-7}) S^3 + $	
	77.034(±1.216)log S	
Quartz (Verma-Santoyo-1)	$-\{44.119(\pm0.438)\}+\{0.24469(\pm0.00573)\}S$	(6)
	$-\{1.7414 {\cdot} 10^{-4} (\pm 1.365 {\cdot} 10^{-5})\}S^2 +$	
	{79.305(±0.427)}log S	
Quartz (Verma-Santoyo-2)	$[140.82(\pm 0.00)] + [0.23517(\pm 0.00179)]$ S	(7)
Quartz (Arnorsson-2)	$-55.3 + 0.3659 \cdot S - 5.3954 \cdot 10^{-4} S^2 + 5.5132 \cdot 10^{-7} S^3 + \\$	(8)
	74.360·log S	
Quartz (Verma)	$\{[1175.7(\pm 31.7)]/[4.88(\pm 0.08)-\log S]\} - 273.15$	(9)

2.6 Circulation depth

With the knowledge of the maximum temperature the spring water has experienced, it is possible to calculate circulation depth z of the spring water using the following equation:

$$z = \frac{t_{max} - t_{air}}{dt/dz} \tag{10}$$

where t_{max} is the maximum water temperature calculated by the silica geothermometers and dt/dz is the geothermal gradient. I used an average geothermal gradient for the Alps, which was calculated from the global heat flow database for 184 boreholes in the Alps by dividing the measured heat flow by the measured thermal conductivity (Hasterok). The calculated average geothermal gradient for the Alps is 29.92 °C/km. The air temperature t_{air} was calculated after Rolland (2003) with an average temperature at sea level of 14 °C and an average lapse rate of 0.56 °C per 100 m (Köhler 2019). The circulation depth was then calculated with equation (10) for every spring with SiO₂ data with the average geothermal gradient and the air temperature for each spring location.

2.7 Heat loss

The heat transport by each spring was calculated using the following equation:

$$HF = c \cdot \rho (T_{max} - T_{spring})Q \tag{11}$$

where c is the specific heat of water with 4184 J/(kg· K), ρ is the density of water with 1000 kg/m³, Q is the spring discharge in m³/s and HF is the heat flux in W/m².

3 Results

3.1 Stable isotopes in precipitation

Figure 3 shows the δ^{18} O values plotted against the elevation (a), amount of precipitation (b) and the average annual temperature (c) at the GNIP stations in Switzerland, Slovenia, Austria, Germany and France. The δ^{18} O, precipitation and temperature values are long time yearly averages from each dataset over the measuring time of each station.

Panel (a) shows the δ^{18} O values plotted against the elevation of the GNIP station. There is a modest correlation (R² = 0.45) between the δ^{18} O values and the elevation.

Panel (b) shows the relation between annual averages in δ^{18} O and the amount of precipitation at the GNIP stations. For Switzerland, Austria and France there is data for more than one station available and therefore a correlation was possible. Only the GNIP stations which contain precipitation data are displayed. For Austria (R² = 0.93) and France (R² = 0.99) the correlation between δ^{18} O values and the amount of precipitation at the GNIP stations is good. For Switzerland the stations Locarno (8) and Sion (13) are located more in the south than the rest of the stations and are viewed separately. For the other stations the correlation (R² = 0.98) between δ^{18} O values and the amount of precipitation is good.

Panel (c) shows the relation between δ^{18} O values and temperature. There is a good correlation ($R^2 = 0.75$) between δ^{18} O values and the temperature.



Figure 3: The relation between $\delta^{18}O$ in precipitation and elevation, amount of precipitation and temperature for GNIP stations in Switzerland, Slovenia, Austria, Germany and France. Panel (a) shows the relation between $\delta^{18}O$ in precipitation and elevation. There is a modest correlation ($R^2 = 0.45$). Panel (b) shows the relation between $\delta^{18}O$ and the amount of precipitation. The dark blue line shows a good correlation ($R^2 = 0.98$) for Switzerland. The light blue line shows a good correlation ($R^2 = 0.93$) for Austria. Panel (c) shows the relation between $\delta^{18}O$ and average annual temperature. There is good correlation ($R^2 = 0.75$).

Figure 4 shows yearly and monthly variations in δ^{18} O and temperature in precipitation from GNIP stations for Austria (a-c), Switzerland (d-f) and Slovenia, France and Germany (e-i).

Panel (a) shows the variation in δ^{18} O over the years from 1960 to 2018 in the GNIP stations Vienna, Klagenfurt and Villacher Alpe in Austria. All three stations show a similar variation pattern and overall the δ^{18} O values are less depleted in 2018 than in the past. Panel (b) shows the variation in δ^{18} O and temperature over the years from 1960 to 2018 for the GNIP station Vienna. The two curves show a similar trend. Overall the temperature increases and the depletion in δ^{18} O decreases. Panel (c) shows the monthly variation in δ^{18} O and temperature for the GNIP station Vienna. In the summer months between May and September the temperature increases and the depletion in δ^{18} O decreases with higher temperature.

Panel (d) shows the variation in δ^{18} O over the years from 1968 to 2008 in the GNIP stations Meiringen, Guttannen and Grimsel in Switzerland. All three stations show a similar variation pattern and overall the δ^{18} O values are less depleted in 2018 than in the past. Panel (e) shows the variation in δ^{18} O and temperature over the years from 1970 to 2010 for the GNIP station Guttannen. The two curves show a similar trend. In 1996 the temperature increases rapidly within one year from 6°C to 9°C. Overall the temperature increases and the depletion in δ^{18} O decreases. Panel (f) shows the monthly variation in δ^{18} O and temperature for the GNIP station Guttannen. In the summer months between May and September the temperature increases and the depletion in δ^{18} O decreased. Overall the depletion in δ^{18} O decreases with higher temperature.

Panel (g) shows the variation in δ^{18} O over the years from 1960 to 2015 in the GNIP stations Ljubljana, Thonon-Les-Bains and Garmisch-Partenkirchen in Slovenia, France and Germany.

The stations are located all over the Alps and do not represent a certain region. All three stations show a similar variation pattern and overall the δ^{18} O values are less depleted in 2015 than in the past. Panel (h) shows the variation in δ^{18} O and temperature over the years from 1978 to 2013 for the GNIP station Garmisch-Partenkirchen. The two curves show a similar trend. Overall the temperature increases and the depletion in δ^{18} O decreases. Panel (i) shows the monthly variation in δ^{18} O and temperature for the GNIP station Garmisch-Partenkirchen. In the summer months between May and September the temperature increases and the depletion in δ^{18} O decreases. Overall the depletion in δ^{18} O decreases with higher temperature.



Figure 4: Yearly and monthly variations in δ^{18} O and temperature in precipitation from GNIP stations for Austria and the station Vienna (a-c), Switzerland and the station Guttannen(d-f) and Slovenia, France and Germany and the station Garmisch-Partenkirchen (e-i).

3.2 Stable isotopes in spring water

Figure 5 and Figure 6 show a map of the Alps with the available samples points for δ^2 H and δ^{18} O (dots) from springs and precipitation (diamonds). The sample points cover the Swiss, Austrian, French and most of the Italian part of the Alps, while for the German part there is no data available. The δ^2 H values ranges from -41 to -115 ‰. The central parts of the Alps with a,

on average, high elevation show a depletion in δ^2 H, while in the topographic lower outer parts of the Alps the depletion in δ^2 H is less. The δ^{18} O values ranges from -5 to -17 ‰. The δ^{18} O isotopes show mostly the same distribution as the δ^2 H values. In lower elevations there is a depletion in δ^{18} O, while in higher elevation the δ^{18} O depletion is less.



Figure 5: Map of the Alps with all the sample points that contain $\delta^2 H$ measurements. The distribution of the $\delta^2 H$ values shows the elevation effect. With increasing elevation, the depletion of $\delta^2 H$ is stronger.



Figure 6: Map of the Alps with all the spring water and precipitation sample points that contain $\delta^{18}O$ measurements. The distribution of the $\delta^{18}O$ values shows the elevation effect, i.e., with increasing elevation the depletion of $\delta^{18}O$ is stronger.

The δ^2 H and δ^{18} O relation in spring water and precipitation is given in Figure 7. Overall stable isotopes in spring water and precipitation from the GNIP stations plot on the GMWL. Single data points show small deviations from the GMWL. Neither spring or GNIP data show an origin from metamorphic or magmatic waters after Yardley (2009).

The Local Meteoric Water Lines for the countries Switzerland, Austria, France and Italy are shown in Figure 8. All four Local Meteoric Water Lines are close to the Global Meteoric Water Line. The LMWL for Austria shows the biggest deviation from the GMWL.



Figure 7: Relation between δ^2 H and δ^{18} O in spring water and in precipitation from the GNIP stations. The data points show the linear correlation between δ^2 H and δ^{18} O. The black dashed line is the GMWL. The blue dots are stable isotopes values from spring water and the brown diamonds are stable isotopes values from precipitation. The fields for the metamorphic and magmatic water sources are modified after Yardley (2009).



Figure 8: Local Meteoric Water Lines from stable isotopes in spring water for the countries Switzerland, Austria, France and Italy.

Figure 9 shows the delta δ^{18} O values plotted against the elevation of the springs. There is a weak correlation (R² = 0.25) between the elevation of the springs and δ^{18} O.



Figure 9: Relation between δ^{18} O in spring water and spring elevation. With increasing spring elevation, the depletion of δ^{18} O is stronger. The correlation with $R^2 = 0.25$ is weak.

The spatial distribution of the GNIP stations Buchs, Pontresina and Sion and the used springs for the calculation of the recharge area is shown in Figure 10. The GNIP stations Buchs and the springs 326 and 353 are located at the northern boundaries of the Alps in the border region Switzerland and Austria. Pontresina is located in southeastern part of Switzerland in the border region to Italy. North of the springs 326 and 353 are located in the central parts of the Alps with elevations up to 2500 m. The rest of the springs are located in the central parts of the Alps with overall higher elevation up to more than 4000 m.

The regression lines for the calculation of the recharge area are shown in equation (12) for the area Buchs and Pontresina.

$$z = -312.97 \cdot \delta^{18}0 - 2579.36 \tag{12}$$

where z is the elevation of the recharge area (m). One point needs to be the highest point in elevation for the regression line. All points need to be in the same region and get rain masses from the same source and side. In an optimal way all points would align along a profile. The calculated recharge elevation for all the springs between the two stations Buchs and Pontresina Figure 11. For the area Buchs and Pontresina the calculation of the elevation of the recharge

area works. The calculated elevation of the recharge area for the springs plots on the regression line between the two GNIP stations.



Figure 10: Spatial distribution of the GNIP stations Buchs, Pontresina and Sion and the used spring for the calculation of the recharge area.



Figure 11: Calculation of the elevation of the recharge area from δ^{18} O in precipitation from the GNIP stations Buchs and Pontresina.

3.3 Spring water chemistry

The main cations and anions concentration of all springs with SiO₂ data are plotted in a piper diagram (Figure 12). After Piper (1944) and Back and Hanshaw (1965) the different parts of the diagram can be assigned to a certain water type. In the diamond shaped diagram most of the springs plot in the area of calcium-magnesium-bicarbonate water type and sodium-chloridesulfate water type. In the cation triangle most of the springs plot in the area of the calcium water type and sodium-potassium water type. In the anion triangle most of the springs plot in the bicarbonate water type and chloride water type. There is no clear distribution for the different lithologies visible. Hem (1985) gives the lithological source of anions and cations in water. Calcium and bicarbonate are common in water and originate mainly from carbonates. Small parts of calcium can originate from pyroxene and amphibole in igneous and metamorphic rocks. Magnesium originates from olivine, pyroxene and amphiboles in igneous and metamorphic rocks and from dolomites, as a sedimentary source. Sodium comes from feldspars in igneous rocks and from sodium salt in evaporites. Potassium comes from feldspars in silicate rocks and from potassium salts in evaporites. Sulfur originates mainly from gypsum and anhydrites as a sedimentary source and in smaller parts from metallic sulfides in igneous and sedimentary rocks. Chloride comes mainly from evaporites and smaller parts from sodalite and apatite in igneous rocks.

Most of the springs in carbonate rocks show a calcium-magnesium-bicarbonate water type as expected. 62 out of 175 springs, however, show a sodium-chloride-sulfate water type, which indicates that they tap a deeper evaporitic layer. They are located in France, in Austria and in Italy (Figure 13).



Figure 12: Piper diagram with the hydrochemistry of spring water from springs in different lithologies.



Figure 13: Spatial distribution of springs with Na-Cl water type.

Panel (a) in Figure 14 shows a histogram of the number of springs plotted against the lithology. Most of the springs are located in carbonate rocks (62) and in metamorphic rocks (36). Less than the half of springs are located in mixed sediments (23), unconsolidated sediments (19), coarse grained sediments (13) and basic plutonic rocks (11). The fewest springs are located in acid plutonic rocks (3) and in basic volcanic rocks (2).

Panel (b) in Figure 14 shows the spring temperature plotted against the different lithologies. The hottest springs are located in unconsolidated sediments, carbonate rocks and in metamorphic rocks with temperatures above 60 °C. Colder temperatures occur in every lithology. The spring temperature varies between 6 °C and 70 °C. The average spring temperature in the Alps is 22 °C.



Figure 14: Histogram of the different lithologies (a) and the spring temperatures in the different lithologies (b).

Figure 15 shows the relation between lithology and spring water temperature. The number of springs in a certain temperature range is displayed in a histogram.

Panel (a) shows that 96 out of 172 springs have water temperatures between 5 °C and 20 °C. 57 springs have temperatures between 20 °C and 50 °C. Only 9 springs show temperatures between 50 °C and 65 °C.

Panel (b) shows a histogram of the number of springs plotted against the spring water temperature for carbonate rocks, metamorphic rocks and basic plutonics. The carbonate and the metamorphic rocks show the same trend. There are 32 springs in carbonate and 23 springs in metamorphic rocks with temperatures between 5 °C and 20 °C. 5 springs in metamorphic rocks show temperatures between 50 °C and 65 °C. The hottest springs (3) in carbonate rocks reach

water temperatures between 50 °C and 55 °C. The two springs in basic volcanics show water temperatures between 50 °C and 20 °C.

Panel (c) shows a histogram of the number of springs plotted against the spring water temperature for unconsolidated sediments, mixed sedimentary rocks and acid plutonics. There are 5 springs in unconsolidated sediments and 15 in mixed sedimentary rocks with temperatures between 5 °C and 20 °C. The hottest spring temperatures in unconsolidated sediments are between 30 °C and 35 °C in two springs. 12 out of 17 springs in unconsolidated sediments have temperatures between 20 °C and 40 °C. The hottest springs in unconsolidated sediments reaches temperatures up to 65 °C. The three springs in acid plutonics have temperatures between 40 °C and 50 °C.



Figure 15: Histogram of the distribution of number of springs and the spring water temperature. Panel (a) shows the number of all springs and the distribution of the temperature. Panel (b) shows the number of springs in carbonates, metamorphic rocks and basic volcanics and temperature distribution. Panel (c) shows the number of springs in unconsolidated sediments, mixed sedimentary rocks and acid plutonics and temperature distribution.

3.4 Tritium in precipitation and groundwater

The peak of tritium concentration in precipitation was reached in 1963 (Figure 16). The GNIP stations Vienna and Thonon-Les-Bains measured tritium concentrations around 3000 TU. From there on the tritium concentrations rapidly decreases to values under 300 TU in 1970 for all stations. Since 1990 the tritium concentrations for all stations are under 20 TU. Only the station in Bern measured tritium concentrations above 20 TU, due to anthropogenic source for tritium by a research reactor in Bern.

Figure 17 shows a map of the Alps with the available sample points for tritium. The tritium values ranges from 1 to 130 TU. Tritium values above 20 TU only occur in the western part of the Alps, except one exception in the eastern part. In total 25 of a total of 60 springs show tritium values that exceed the background value of 20 TU, which indicates that these springs discharge a component of young (post 1950s) groundwater.



Figure 16: Decrease of tritium in precipitation since 1960 in the GNIP stations, Thonon-Les-Bains, Garmisch-Partenkirchen, Bern and Vienna.



Figure 17: Map of the Alps with all the sample points that contain Tritium (TU) measurements. The western and northwestern parts of the Alps show higher Tritium concentrations, than the southern parts.

3.5 Silica geothermometers in springs

Figure 18 shows a map of the Alps with the available sample points for SiO_2 . The sample points cover the Swiss, Austrian, French and the Slovenian part, while for most of the Italian and German part of the Alps there is no available data. The central part of the Alps in the border area between Switzerland, Austria and Italy has a low data density. The values range from 3 mg/l to 78 mg/l. The highest SiO₂ concentrations are in the eastern part of the Alps compared to the western part of the Alps.



Figure 18: Map of the Alps with all the sample points that contain $SiO_2 (mg/l)$ measurements. The northwest and southeast part of the Alps show lower SiO_2 concentration in comparison to the rest of the Alps.

The theoretical relation between SiO_2 and maximum fluid temperature is shown in Figure 19. The calculated maximum temperature increases with higher SiO_2 concentrations. For SiO_2 concentrations under 3 mg/l the calculated temperature becomes negative. All equations show a similar pattern and the values are close to each other. The method after Verma-Santoyo 2 shows a bigger derivation and higher calculated maximum temperatures overall.



Figure 19: Theoretical relation between SiO_2 concentration and maximum temperature, following equation(3-9) after Verma et al. (2008).

In Figure 20 panel (a) the SiO₂ concentration is plotted against the temperature of the spring. The correlation ($R^2 = 0.2$) between SiO₂ concentration and spring temperature is weak. The hottest springs do not have the highest concentrations in SiO₂, but instead the highest concentrations in SiO₂ are from springs with temperatures between 10 °C and 20 °C. There are two different trends visible. Trend one is between 10 °C and 15 °C where the SiO₂ concentration increases with consistent temperature and the trend two is between 10 °C and 75 °C where the SiO₂ concentration shows a linear rise.

Panel (b) shows the relation between calculated maximum fluid temperature and spring temperature. The overall correlation ($R^2 = 0.19$) is weak. There are two trends visible. Trend one is for temperatures between 10 °C and 15 °C where the calculated maximum fluid temperature increases without an increasing spring temperature. Trend two is for temperatures between 10 °C and 75 °C where the calculated maximum temperature increases linear.



Figure 20: Relation between SiO₂ and the spring temperature (a). The overall correlation ($R^2 = 0.20$) is weak. Panel (b) shows the relation between calculated maximum fluid temperature and spring temperature (b). The overall correlation ($R^2 = 0.19$) is weak

Figure 21 shows a histogram with the calculated mean maximum temperature distribution springs. Panel (a) shows the distribution in all springs. 123 out of 175 springs have mean maximum fluid temperatures between 20 °C and 80 °C. 44 springs have temperatures between 80 °C and 130 °C. The average maximum fluid temperature for all springs is 61 °C.

Panel (b) shows a histogram of the number of springs plotted against the mean maximum fluid temperature for carbonate rocks, metamorphic rocks and basic plutonics. The mean maximum temperature in carbonates varies between 10 °C and 90 °C and shows a normal distribution. The mean maximum temperature in metamorphic rocks shows two distributions. One between 10 °C and 50 °C and the second one between 60 °C and 90 °C. The two springs in basic volcanics have mean maximum temperature between 100 °C and 120 °C. These are the highest mean maximum temperatures.

Panel (c) shows a histogram of the number of springs plotted against the mean maximum fluid temperature for unconsolidated sediments, mixed sedimentary rocks and acid plutonics. The mean maximum temperature in unconsolidated sediments shows two distributions. One between 20 °C and 50 °C and the second one between 60 °C and 100 °C. The mean maximum temperature in mixed sedimentary rocks ranges from 10 °C to 80 °C, with a maximum between 60 °C and 70 °C. The three springs in acid plutonics have mean maximum temperature between 90 °C and 110 °C:



Figure 21: Histogram of the distribution of temperature for spring water and the mean maximum temperature. The average calculated maximum fluid temperature is 61 °C.

The mean maximum temperature for each spring is displayed on a map of the Alps (Figure 22). The mean maximum temperature ranges from 11 °C up to 128 °C. In Austria most of the warmer springs are located in the eastern part of Austria. In the western part of the Alps the hottest springs are located in the southern branch.



Figure 22: Map of the Alps with the calculated maximum temperature in spring water for all springs with existing SiO_2 data. The value is an average from different equations.

The calculated circulation depth is displayed in Figure 23 with the mean maximum temperature. The correlation ($R^2 = 0.19$) is weak. The spring temperature shows two different trends. The first trend is for spring temperatures between 10 °C and 15 °C and the second for temperatures

between 10 °C and 70 °C. In the first case, circulation depth increases without an increase in fluid temperature. In the second case, the fluid temperature increases with circulation depth. In some springs the spring temperature is higher than the calculated maximum fluid temperature. The average circulation depth is 1692 m.



Figure 23: Relation between the calculated circulation depth and the spring temperature for all springs with SiO₂ data. There is a weak correlation ($R^2 = 0.19$).

Figure 24 shows the relation between heat loss and the different spring lithologies panel (a), the distribution of the heat loss in panel (b) and panel (c). Panel (a) shows a similar distribution between heat loss and the different lithologies. The highest heat loss with 11.7 W/m² occurs in metamorphic rocks. Panel (b) shows that 40 out of 61 springs have a heat loss between 0.003 W/m² and 0.4 W/m². 8 springs show a heat loss between 0.4 W/m² and 1 W/m². Panel (c) shows that 9 out of 61 springs have a heat loss between 1 W/m² and 2.5 W/m². 3 springs have a heat loss between 4 W/m² and 5 W/m². The average heat loss is 0.79 W/m².

The relation between heat loss and spring water temperature is shown in Figure 25 panel (a). The correlation ($R^2 = 0.001$) is weak.

Panel (b) shows the relation between heat loss and calculated circulation depth of spring water. The correlation ($R^2 = 0.03$) is weak



Figure 24: Relation between heat loss and lithology (a), histogram of the heat loss (a) and (c).



Figure 25: Relation between heat loss and spring water temperature (a). The correlation ($R^2 = 0.001$) is weak. Relation between heat loss and calculated circulation depth of spring water (b). The correlation ($R^2 = 0.03$) is weak.

4 Discussion

4.1 Fluid source

The cycle of spring water begins with meteoric water in precipitation. I found that δ^{18} O is strongly dependant on the atmospheric temperature. The long-time observed decreasing depletion in δ^{18} O in precipitation in the GNIP stations is mostly caused by an increasing temperature since 1960. Besides the temperature effect, the elevation effect plays a major role in the behaviour of stable isotopes. With increasing elevation, the depletion in δ^{18} O increases. Overall the GNIP stations recorded data that is in accordance with this statement, however, some stations show different trends. The deviant trends are caused by geographical and climatic differences. Mostly by different origin of the rain fall, either from the Atlantic Ocean or the Mediterranean Sea, and by rain shadow of mountains and valleys in the Alps.

Because of long residence time and slow response to changes the groundwater expresses the mean isotopic composition over a long timescale and a mixing from different sources. The isotopic composition of a shallow groundwater can be interpreted as the weighted mean annual composition of precipitation for the same region (Giustini et al. 2016). Even though I was not able to estimate the elevation of the recharge area for all springs in this study, I was able to show that stable isotopes in precipitation can be used as a tool to estimate the recharge elevation. It was difficult to find another station pair besides Buchs and Pontresina, because most of the stations are located at lower elevations. For the regression line it is necessary to have the stations as endmember. One station has the highest elevation and the other one the lowest elevation in the profile. Another problem was to find enough springs, which are located between the stations.

Spring lithology only refers to the top layer (GLIM) of the source rock. The water itself flows through several lithologies that influence the overall fluid composition. Since the spring lithology only corresponds to the surface rocks where the water is discharged it does not reveal any information about the geological subsurface and structure. The Alps can show a complex structural setting; especially in deep faults fluid pathways can pass through many lithologies.

There are several springs distributed all over the Alps that show a Na-Cl water type. The only thick evaporites in the Alps are in the Northern Calcareous Alps (Mandl 2000). The distribution of most of the springs is not consistent with the location of the evaporites. Only 6 springs in Austria are located in the area of the Northern Calcareous Alps. Natural springs near urban areas can be influenced by salt from road de-icing (Williams et al. 2000). But this is not a sufficient explanation for the occurrence of the Na-Cl water type in so many springs.

Even though tritium concentrations in precipitation are nowadays at the concentration of the natural background, I can still use it to estimate the groundwater age. Spring water with tritium concentrations higher than the natural background of 20 TU is influenced by the nuclear test from the 1950s and 1960s. It therefore must be young groundwater with ages less than ~70 years. The interpretation of spring water with tritium concentrations under 20 TU is more difficult. This can be old groundwater that reacts slowly to changes or it can be also fast-changing young groundwater, where the tritium concentration reflects the recent concentration. For this work, I simply assume that it must be old groundwater.

4.2 Fluid flow path

There is no SiO_2 data for Switzerland available. This complicates the comparison between the western and the eastern part of the Alps.

The application of the quartz geothermometer usually underestimates the maximum temperature of the fluid by 10 - 35 %, due to mixing between deep and shallow groundwater (Ferguson et al. 2009). Based on this underestimation, I assume that the actual circulation depth must be higher than the calculated circulation depth.

When looking at the relation between spring temperature and SiO₂ concentration, two trends are visible. The first trend is at low spring temperatures around 10 °C and the second trend above temperatures of 20 °C. The same trends are visible for the relation between spring temperature and calculated maximum fluid temperature and the relation between spring temperature and calculated maximum circulation depth. On one hand, the two trends can be explained by different ascent rates of fluid from the subsurface (Dzikowski et al. 2016). The first trend has a low ascent rate and the fluid loses more heat. The second trend is faster and the fluid retains more heat. Different ascent rates can be caused by the variation of permeability in faults. But I have no options to verify this explanation in this thesis. On the other hand, the two trends may be due to a reproductive artefact, because the calculation of maximum fluid temperature and circulation depth are based on the SiO₂ concentration and there are no two different distributions.

5 Conclusion

I used a new data set of thermal springs in the Alps (Luijendijk et al.) to study the spatial distribution of δ^2 H, δ^{18} O, tritium and SiO₂ and to quantify fluid sources and pathways.

In this study I found that most of the springs in the Alps are located in carbonates (62) and in metamorphic rocks (36). The highest temperatures occur in springs that are located in unconsolidated rocks, metamorphic rocks and in carbonates, while springs with lower temperatures occur in every lithology.

The stables isotopes in precipitation show different regional trends, caused by the geographical location and different origin of the rain masses. The parameters that control the δ^{18} O values in precipitation are mainly temperature, elevation and amount of precipitation.

The correlation between δ^2 H and δ^{18} O in precipitation and in spring water plots on the Global Meteoric Water Line. This indicates that the origin of the spring water in all analysed springs is meteoric water. There is no obvious influence from a magmatic or metamorphic water source.

The correlation between spring elevation and δ^{18} O in spring water shows a weak correlation, caused by a δ^{18} O signal, which is related to a higher recharge elevation. The higher elevation of the recharge area of springs can be calculated from stable isotopes in precipitation, if they belong to the same geographical and climatic setting.

Most of the spring water in the Alps is old groundwater. However, there are 25 out of 60 springs, which show tritium values above 20 TU. These springs discharge young groundwater with ages less than ~70 years. Springs with young groundwater are limited to the western part of the Alps.

The heating of the fluid can be explained by a normal geothermal gradient and does not require a heat anomaly.

There are 113 out of 175 springs that show an expected water type that coincides with the hydrochemistry of the surrounding rocks. However, there are 62 springs that show a Na-Cl water type, which could not be explained for all the springs.

6 References

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7 Appendix

Appendix 1: Overview of the GNIP stations in Switzerland, Slovenia, Austria, France and Germany and the respective parameters that were measured at each station. The averages are yearly averages.

Number	r Site	Country	Latitude	Longitude	Elevation	Period	δ ¹⁸ O (‰) Error	$\delta^2 H$	Error	d-excess (‰)	Error A	ir Temperatu	re Error P	recipitation (m	m) Error
					(m)		Avg	,	(‰)		Avg	(°	C) Avg	A	vg	
1	Basel	СН	47.54	7.58	316	2004-2016	-9.21	±0.93	-66.3	±7.2	7.3	± 0.8	11	±0.7	844.3	±141.3
2	Belp	CH	46.89	7.49	520	2011-2016	-9.95	n.a	-72.1	n.a	7.51	n.a	n.a	n.a	n.a	n.a
3	Bern	CH	46.95	7.44	511	1996-2012	-9.7	± 0.91	-69.7	±5.3	9.5	± 1.4	9.1	±0.9	1058.9	230.3
4	Buchs	СН	47.37	8.08	397	1994-2016	-9.51	n.a	-68.8	n.a	7.28	n.a	n.a	n.a	n.a	n.a
5	Grimsel	CH	46.57	8.33	1950	1970-2008	-13.61	± 0.68	-94.9	±5.7	12.5	± 1.0	1.7	±0.7	2053	± 352.6
6	Guttannen	CH	46.66	8.29	1055	1970-2008	-12.46	± 0.85	-85.3	± 2.4	10.2	± 1.1	7.2	± 1.4	1698.6	± 246.8
7	La Brevine	CH	46.98	6.61	1042	1994-2016	-9.72	n.a	-67.87	n.a	9.94	n.a	n.a	n.a	n.a	n.a
8	Locarno	CH	46.17	8.79	379	1966-2008	-8.68	± 1.06	-60.4	± 8.5	9.1	± 1.4	12.1	±0.6	1846.6	± 398.3
9	Meiringen	CH	46.73	8.19	632	1970-2008	-11.39	± 1.07	-79.3	±6.5	8.7	±1.3	8.4	±0.7	1372.6	±212.6
10	Nyon	CH	46.40	6.23	436	1992-2016	-8.48	n.a	-61.05	n.a	6.82	n.a	n.a	n.a	n.a	n.a
11	Pontresina	CH	46.49	9.90	1724	1994-2016	-13.75	n.a	-102.1	n.a	7.97	n.a	n.a	n.a	n.a	n.a
12	Sevelen	CH	47.12	9.49	450	2012-2016	-11.37	n.a	-84.24	n.a	6.77	n.a	n.a	n.a	n.a	n.a
13	Sion	CH	46.22	7.34	482	2009-2016	-10.21	± 1.30	-76.8	±10.2	5.2	±1.5	11	±0.6	534.9	±49.7
14	St. Gallen	CH	47.43	9.40	779	2004-2016	-11.19	n.a	-79.36	n.a	10.2	n.a	n.a	n.a	n.a	n.a
15	Ljubljana	SI	46.10	14.60	282	1981-2010	-8.7	± 0.75	-60.3	± 5.6	9.4	± 1.7	10.6	± 0.8	1345	± 149.7
16	Graz	AT	47.08	15.45	366	1973-2002	-9.91	± 0.67	-70.5	± 5.3	8.7	± 1.1	n.a	n.a	813.3	±114.3
17	Klagenfurt	AT	46.65	14.32	450	1973-2002	-10.57	± 0.81	-75.6	±5.6	9.7	± 1.0	n.a	n.a	890.9	±111.9
18	Petzenkirche	AT	48.15	15.15	252	1965-1978	-9.73	± 0.88	-72.8	±6.4	8.8	± 2.5	8.7	± 0.4	725.8	±118.9
19	Podersdorf	AT	47.85	16.84	121	1965-1968	-9.41	n.a	-68.57	n.a	5.17	n.a	n.a	n.a	550	n.a
20	Vienna	AT	48.25	16.36	198	1960-2018	-9.69	± 0.94	-70.2	±6.7	6.8	± 2.2	10.4	± 0.8	639.8	± 108.7
21	Villacher Alpe	AT	46.60	13.67	2156	1970-2002	-11.16	±0.93	-77.9	±7.3	11.4	±1.1	n.a	n.a	1282.7	±211.7
22	Garmisch-	DE	17 18	11.06	710	1078 2016	11.2	+0.82	82.2	+7.0	74	+1.6	7.2	+0.8	1264 7	+160.4
22	Partenkirchen	DE	47.40	11.00	/19	1976-2010	-11.2	±0.62	-02.3	±7.0	7.4	± 1.0	1.2	±0.8	1304.7	±100.4
23	Carpentras	FR	44.95	5.78	99	1997-1998	-5.3	n.a	-36.8	n.a	5.6	n.a	n.a	n.a	434	n.a
24	Draix	FR	44.13	6.33	851	2004-2013	-8.05	± 1.21	-54.1	± 9.2	8	± 1.0	10	±0.6	815.7	±116.9
25	Thonon-Les- Bains	FR	46.37	6.47	385	1963-2012	-9.37	±0.81	-63.5	±5.3	7.5	±1.3	10.7	±0.7	994.6	±158.4



Appendix 2: Relation between the elevation of the GNIP stations and the amount of precipitation. With increasing elevation, the amount of precipitation increases. The dark blue line shows a good correlation ($R^2 = 0.89$) for Switzerland. The light blue line shows a weak correlation ($R^2 = 0.31$) for France and the red line shows a good correlation ($R^2 = 0.98$) for Austria.

Eigenständigkeitserklärung

Hiermit versichere ich, dass ich die vorliegende Arbeit selbstständig verfasst habe. Es wurden keine Quellen außer den ausdrücklich genannten verwendet. Alle Teile meiner Arbeit, die wortwörtlich oder dem Sinn nach anderen Werken entnommen sind, wurden unter Angabe der Quelle kenntlich gemacht. Die Richtlinien zur Sicherung der guten wissenschaftlichen Praxis an der Universität Göttingen wurden von mir beachtet.

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