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Hydrochemical characterisation of a major central European heat flux anomaly: the Bürchau geothermal spring system, Southern Black Forest, Germany

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Abstract

Background: The possible signature of deep fluids originating from processes occurring during infiltration or circulation in a remote valley in the Black Forest (Germany), a typical infiltration area in the crystalline basement which represents a possible recharge zone of one of the major heat flux density anomalies in central Europe, has been hydrochemically characterised. Chemical and isotopic compositions of two warm springs and several cold springs in Bürchau as well as water from the Badenweiler Spa were sampled three times during June and October 2013.

Methods: A number of 70 water samples were taken at natural outlet conditions and analysed for major and trace elements, water H/O-isotope ratios and sulphur isotope ratios of dissolved sulfate. A chlorofluorocarbon (CFC) analysis was conducted to determine the underground residence time of the thermal water. To assess water-rock interactions seven rock samples representing the occurring lithological units of the study area were prepared to thin sections for polarization microscopic analysis.

Results: The main spring in Bürchau discharging water with a temperature up to $T = 18.1^\circ\text{C}$ at flow rates of approximately 0.2 L s^{-1} is Na-Ca- HCO_3 -dominated and generally low mineralised (total dissolved solids (TDS) of about 150 mg L^{-1}). Even lower mineralisation and temperature of a nearby spring indicates further dilution with shallow groundwater. With respect to cold springs in the vicinity, the thermal water in Bürchau is slightly enriched in Cl, B, Li, Rb and Cs. In nearby granites, sericitisation of plagioclase and oxidation of pyrite to goethite have been identified. The stable isotope composition of H and O suggests meteoric origin of the water. Chlorofluorocarbon (CFC) analyses indicate that 30% to 40% of the thermal water in Bürchau is younger than 60 to 70 years. Reservoir temperatures have been estimated to 40°C to 80°C using sulphate and quartz geothermometers.

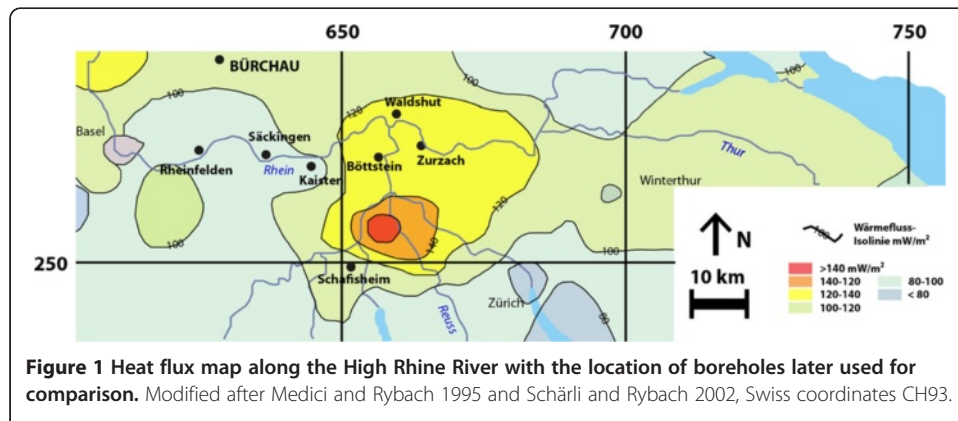
Conclusions: Thus, the circulation time of the other 60% to 70% of the thermal water is longer than 70 years. Estimated reservoir temperatures in a range of 40°C to 80°C correspond to an infiltration depth of about 1,600 to 1,800 m.

Background

Very low-temperature and natural subsurface flow systems have been observed worldwide, especially in mountain ranges such as the Alps, the Himalayas and the Black Forest (e.g. Sonney 2010, Bucher et al. 2009). These systems are often characterised by water of meteoric origin that percolates in the uppermost crust along permeable structures (Baietto et al. 2005). It can reach elevated temperatures and considerable total dissolved solids (TDS) through water-rock interaction (e.g. Evans et al. 2005). Subsurface circulation in such settings is mainly driven by pressure differences due to the topography (Tóth 1978). Ascent paths are generally controlled by faults and fracture zones, i.e. by zones of enhanced permeability (Guglielmetti et al. 2013, Giersch 2006).

Central Europe hosts a number of important heat flux anomalies that are linked to upwelling fluids of enhanced temperature in a specific geological and tectonic setting. Major anomalies are located in the central Upper Rhine Graben to the east of the Black Forest (e.g. Baillieux et al. 2013) and to the south of the Black Forest at the High Rhine (Medici and Rybach 1995; Figure 1). They are thoroughly investigated and reach a heat flux density up to 150 mW m^{-2} . Differences in ^3H - and ^{14}C -contents for the Ca-Na-HCO₃-type water in the springs at Bürchau and Rothaus compared to the Na-SO₄-HCO₃-Cl-type in Northern Switzerland led to the interpretation that fluids in the crystalline basement of Northern Switzerland were recharged in the Black Forest (Pearson et al. 1991).

The basement rock in this area can be characterised by a heat flow pattern between the elevated temperatures at the Rhine Graben and the anomaly in Northern Switzerland (Kohl et al. 2003). Since there are no data from deep wells near Bürchau, the temperature field is only accessible through indirect observations such as hydrochemistry. The warm spring at Bürchau was first documented with a flow rate of 0.2 L s^{-1} and a TDS of 100 mg L^{-1} in the early 1920s (Badisches Geologisches Landesamt 1930). Extensive hydrochemical and isotopic investigations were carried out at this source by Schmassmann et al. (1984) to examine its regional relation to water from deep wells in Northern Switzerland. They concluded that the Bürchau water is probably a mixture of older crystalline water with recent water. Isotopic investigation indicated a rather local catchment area (Pearson et al. 1991). The residence time of the water is estimated to be over 25 to 30 years. However, the likely mixing leads to high uncertainty of the flow model.

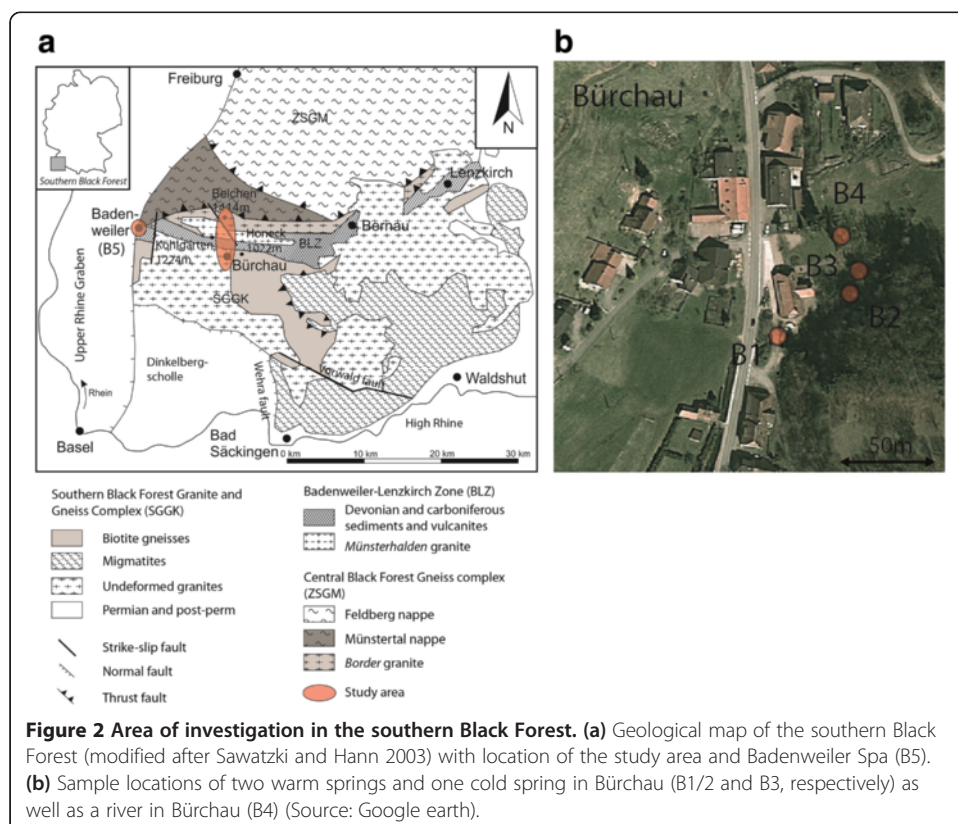


In this respect, this study aims on characterising hydrothermal processes occurring in the infiltration zone of this large scale heat flux density anomaly.

Study area

The study area includes a large part of the *Kleines Wiesental*, a high-situated valley in the Southern Black Forest, SW-Germany. The Black Forest represents an erosional window into the Variscan crystalline basement that consists in its central part predominantly of ortho- and paragneisses (Geyer and Gwinner 2011). The boundary between the Central Black Forest Gneiss Complex to the north and the Southern Black Forest Granite and Gneiss Complex to the south is located about 2 km north of Bürchau (Figure 2). Both complexes are considered to be part of the Moldanubian zone of the Central-European Variscan orogen. They are separated by the Badenweiler-Lenzkirch Zone, presumably a suture zone, consisting of Ordovician to lower Carboniferous sediments and volcanic rocks as well as successions of metamorphosed volcano sediments (Sawatzki and Hann 2003). South of the Badenweiler-Lenzkirch Zone, gneisses are characterised by extensive intrusions of granitoids (Kalt et al. 2000, Figure 2).

The warm springs are located at Bürchau (628 m above sea level (a.s.l.)), about 25 km south of Freiburg i.Br. (Figure 2). The topography of this region is dominated by Mt. *Belchen* (1,414 m) north of Bürchau, Mt. *Honeck* (1,022 m) in the east and Mt. *Köhlgarten* (1,224 m) in the northwest. There are two discharges of warm water in Bürchau. The main discharge B1 is located within the river and reveals a temperature of 15°C to 18°C. Its flow rate has dropped after construction work to about 0.16 L s⁻¹. A second discharge B2 with a

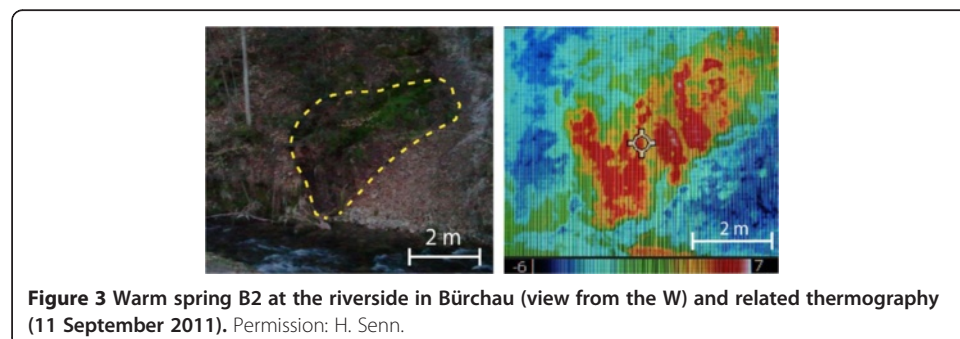


temperature around 9.5°C occurs at the rim of the riverbed 50 m northeast of B1 (Figure 2b). The thermal image of the slope at B2 (Figure 3) reveals a surface temperature of up to 7°C in contrast to the ambient temperature of -6°C in October 2011, when the picture was taken (Figure 3). In Badenweiler, west of Büschau, another thermal spring (B5) was investigated for comparison. Its water is of meteoric origin (Berg and Genser 1961) and reveals a lower mineralisation in contrast to other thermal waters in similar tectonic settings close to the eastern boundary fault of the Upper Rhine Graben in Baden-Baden or Ohlsbach (Stober and Bucher 2000). The host rock of the springs is the Southern Black Forest Granite and Gneiss Complex occurring at the lithological contact between the biotite gneisses to the east and the un-deformed granites to the west (Figure 2a).

Regional fault systems reveal mainly Hercynian and Rhenian strike directions with the ESE-WNW striking Vorwald fault and the N-S striking normal fault system of Wehr, respectively (Figure 2). All geological units are cut by granite porphyry dykes with late Viséan intrusion ages (Schaltegger 2000). The orientation of a number of these dikes is in agreement with the ESE-WNW striking fault zones. The Vorwald fault, approximately 20-km long, is assumed to be a pathway for hydrothermal circulation from the area of investigation to the area of high heat flux density in Northern Switzerland (Medici and Rybach 1995, Figure 1). The origin of the fault is assumed to be pre-Variscian (Wirth 1984). The likely hydrothermal circulation along the fault zone may be indicated by the present stress field. Recent displacement is observed at the Kandern fault, a prolongation of the Vorwald fault, e.g. by the Schopfheim earthquake on 5 May 2009 with a magnitude of $M_L = 4.5$ with an epicentre located about 5 km to the SW of Büschau (Bundesanstalt für Geowissenschaften und Rohstoffe BGR 2009). A regional strike-slip stress regime that was determined for the study area using inversion of focal mechanism (Kastrup et al. 2004) is consistent with the recent Schopfheim earthquake. The maximum horizontal stress (SH_{max}) is oriented sub-horizontally in approximately NW-SE direction, while the minimum horizontal stress (Sh_{min}) is orientated approximately NE-SW (Müller et al. 2003). Towards Northern Switzerland in the area of high heat flux density, the orientation of the stress field in the granitic basement is consistent with the one observed around Büschau; the type of stress, however, changes into strike-slip/normal faulting regime (Kastrup et al. 2004).

Methods

For chemical characterisation of the circulation system in Büschau, water samples were taken at natural outlet conditions. In total, seven rock samples were cut and prepared



to 30- μm -thin sections for polarisation microscopic analysis. The fresh rock samples representing the occurring lithological units of the Southern Black Forest Granite and Gneiss Complex and the Badenweiler-Lenzkirch zone were taken in a radius of <5 km from the spring B1. One additional sample was taken from the slightly altered rock sample of the Mambach granite in the fracture at B1 (Figure 4) where discharge occurs.

A number of 70 water samples were taken during three field campaigns in 2013 at two warm springs (B1/2), a cold spring (B3) and the river water (B4) at Bürchau, as well as at the thermal spring near Badenweiler (B5). A seasonal monitoring of the springs was not conducted, since steady chemical composition of the fluid is indicated over decades by comparison with earlier measurements (Carlé 1975; Schmassmann et al. 1984). In order to investigate a possible effect of near surface inflow, the concentrations of major and trace elements, water H/O-isotope ratios and sulphur isotope ratios of dissolved sulphate, were determined for samples of the first two campaigns. In this respect campaign I was conducted after a period of 3 days of heavy rainfall with a total precipitation of >100 L m⁻². Campaign II was carried out after a period of 10 days without precipitation. Although temperature appears different between the JUN13 and JUL13 sampling, no significant difference in the chemical composition of the spring waters between campaigns I and II for B1 has been observed (Table 1). Campaign III for chlorofluorocarbon (CFC) analyses was conducted at B1 after a period of low precipitation (<50 L m⁻² over 10 days). This observation is underlined by comparison with earlier measurements (Schmassmann et al. 1984; Carlé 1975) showing that the water chemistry is distributed homogenous (especially for trace elements) over decades.

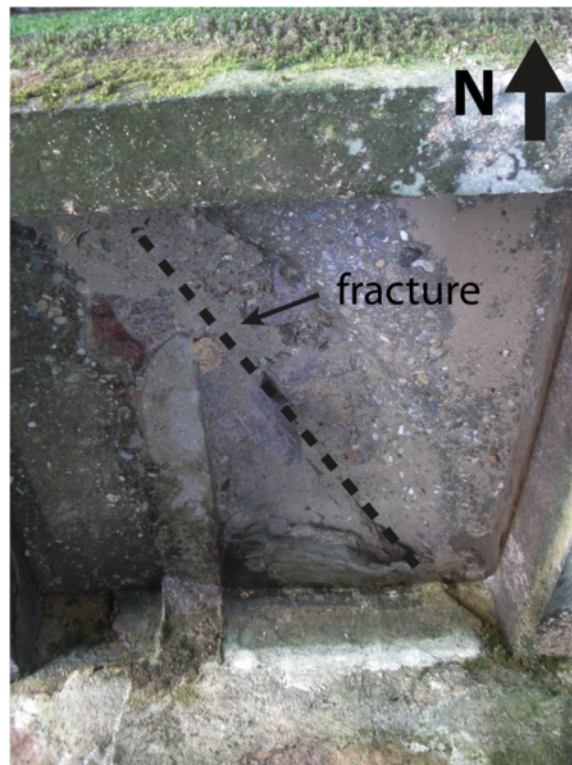


Figure 4 Warm water, tapped spring B1 in Bürchau. The strike of the fracture along which water is ascending is highlighted by the dashed line.

Table 1 Chemical composition and stable isotope contents of waters in the study area (Bürchau, B1-4, Badenweiler, B5): results for the two sampling campaigns in June and July 2013 and earlier studies

Spring	B1		B2		B3		B4		B5		B1 Schmassmann et al. (1984)	B1 Carlé (1975)
	JUN13	JUL13	JUN13	JUL13	JUN13	JUL13	JUN13	JUL13	JUN13	JUL13	1981 to 1983	1958
Temperature [°C]	15.1	18.1	9.3	9.7	-	-	8.3	-	18.7	20.4	16.8	-
Conductivity [$\mu\text{S cm}^{-1}$]	152	149	49	61	49	46	46	55	429	420	-	-
O ₂ concentration [%]	62	66	92,8	77	105	97	98	90	72	71	-	-
Redox potential [mV]	221	245	294	270	-	290	242	237	227	252	-	-
pH	7.45	7.5	6.7	6.8	7.2	6.3	7.4	7.2	7.6	7.7	8.06	6.8
$\delta^{18}\text{O}$ [‰]	-9.77	-10.25	-9.82	-10.1	-	-10.6	-	-10.12	-9.58	-10.1	-9.86	-
$\delta^2\text{H}$ [‰]	-68.1	-68.7	-68.9	-68.4	-	-70.9	-	-68.0	-67.4	-69.2	-69.5	-
$\delta^{34}\text{S}$ [‰] (from BaSO ₄ precipitation)	5.11	5.00	-	4.12	-	-	-	-	12.88	12.95	-	-
$\delta^{18}\text{O}$ [‰] (from BaSO ₄ precipitation)	3.72	3.61	-	3.17	-	-	-	-	6.04	5.88	-	-
Amount [mg L ⁻¹]												
Na	15.0	15.4	2.88	2.88	-	2.14	-	3.66	31.4	33.3	14.9	11.7
K	1.21	1.21	0.55	0.54	-	0.33	-	0.6	3.1	3.27	1.21	-
Ca	14.6	15.3	4.55	6.88	-	5.37	-	5.72	46.9	54.8	33.3	12.6
Mg	1.21	1.3	0.85	1.33	-	1.11	-	0.84	6.58	7.16	2.80	3.7
Li	0.0405	0.0419	0.0009	0.0011	-	0.0006	-	0.0007	0.134	0.138	0.048	-
Sr	0.155	0.181	0.028	0.042	-	0.042	-	0.03	0.455	0.487	0.298	-
Cl	1.85	1.79	3.3	3.59	-	1.48	-	3.73	8.58	8.93	1.91	4.5
HCO ₃	85.4	79.3	18.3	24.4	-	42.7	-	42.7	159	165	71.0	67.1
SO ₄	12.0	12.1	2.89	3.32	-	2.36	-	2.99	67.9	67.8	23.8	12.3
F	1.85	1.9	0.13	0.23	-	0.2	-	0.12	0.82	0.8	1.86	-
SiO ₂	-	22.3	-	4.1	-	4.4	-	5.3	-	19.6	23.8	7.5

Table 1 Chemical composition and stable isotope contents of waters in the study area (Bürchau, B1-4, Badenweiler, B5): results for the two sampling campaigns in June and July 2013 and earlier studies (Continued)

Amount [$\mu\text{g L}^{-1}$]												
B	14.2	13.6	2.73	2.68	-	2.61	-	2.74	162.9	164	-	-
Fe	1.32	2.32	2.51	1.59	-	1.78	-	10.7	2.03	2.39	-	-
Cu	0.17	0.27	0.15	0.14	-	0.17	-	0.37	3.09	3.58	-	-
Zn	1.03	1.9	1.59	2.37	-	1.88	-	1.85	98.6	96.4	-	-
As	62.3	64.2	4.97	5.2	-	1.91	-	4.8	101.5	104	-	-
Rb	6.67	8.12	2.29	2.67	-	1.74	-	2.29	15.6	17.1	-	-
Mo	1.66	1.65	0.05	0.1	-	0.05	-	0.08	1.34	1.33	-	-
Cs	2.65	3.92	0.7	0.82	-	0.54	-	0.38	14.29	15.1	-	-
U	6.51	7.1	0.09	0.14	-	0.03	-	0.12	5.59	5.79	-	-
Ba	156	187	254	333	-	199	-	75.6	56.7	59.5	-	-
TDS [mg L^{-1}]	135	153	35.6	49.8	-	61.7	-	67.8	328	365	-	-

During the field campaigns, physico-chemical parameters of the springs, including temperature, pH, oxygen concentration, redox potential and electrical conductivity, were measured *in situ* using a WTW Multiline P4 (WTW Wissenschaftlich-Technische Werkstätten GmbH, 82362 Weilheim, Germany). Additionally, the alkalinity was determined by titration with an alkalinity field set (Aquamerck, Merck KGaA, 64293 Darmstadt, Germany) immediately after sampling.

Water samples were collected in new 60-, 100- and 1,000-mL polyethylene (PE) bottles. Before collecting water samples, all materials were well flushed with the water that was to be sampled later. Samples for the anion and cation analytics were filtered with a 0.45- μm membrane filter. To prevent the formation of metal hydroxide complexes, samples for the major and trace elements were acidified with sub-boiled nitric acid (HNO_3) to $\text{pH} < 2$ immediately after sampling. Samples for anion analytics (SO_4 , F, Cl) were darkened with aluminium foil and frozen until the day of analysis. Water samples for CFC measurements were collected from the outflow B1 in 1-L faceted glass bottles locked in water-filled gas-tight brass tubes. The empty glass bottle is plunged completely in a metallic tin. The water is filled in the glass bottle using a rubber tube positioned at its bottom. The sampling is carried out in a 10-L plastic bucket. After complete overflow of the bottle and the tin and continuous flushing for at least several minutes to remove atmospheric air from the sample bottle, the tube was pulled out and the bottle was closed under water in the tin. The tin was closed with a sealing rubber ring to avoid exchange with air.

Different analytical methods like the atomic absorption spectroscopy (ASS), the atomic emission spectroscopy (AES), the ion chromatography (IC) and the inductive-coupled-plasma mass spectroscopy (ICP-MS) had been successfully applied for analysing geothermal waters (Arnórsson et al. 2006, Armannsson and Olafsson 2007). The analyses of the acidified samples for major (Na, K, Ca, Mg) and trace elements (Li, B, Fe, Cu, Zn, As, Rb, Sr, Mo, Cs, U, Ba) with ICP-MS at the Institute of Mineralogy and Geochemistry IMG at KIT showed a high reproducibility. Certified reference material HPS VF 5 from *High Purity Standards* was used. The detection limit for major elements is $<0.01 \text{ mg L}^{-1}$ and $<0.013 \mu\text{L}^{-1}$ for trace elements except B and Fe with a detection limit of $0.56 \mu\text{L}^{-1}$ and $1.41 \mu\text{L}^{-1}$, respectively.

Samples for anion analytics (SO_4 , F, Cl) were analysed with ion chromatography at the IMG laboratory at the KIT. The coefficient of determination at the calibration for the standard solution was 99.9972% in average.

The dissolved silica content was measured by ultraviolet-visible (UV/VIS) photometer (Lambda 2, PerkinElmer, Waltham, MA, USA) and the molybdenum blue method. The basis of this method is the formation of a silica-molybdenum blue complex in the presence of ascorbic acid. The intensity of the blue coloration after adding specific solutions depends on the amount of dissolved silica. The absorption of light determined with a UV/VIS photometer can be used to quantify the amount of dissolved silica.

Water samples for H/O-isotope measurements were collected in 100-mL PE bottles. The bottles were closed under water to prevent contamination by air. The hydrogen and oxygen isotope ratios were determined with the Liquid Water Isotope Analyser (LWIA, Los Gatos Research Inc., Mountain View, CA, USA). As a calibration standard, LGR5A, LGR6A and LGR7A were used. The mean standard deviation for $\delta^2\text{H}$ is 0.35‰ and for $\delta^{18}\text{O}$ 0.09‰.

Sulphur and oxygen isotope composition of dissolved sulphate was measured with an isotope-ratio mass spectrometer (IRMS) at the IMG laboratory of the KIT. Therefore, dissolved sulphate was precipitated from water samples by adding barium chloride. The precipitated barium sulphate was dried and analysed with an IRMS. The mean standard deviations are 0.03‰ and 0.14‰ for $\delta^{34}\text{S}$ and for $\delta^{18}\text{O}$, respectively.

The concentration of different CFCs in groundwater, emitted during different periods since the 1930s into the air, provides a useful tracer to indicate underground residence times due to high chemical stability under aerobic conditions (Rowland and Molina 1975). Generally, low CFC concentrations in groundwater suggest a relatively long residence time of >60 to 70 years indicating a deep circulation system in the study area. During groundwater recharge, the CFCs are incorporated in the groundwater based on the specific gas solubility. Due to CFC input curves, the proportion of young water and ideally also the mean residence time can be distinguished (Plummer and Busenberg 1999).

CFC samples were analysed at the *Spurenstofflabor* Dr. Harald Oster (Wachenheim, Germany). The water samples were analysed for trichlorofluoromethane (CFC-11), CFC-12 and trichlorotrifluoroethane (CFC-113) using purge and trap gas chromatography with an electron capture detector. The measurements generally are performed by direct injection of about 20 mL of water to the stripping chamber. A transfer gas is used to extract the CFCs from the water sample. The reconstruction of the age of the water is based on the historic data of atmospheric CFC concentrations. The concentrations in the sample are determined by atmospheric CFC concentrations and Henry's law describing the proportionality of gas dissolution to its partial pressure. An altitude of 1,100 m a.s.l. with an annual mean temperature of 6°C was assumed according to the weather history at the study area. Furthermore, the salinity of the water samples was taken into account for the descriptions of distinct input functions for the area of recharge. These distinct input functions are integrated in a lumped parameter program using the exponential model after Malloszewski and Zuber (1992).

Resampling the Bürchau springs allows for comparing the results with former investigations and for enlarging the existing dataset. We collected water samples to measure CFC to tackle the above mentioned uncertainty due to mixing processes in a quantitative way.

With respect to the possible temperature distribution at depth, we compared different silica-geothermometers with SO_4^{2-} - H_2O geothermometers, obtained from S-isotopy.

Data from Schmassmann et al. (1984) and Carlé (1975) were included in the interpretation to determine possible changes in the hydrochemical characteristics.

Results and discussion

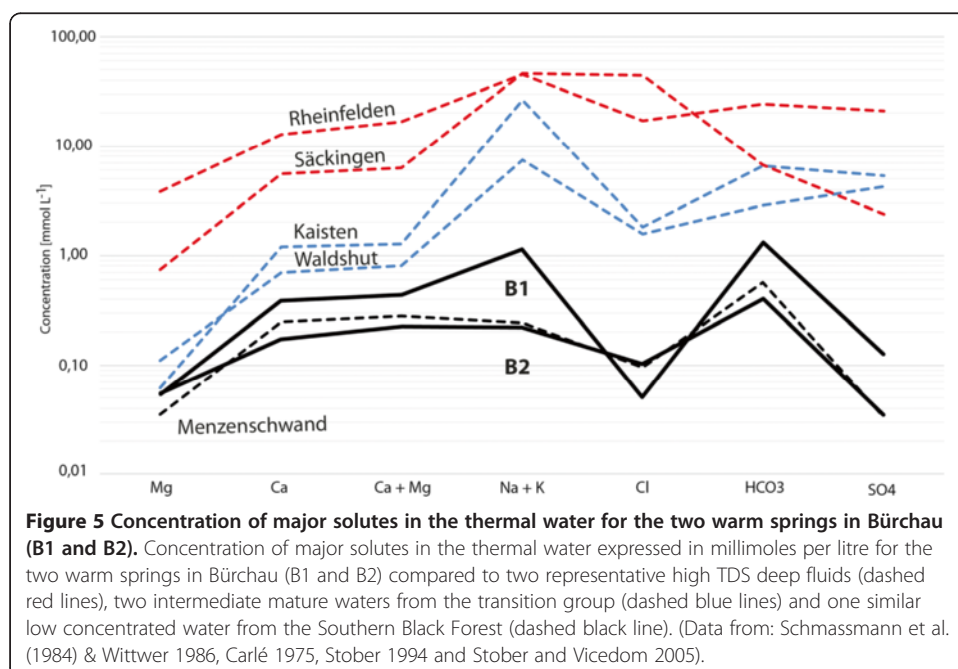
The analysis of the tectonic structures reveals that three to four tectonic features of different type or orientation join directly at Bürchau or a few kilometres in the north. In the direct vicinity of the spring, a number of different arms of dikes of a late-Variscian, porphyric granite join in a kind of triple junction. The major arm is oriented N-S following the valley of Kleines Wiesental and is transforming towards the north of Bürchau in a fault zone cutting through the Badenweiler-Lenzkirch zone.

The two minor arms of the intrusion are orientated NE-SW and NW-SE. The orientation of the outflow fracture of B1 at Bürchau coincides with the latter direction (Figure 4).

Hydro-geochemical characteristics

In the following, we will discuss the results listed in Table 1. The discussion is focused on the Bürchau (B1) and Badenweiler (B5) waters since they reveal the highest total mineralisation in the area. We observe temperature differences of 1.7°C to 3.0°C between the JUN13 and JUL13 campaigns for B5 and B1, respectively. The specific electric conductivity is rather stable with 152 and 429 $\mu\text{S cm}^{-1}$ in JUN13 and 149 and 420 $\mu\text{S cm}^{-1}$ in JUL13 for B1 and B5, respectively. Redox potential is observed to increase slightly from JUN13 to JUL13 from 221 (B1) and 227 mV (B5) to 245 (B1) and 252 mV (B5), while the pH increases from pH = 7.45 (B1) and 7.6 (B5) to 7.5 (B1) and 7.7 (B5). The chemical composition of the B1 water of (Figure 5) is dominated by Ca, Na and HCO_3 . Its mineralisation with TDS = 153 mg L^{-1} differs from the other samples B2 to B4 with TDS between 50 and 68 mg L^{-1} , respectively, and B5 with TDS of 365 mg L^{-1} . It should be mentioned that the thermal water of B1 is enriched in Li, Cl, F, B, Rb and Cs with respect to B2 and B4 (see Table 1). The enrichment of trace elements like fluorine is often documented for water from fractured granite in the Black Forest (Göb et al. 2013, Hofmann 1989). Changes in the concentration of some elements of the different sources and in particular temperature changes in B1 and B5 may indicate a possible increased influx of shallow subsurface water after rainfall in the JUN13 campaign. Most of the variation is however within the uncertainty of the measurements.

Since a link between the Bürchau waters and the High Rhine region in terms of infiltration and discharge has been postulated by Schmassmann et al. (1984) and reactivated Variscian fault zones are suspected to provide sufficient permeability for fluid transport (Schill et al.

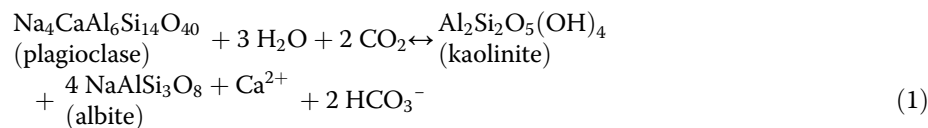


2011), we have compiled the major solutes of the waters in Figure 5. It results that the thermal water in the study area is Na-Ca-HCO₃-dominated revealing chemical characteristics that are similar to representative crystalline basement groundwater from the Black Forest, but of lower mineralisation and a significant influence of surface water.

The relationship between δ¹⁸O and δ²H is shown in Figure 6. Since the isotope ratio follows the global meteoric water line, there is no isotopic shift due to boiling processes. The values show a difference between sampling campaign I to II. The δ¹⁸O values in campaign II are more negative. Most likely, this can be attributed to the heavy rainfall before sampling of campaign II. This resulted in a backshift to lighter δ¹⁸O values in campaign I due to significant infiltration of surface water in the direct vicinity of the source. In campaign II, water originates mainly from higher recharge areas. The decrease of δ¹⁸O and δ²H values between the Mt. Belchen and B1 to B3 and B5 can be attributed to altitude effects since there is a difference in altitude of several hundred metres between Bürchau and Mt. Belchen as well as Badenweiler and Mt. Belchen. A minimum value for the altitude of infiltration of about 870 m a.s.l. with an annual mean temperature of 6°C has been inferred using the δ¹⁸O to altitude ratio of Pearson et al. (1991) for the NE Jura Mountains and the Black Forest.

Petrography

Petrographic analyses of the thin sections of all granite samples from the study area (Figure 7) reveal sericitisation of plagioclase. Although the TDS between 35 to 153 mg L⁻¹ at Bürchau indicates only little water-rock interaction, this sericitisation may among others represent one possible source of alteration of plagioclase in the presence of CO₂ (Equation 1).



From the isotopic composition of the Bürchau water, it should be mentioned that it is inconclusive to prove sericitisation. Furthermore, the exact composition of plagioclase was not identified in this study.

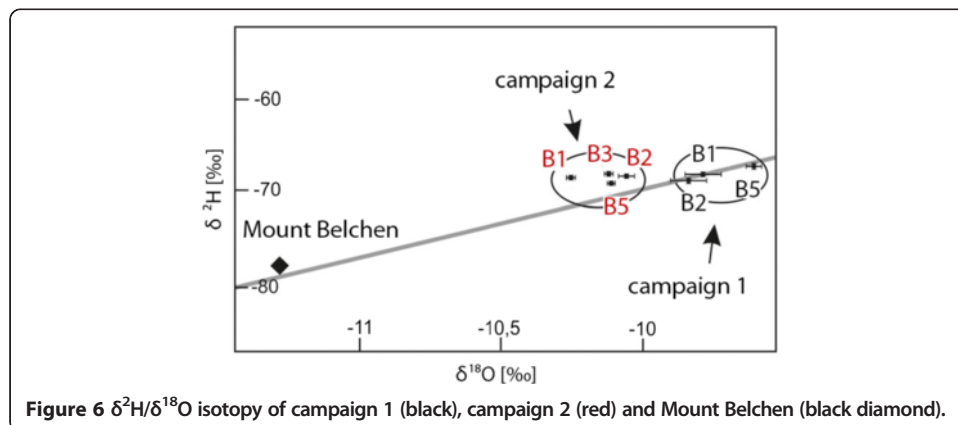


Figure 6 δ²H/δ¹⁸O isotope of campaign 1 (black), campaign 2 (red) and Mount Belchen (black diamond).

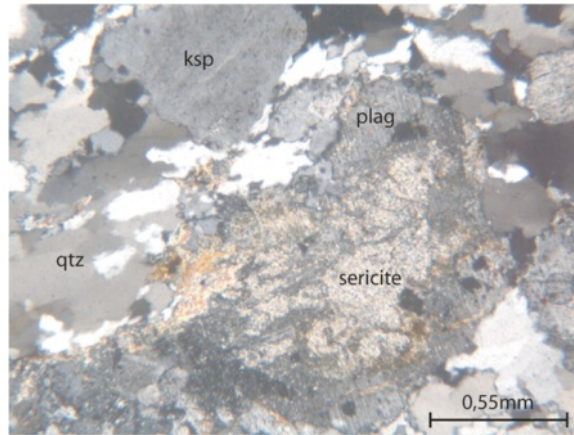
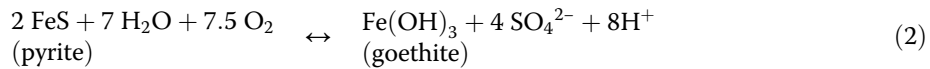


Figure 7 Representative example of the Mambach granite with sericitised plagioclase (sample taken at the discharge B1). Ksp = alkali feldspar, qtz = quartz.

Thin sections of the granite sample from B1 show distinct weathering reactions of opaque minerals to reddish secondary minerals that indicate the oxidation of pyrite to goethite (Figure 8). The oxidation of pyrite can be described with the following equation:



Chlorofluorocarbon analysis

The amount of specific CFCs for B1 obtained from the sampling campaign III are listed in Table 2. Assuming a contamination of surface water as shown by the stable isotope results of campaign I and II, the infiltration altitude for the groundwater recharge is estimated iteratively using the below presented results to about 500 m above B1 at a mean temperature of 5°C. For this case, specific harps were constructed using the exponential model of Malloszewski and Zuber (1992) for further interpretation. In Figure 9,

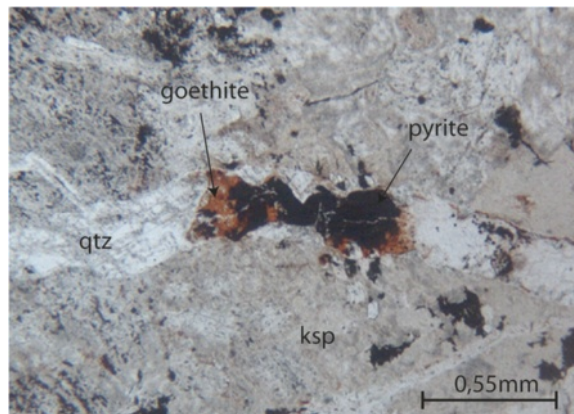


Figure 8 Pyrite oxidation in quartz (qtz) vein surrounded by alkali feldspar (ksp).

Table 2 Amount of CFCs and standard deviation at B1 from the sampling campaign III

Sample name	Trace gases					
	Trichlorofluoromethane (F11)		Dichlorodifluoromethane (F12)		1,1,2-Trichlorotrifluoroethane (F113)	
	[pmol L ⁻¹]		[pmol L ⁻¹]		[pmol L ⁻¹]	
Spring B1	1.5	±0.2	0.81	±0.05	0.13	±0.05

the results of the CFC analysis are represented for the specific sampling period and recharge area for CFC-113 and CFC-11. Data points at the top on the right of the harp would indicate a young water amount of 100%. The results indicate a mixed ground water composition of minimum two components. The younger component appears to be younger than 60 years and has a proportion of about 30% to 40%. The major groundwater component of B1 (60% to 70%) is older than 60 years.

Geothermometers

Geothermometers are based on temperature-dependant chemical reactions or isotope equilibrium fractionation relations from which the equilibrium temperatures can be calculated. The applicability to low-temperature reservoirs is a matter of debate, since the majority of geothermometers were developed and calibrated for high-enthalpy geothermal systems (Fournier 1977, Arnórsson 1983). To obtain higher reliability of estimated reservoir temperatures, in this study, we tested sulphate geothermometers that have recently been successfully applied for low-enthalpy systems (T < 150°C) in

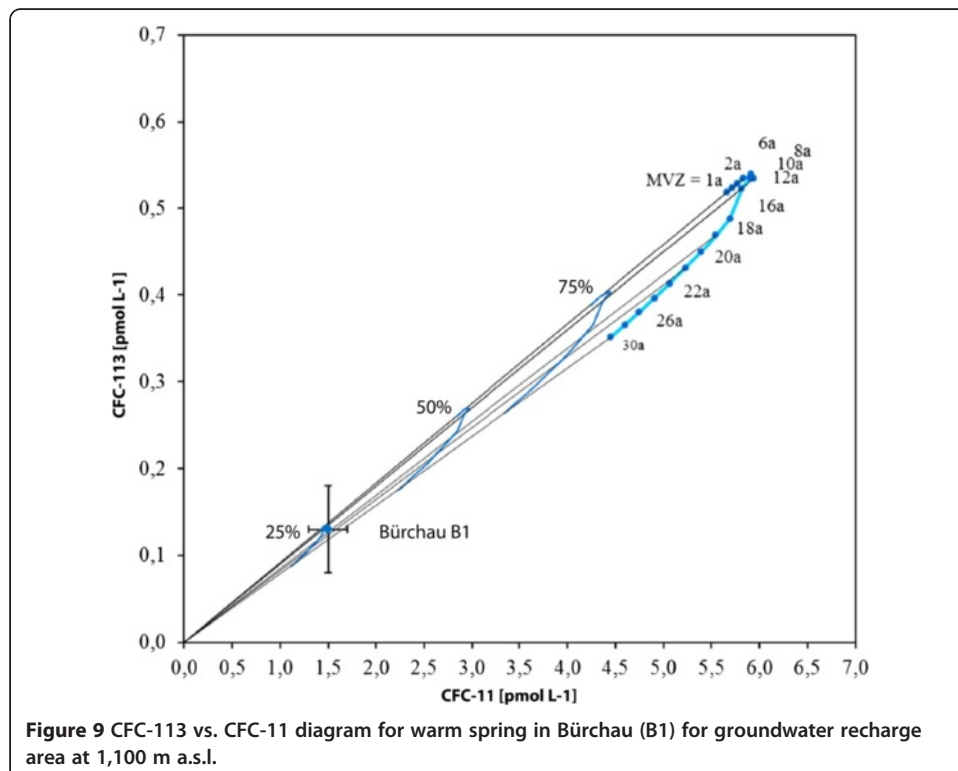


Table 3 Calculated reservoir temperatures

Geothermometer	Temperature calculation [t in °C] S = Si-concentration as SiO ₂ in mg kg ⁻¹ α = isotopic relation between SO ₄ and H ₂ O (fractionation factor)	Calculated reservoir temperature for B1 [°C]	Calculated reservoir temperature for B5 [°C]
Quartz (Fournier 1977)	$t = \frac{1,309}{5,19 - \log S} - 273.15$	68	63
Quartz (Arnórsson et al. 1998a)	$t = -55.3 + 0.3659S - 5.3954 \times 10^{-4}S^2 + 5.5132 \times 10^{-7}S^3 + 74.36 \log S$	55	49
Quartz (Verma 2000)	$t = \frac{1,175}{4,88 - \log S} - 273.15$	60	55
Chalcedony (Fournier 1977)	$t = \frac{1,032}{4,69 - \log S} - 273.15$	36	31
Chalcedony (Arnórsson et al. 1983b)	$t = \frac{1,112}{4,91 - \log S} - 273.15$	39	34
SO ₄ ²⁻ -H ₂ O (Halas and Pluta 2000)	$10^3 \ln \alpha_{(SO_4-H_2O)} = 2.41 \cdot 10^6 / t^2 - 5.77$	77	59
SO ₄ ²⁻ -H ₂ O (Zeebe 2010)	$10^3 \ln \alpha_{(SO_4-H_2O)} = 2.68 \cdot 10^6 / t^2 - 7.45$	81	65

addition to silicate geothermometers (Boschetti 2012). A sulphate geothermometer is derived from the oxygen isotope composition of dissolved sulphate and water.

Calculated reservoir temperatures for B1 and B5 are listed in Table 3. Temperatures derived from silica geothermometers for B1 are in the range of 55°C to 68°C for the quartz geothermometer and slightly below 40°C for the chalcedony geothermometer. Within the range of up to 80°C, the calculated reservoir temperatures derived from

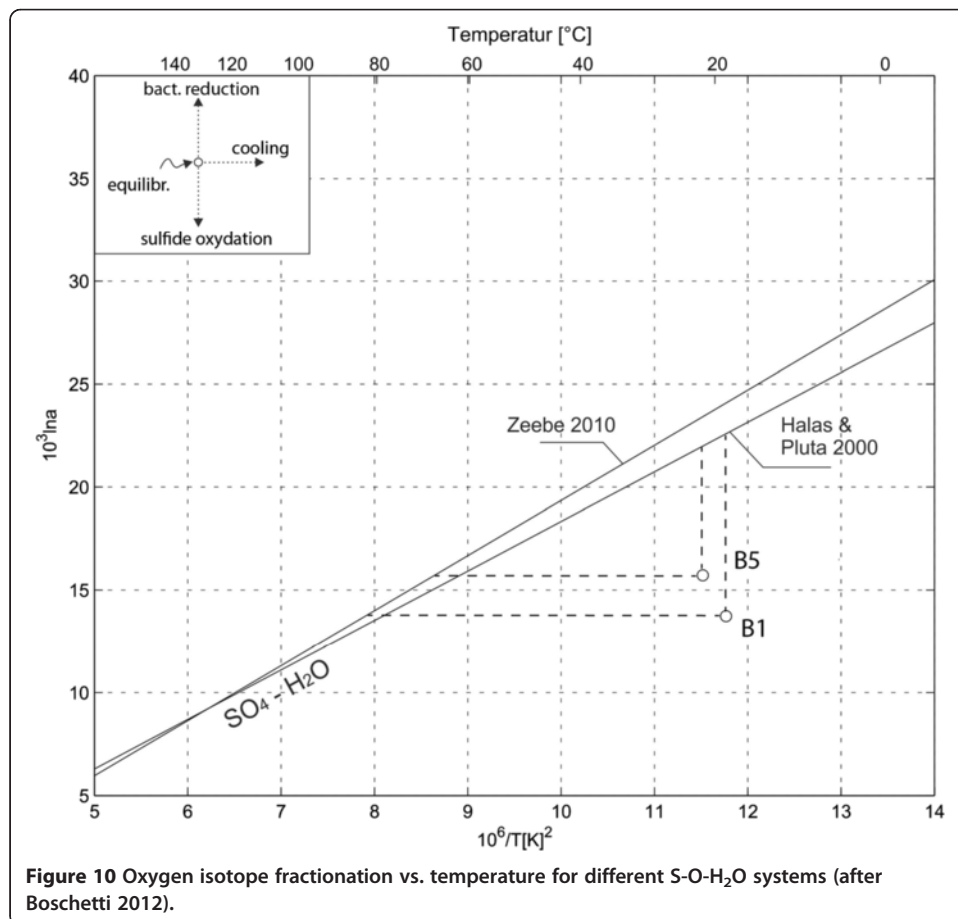


Figure 10 Oxygen isotope fractionation vs. temperature for different S-O-H₂O systems (after Boschetti 2012).

sulphate geothermometers are higher than those derived from silica geothermometers. Similar to spring B1, the calculated temperatures for the Badenweiler Spa (B5) are uniform and show reasonable results in the range of 49°C to 63°C for silicate geothermometer and $\pm 60^\circ\text{C}$ for sulphate geothermometer. Since we observe massive sericitisation of plagioclase in thin sections, enough SiO_2 in solution is assumed to form equilibrium with quartz over time.

All water samples (B1, B2 and B5) fall into the zone of immature water in the ternary Na-K-Mg^{1/2} diagram (Giggenbach 1988) indicating little water-rock interaction, i.e. no equilibrium condition. Reservoir temperatures for B2, B3 and B4 are not listed, since dilution with surface groundwater leads to inconsistent temperatures. This leads to the conclusion that calculated reservoir temperatures for the Bürchau side are questionable.

For evaluating the sulphate-water oxygen isotope geothermometers, the theoretical (Zeebe 2010) and empirical (Halas and Pluta 2000) isotope fractionation factors within the range of 0°C to 150°C were considered (Figure 10). Due to a very likely dilution by near surface water, B2 has been excluded from further analyses. Both samples, B1 and B5, are shifted from the SO_4^{2-} -H₂O equilibrium area. This shift may result from conductive cooling during the ascent of the fluid and/or from isotopic effects due to sulphide oxidation (Boschetti 2012). Since indication for oxidation of pyrite to goethite is found in the thin sections (Figure 8), the calculated reservoir temperatures with the sulphate isotope geothermometers tend to be overestimated. In this case, both conductive cooling and sulphidic oxidation influence the oxygen isotopic fractionation within the geothermal water.

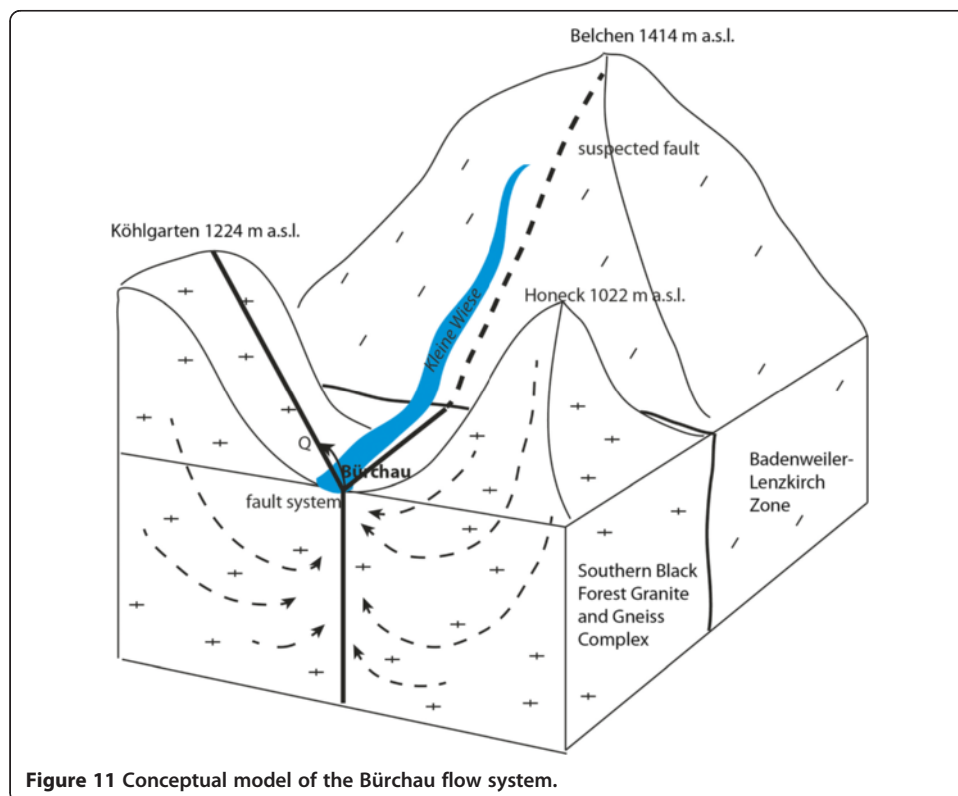


Figure 11 Conceptual model of the Bürchau flow system.

Conclusions

The very low-temperature fluid that rises along open NW-SE discontinuities in the Mambach granite is of meteoric origin with a low mineralisation of Na-Ca-HCO₃ type. All samples plotted in the $\delta^{18}\text{O} / \delta^2\text{H}$ diagram occur close to the meteoric water line indicating only little significant water-rock interactions. Sericitisation of plagioclase and pyrite oxidation in quartz vein is observed in thin sections. Infiltration of the water has been estimated iteratively to occur at an altitude of approximately 1,100 m at an annual mean temperature of 5°C. Figure 11 shows a conceptual flow model of the Bürchau flow system. Sulphate isotope geothermometer appears to be applicable to the very low-temperature reservoirs of the Black Forest. Although possibly slightly overestimated, it provides most-consistent temperatures ranging between 77°C and 87°C for B1 and 59°C to 65°C for Badenweiler. CFC analyses show that 30% to 40% of the thermal water in Bürchau is younger than 60 to 70 years. Thus, the circulation time of the other 60% to 70% of the thermal water is longer than 70 years.

Finally, our results provide a reference for processes occurring already in the infiltration area of the Black Forest. A thermo-hydraulic model will be established in a forthcoming paper.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

The manuscript is based in JR's master thesis with the sampling, laboratory measurements and interpretation of the geochemical and petrological analyses. ES linked the results with the heat flux anomaly in the northern Switzerland and wrote a significant part of the manuscript. IS supervised the work on the sericitization. JS interpreted the CFC measurements. TN supervised the laboratory work. TK provided input on topography-driven systems.

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