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The origin of thermal waters in the northeastern part of the Eger Rift, Czech Republic

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ABSTRACT

An investigation of the thermal waters in the Ústí nad Labem area in the northeastern part of the Eger Rift has been carried out, with the principal objective of determining their origin. Waters from geothermal reservoirs in the aquifers of the Bohemian Cretaceous Basin (BCB) from depths of 240 to 616 m are exploited here. For comparison, thermal waters of the adjacent Teplice Spa area were also incorporated into the study. Results based on water chemistry and isotopes indicate mixing of groundwater from aquifers of the BCB with groundwater derived from underlying crystalline rocks of the Erzgebirge Mts. Unlike thermal waters in Děčín, which are of Ca–HCO_3 type, there are two types of thermal waters in Ústí nad Labem, Na–HCO_3–Cl–SO_4 type with high TDS values and Na–Ca–HCO_3–SO_4 type with low TDS values. Carbon isotope data, speciation calculations, and inverse geochemical modeling suggest a significant input of endogenous CO_2 at Ústí nad Labem in the case of high TDS groundwaters. Besides CO_2 input, both silicate dissolution and cation exchange coupled with dissolution of carbonates may explain the origin of high TDS thermal waters equally well. This is a consequence of similar $\delta^{13}C$ and ^{14}C values in endogenous CO_2 and carbonates (both sources have ^{14}C of 0 pmc, endogenous CO_2 $\delta^{13}C$ around −3‰, carbonates in the range from −5‰ to +3‰ V-PDB). The source of Cl^- seems to be relict brine formed in Tertiary lakes, which infiltrated into the deep rift zone and is being flushed out. The difference between high and low TDS groundwaters in Ústí nad Labem is caused by location of the high mineralization groundwater wells in CO_2 emanation centers linked to channel-like conduits. This results in high dissolution rates of minerals and in different $\delta^{13}C$(DIC) and ^{14}C(DIC) fingerprints. A combined $\delta^{34}S$ and $\delta^{18}O$ study of dissolved SO_4 indicates multiple SO_4 sources, involving SO_4 from relict brines and oxidation of H_2S. The study clearly demonstrates potential problems encountered at sites with multiple sources of C, where several evolutionary groundwater scenarios are possible.

1. Introduction

Geothermal reservoirs have been studied extensively because of their potential for power generation and heating (Huttrer, 2001; Birkle et al., 2001) and also as analogs of paleo- and recent hydrothermal systems (Brugger et al., 2005). A wide range of approaches are used in these types of studies including the applications of structural, hydraulic, hydrogeochemical and isotopic methods, and the investigation of fluid inclusions (González et al., 2000). These studies provide useful information about origin and genesis of thermal waters, which is necessary for their protection and determination of regime of exploitation.

In the towns of Děčín and Ústí nad Labem (Fig. 1) geothermal energy is exploited by pumping of groundwater with a temperature of up to 40 °C in the tectonic structure of the Ohře/Eger Rift zone. Groundwater pumped from these wells is used in local spas and swimming pools. Several geothermal wells are also used for heating houses in Děčín.

Geothermal wells at both sites pump groundwater from the aquifers developed in sedimentary rocks of the Bohemian Cretaceous Basin (BCB), but their hydrogeochemical fingerprints are quite different. Groundwater chemistry of wells in Ústí nad Labem does not correspond to typical BCB groundwaters because of mineralization (TDS about 1 g/L) and concentration of F (about 10 mg/L) are both high. There is a hydrogeochemical similarity between this groundwater and groundwater exploited in the Teplice Spa located to the SW, where groundwater used in the spa is linked to a rhyolite body, covered partly by Cretaceous, and partly by Tertiary pelitic and argillous sediments (Fig. 1). However, direct communication between aquifers of the BCB and the rhyolite aquifer has not been proved by a long-term pumping test (Hazdrová et al., 1964).

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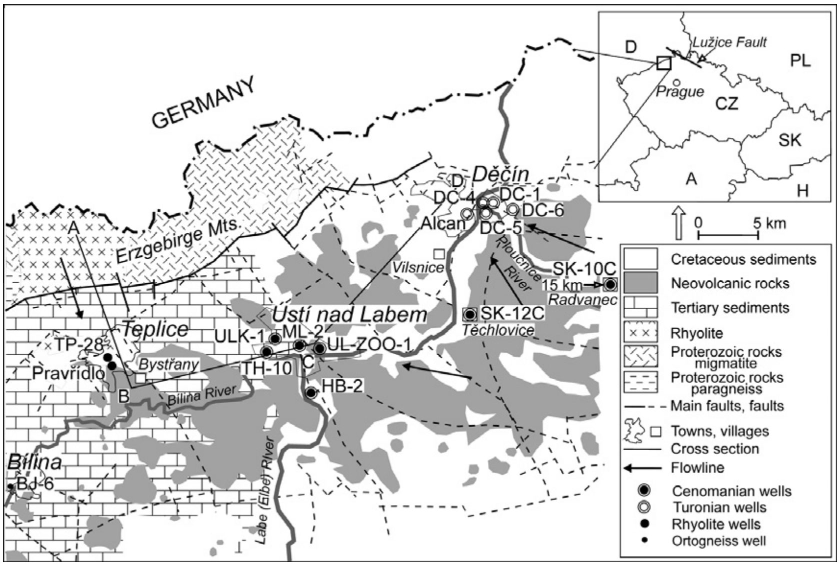

Fig. 1. Map of the study region and location of sampled wells. Assumed flow pattern is based on Herčík et al. (2003).

The occurrences of thermal waters in Ústí nad Labem and Děčín had been reported in the late 19th and early 20th century. The first wells, which encountered thermal waters, were drilled in Bystřany SE of Teplice (1888, 1897). Later other wells were drilled in Vilsnice south from Děčín (1906), in Děčín (1911–1912) and in Ústí nad Labem (1911–1932). A long time before the discovery of thermal waters in deep aquifers in the sediments of the BCB natural discharges of thermal waters related to tectonically disturbed zones within the rhyolite body were known in Teplice. The first exploration studies started almost immediately after the discovery of thermal waters. Hynie (1963) studied thermal waters in Ústí nad Labem from the 1930s. In the 1960s and 1970s, as a consequence of groundwater protection zone delimitation for the Teplice Spa, regional hydrogeological exploration was performed to determine a possible connection between thermal waters in Teplice and Ústí nad Labem (Hazdrová et al., 1964). In the 1970s Hazdrová (1971) studied thermal waters in Ústí nad Labem. In this period, several wells were drilled for regional hydrogeological exploration. In the 1980s the structure was evaluated in the framework of regional hydrogeological synthesis of the BCB (Herčík et al., 2003). Brines of Na–SO_4–Cl type in the crystalline rocks in the deep zone of the western part of the Ohře/Eger Rift zone were studied by Paces and Smejkal (2004). They presented a multi-stage conceptual model of their evolution. Isotopic composition of groundwater in the study area with emphasis on radiocarbon dating was investigated by Šilar (1976, 1989, 2007). Pačes (1962, 1974), Šmejkal (1979) and Šmejkal et al. (1981) studied isotopes of O, H and S. The origin of thermal waters of the north-western part of the BCB was discussed based on older chemical, $\delta^{13}C$ and radiocarbon data by Jiráková et al. (2010). The Eger Rift is the zone of subcrustal CO_2 ascent via localized preferential transport conduits linked to deep faults (Weinlich et al., 1999; Weise et al., 2001). The source of CO_2 is active degassing of magma in the upper mantle (Weinlich et al., 1999).

The principal objective of this study was to determine the origin of thermal waters in Ústí nad Labem because this information is necessary for their protection. In the study, hydrostratigraphic, hydrogeochemical, and isotopic data were integrated. Another outcome of this study is the development of a methodology for interpretation of ^{14}C data in very complex conditions of the northeastern part of the Eger Rift.

2. Materials and methods

2.1. Water chemistry

In the study region there are several exploited wells. Currently, four wells are used for pumping of thermal waters in Ústí nad Labem: ULK-1, HB-2, ML-2, UL-ZOO-1. In Děčín thermal water is pumped from five wells: Alcan, DC-1, DC-4, DC-5 and DC-6. Several monitoring wells of the Czech Hydrometeorological Institute (CHMI) are also relevant for the study: well TH-10 with thermal water in Ústí nad Labem and two wells in the Cenomanian aquifer: SK-10C and SK-12C. There are two thermal wells in Teplice with a similar composition of groundwater compared to Ústí nad Labem: Pravřídlo and TP-28. More information about sampled wells is in Table 1.

Groundwater from pumped wells was sampled for chemical analyses. In total, five wells in Děčín and four wells in Ústí nad Labem were sampled. Wells sampled in Děčín were DC-1, DC-4, DC-5 and DC-6 and well Alcan. In Ústí nad Labem sampled wells were ML-2, ULK-1 and HB-2 and well UL-ZOO-1. Samples were collected in the period from December 2007 to January 2008. They were analyzed in the laboratory of the Monitoring Ltd company. Temperature, pH and electrical conductivity (EC) were measured on-site. Chemical analyses of CHMI wells (TH-10, SK-10C and SK-12C) and Teplice Spa wells (Pravřídlo, TP-28) were taken from the databases of these institutions.

2.2. Isotopes

The wells were sampled for isotopic analyses in December 2008. This sampling was focused especially on the wells in Ústí nad Labem, where four samples were taken from wells ML-2, ULK-1, UL-ZOO-1 and well TH-10 (Fig. 1). One sample was also taken from well SK-12C and one sample from SK-10C well. Several isotopes including ^{18}O, ^{2}H, ^{3}H, $^{34}S(SO_4)$, $^{18}O(SO_4)$, $^{13}C(DIC)$, $^{14}C(DIC)$, $^{87}Sr/^{86}Sr$ were determined on selected samples.

In January and June 2009 samples for isotopic analyses were taken from Pravřídlo (Teplice Spa) and TP-28 well (Teplice Spa). Isotopes determined were ^{18}O, ^{2}H, ^{3}H, $^{34}S(SO_4)$, $^{18}O(SO_4)$, $^{13}C(DIC)$, $^{14}C(DIC)$, and $^{87}Sr/^{86}Sr$. Several samples were also analyzed for trace elements including samples from ML-2, ULK-1

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Table 1
Water chemistry data.

Parameter/well		Děčín Sandstone-Turonian					Ústí nad Labem Sandstone-Cenomanian					Teplice Rhyolite		Radvanec s.-Cenoman	Těchlovice s.-Cenoman	Bílina
		Alcan	DC-1	DC-4	DC-5	DC-6	UL-ZOO-1	ML-2	HB-2	ULK-1	TH-10	Pravřídlo	TP-28	SK-10C	SK-12C	BJ-6
X		−747311	−746,650	−746,911	−746,731	−745,453	−759,240	−761,402	−759,538	−762,867	−763,721	−776,056	−776,068	−720,428	−748,000	−782,566
Y		−966,098	−965,500	−965,405	−965,713	−965,880	−975,929	−975,927	−980,147	−975,156	−976,443	−976,474	−976,278	−970,522	−974,213	−986,169
Z	m	131	129	128	137	142	144	146	142	193	144	217	217	308	207	231
Depth	m	240	420	473	520	545	515	390	400	511	500.2	54.3	973	616	598	191
Year of drilling		1998	1977	1989	1997	1999	2001	2002	2003	1998	1961	1835	1972	1982	1982	1984
Open interval	m	188–240	150–399	231–473	440–504	459–545	400–515	235–387	286–400	439–511	374–441	–	883–942	559–601	407–527	121–187
T after drilling	°C	27	27	31	25	31	31.2	31.4	32	35	30	49	45.7	14	28	16
T (sample)	°C	21.3	27	30.8	24.9	30.2	30	28	26	30	24.2	40	41	10.2	26.6	16
pH		7.7	7.9	7.5	7.6	7.5	7.4	7.5	7.3	7.3	6.84	7.14	7.26	7.24	7.64	7.00
pH in situ		7.19	7	6.7	7.1	6.65	7.27	7.06	6.92	6.96	6.8	–	–	7.2	7.4	–
Conductivity (EC)	mS/m	28	27.7	26.8	27.2	27.1	235	222	235	95	96.8	116	156	19.7	31.2	642
Alkalinity	mmol/L	2.5	2.5	2.4	2.5	2.5	20	18	20	6.5	5.18	–	–	1.95	2.61	75.3
Ca	mg/L	48	48	48	48	50	26	27	20	66	24	37.2	33.6	39	38	134.3
Mg	mg/L	4	4	2	4	4	8	9	5	11	6.3	5.77	5.76	0.89	5.7	76.6
Na	mg/L	3.7	2.7	3.9	1.9	1.8	620	560	600	150	160	229	335	1.4	16	1840
K	mg/L	1.4	1.5	1.3	1.1	0.91	14	18	17	13	20	10.6	11.3	1.1	7.6	83.1
Fe	mg/L	0.52	1.3	0.62	0.57	0.4	0.28	0.19	0.044	2.4	2.3	0.022	0.516	6.9	0.59	1.09
Mn	mg/L	0.016	0.031	0.02	0.025	0.018	<0.01	0.053	0.014	0.034	0.012	<0.013	0.016	0.18	0.012	0.07
NH_4^+	mg/L	0.13	0.22	<0.1	<0.1	<0.1	0.4	0.67	0.39	0.55	0.55	0.023	0.104	<0.05	0.991	3.1
SO_4^{2-}	mg/L	25	37	29	25	29	236	234	207	183	180	116	275	<1	21	598
Cl^-	mg/L	2	<2	<2	<2	2	142	121	135	14	14	49.8	56.6	1.1	1.2	237.6
HCO_3^-	mg/L	153	153	146	153	153	1210	1120	1190	397	320	528	600	120	160	4594.7
NO_3^-	mg/L	<1	1.3	<1	<1	<1	<1	1.4	<1	<1	<1	0.531	<0.05	<1	<1	0.2
F^-	mg/L	0.33	0.1	0.14	0.11	0.1	9.7	10	12	6.2	5.7	7.22	6.75	<0.05	1	4.8
COD-Mn	mg/L	<0.5	<0.5	<0.5	<0.5	<0.5	0.7	0.5	0.63	<0.5	<0.5	–	–	<0.5	<0.5	1.5
SiO_2	mg/L	–	12.7	14	–	13.6	12	–	14	13	12	40.86	45.66	3.8	13	43
As	mg/L	–	–	0.002	–		0.0043	–	<0.002	0.028	0.0089	<0.018	0.045	<0.002	0.005	0.14
Ba	mg/L	–	0.054	0.06	–	0.054	<0.05	–	<0.05	<0.05	0.095	0.0899	0.083	0.1	0.24	–
Cr	mg/L	–	<0.01	0.0034	–	<0.01	0.003	–	<0.001	<0.001	<0.002	<0.001	<0.001	<0.002	<0.002	<0.01
Sr	mg/L	–	–	0.083	–	–	0.84	–	0.74	0.82	0.48	0.285	0.319	0.061	0.45	–
Li	mg/L	–	–	<0.01	–	–	0.72	–	0.7	0.31	0.96	0.385	0.528	0.0009	0.032	3.98
Ni	mg/L	–	0.027	<0.003	–	0.008	0.0032	–	0.0032	0.063	<0.002	0.0016	0.0009	<0.002	<0.002	–
TDS	mg/L	162	174	159	158	165	1660	1540	1590	645	740	1039	1386	170	260	7621

The Y and X coordinates show the position of the wells in local coordinate system S-JTSK.

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and UL-ZOO-1. Groundwater from HB-2 and DC-4 was analyzed for trace metals and isotopes ^{18}O, ^{2}H, $^{34}S(SO_4)$ and $^{18}O(SO_4)$.

Isotope values $\delta^{18}O$ and δD in water were determined in the Slovak Geological Survey in Bratislava, Slovakia. Oxygen isotope data were obtained by the water–CO_2 equilibration method, followed by analysis on a Finnigan MAT-250 mass spectrometer with precision ±0.1‰. The δD values were measured by the LWIA apparatus, model DLT-100 (producer Los Gatos Inc., California, USA). Calibration curves were based on standards LGR-2,3,4. Precision of measurement was ±0.15‰. Results were expressed relative to the VSMOW standard.

For the radiocarbon analyses samples were concentrated by the addition of $FeSO_4$ to 100 L of water and pH was increased to about 12. Then 300 g of $BaCl_2$ were added. Precipitated $BaCO_3$ was used for ^{14}C analyses. Analyses were performed at the Faculty of Science of Charles University, Prague, using liquid scintillation spectrometer TriCarb 3170TR/SL. Scintillation agent was a mixture of 3 mg of MSB and 15 mg of PBD. Each sample was measured 4× for 1000 min.

Measurements of ^{3}H were performed at the Faculty of Science of Charles University by TriCarb 3170TR/SL apparatus. Samples for ^{3}H analyses were enriched by electrolysis in a solution of Na_2O_2 and each sample was measured 4× for a period of 700 min.

Isotopes $^{34}S(SO_4)$, $^{18}O(SO_4)$, $^{13}C(DIC)$ and $^{87}Sr/^{86}Sr$ were determined in the stable isotopes laboratory of the Czech Geological Survey, Prague. Samples for $\delta^{34}S(SO_4)$ determination were precipitated after sample acidification by addition of a 10% solution of $BaCl_2$ and $BaSO_4$ precipitate was collected. Determination of $\delta^{34}S(SO_4)$ in samples of $BaSO_4$ was performed by decomposition with a mixture of V_2O_5 and SiO_2 at 1000 °C in vacuum according to Haur et al. (1973) based on the method of Yanagisawa and Sakai (1983). Released SO_2 was determined by Finnigan MAT 251 mass spectrometer. Total error of $\delta^{34}S(SO_4)$ was ±0.15‰ and results were expressed relative to the CDT standard.

Values of $\delta^{18}O(SO_4)$ were determined on $BaSO_4$ precipitate, which was reduced by pure C in vacuum on Pt at 1050 °C, according to Longinelli and Craig (1967), as modified by Sakai and Krouse (1971). Released CO_2 was captured and determined with a Finnigan MAT 251 mass spectrometer. Total error of $\delta^{18}O(SO_4)$ determination is ±0.3‰ and results are given relative to the VSMOW standard.

The $BaCO_3$ precipitate used for ^{14}C measurement was also used for $\delta^{13}C(DIC)$ determination. The precipitate was decomposed in 100% H_3PO_4 in vacuum, at 25 °C. The composition of C isotopes in released CO_2 was determined by the Finnigan MAT 251 mass spectrometer. Total error of isotopic determination was ±0.1‰. Results were expressed with respect to the PDB standard.

Samples for $^{87}Sr/^{86}Sr$ determination were prepared by chromatographic separation on ion exchanger "Sr Resin" of the Eichrom company (Míková and Denková, 2007). The solution of Sr was evaporated with H_3PO_4 and precipitate was transferred to a Re fibre in a Ta activator solution. The measurement was performed on a Finnigan MAT262 mass spectrometer with thermal ionization in dynamic mode. Long-term reproducibility of results was confirmed by repeated analyses of reference material NBS 987 with an average value from 10 measurements of 0.710244 ± 0.000030 (2 sigma).

Multivariate statistical analyses were performed using the program PAST (Hammer et al., 2001). Speciation modeling was performed by the program PHREEQC (Parkhurst and Appelo, 1999) with combined databases of minteq4.dat and llnl.dat. The NETPATH code (Plummer et al., 1994) was used for inverse geochemical modeling.

3. Geology and hydrogeology

Thermal waters in Ústí nad Labem and Děčín are a part of the Benešov–Ústí hydrogeological system, which belongs to the western part of the BCB (Herčík et al., 2003). The basin represents platform sedimentary cover of the NE part of the Bohemian Massif. The Bohemian Massif was consolidated during the Hercynian orogeny. In the northwestern part of BCB Cretaceous sediments reach their maximum thickness, in the deepest zone up to 1000 m. The Benešov–Ústí hydrogeological system is the most complicated part of the BCB because of its heterogeneous sedimentary layers and frequent presence of faults.

In Ústí nad Labem and Děčín, the Cretaceous sediments are underlain by the Erzgebirge Mts. crystalline basement, composed mostly of medium-grained two-mica orthogneiss and migmatites of Proterozoic age (Mísař et al., 1983). These rocks are locally penetrated by well-fractionated granitic bodies of Upper Carboniferous age. Carboniferous–Permian sediments of Česká Kamenice, part of the Lužický Basin, underlie the Cretaceous rocks in the area east of Děčín. The thickness of these sediments is locally up to 600 m here (Malkovský et al., 1974).

The Paleozoic crystalline bedrock or the Permian–Carboniferous sediments are covered by Cretaceous sediments. The basal part of the BCB sediments is represented by freshwater continental sediments, but most of the basin filling is represented by shallow-water marine sediments. The sedimentary sequence of the Benešov–Ústí hydrogeological system exhibits significant lithological changes in a NE–SW direction. The northeast zone is the source area of sedimentation and a main part of the stratigraphic sequence from Cenomanian to Coniacian present here is composed of psammitic material. There are important aquifers developed in the BCB (Fig. 2).

In the Ústí nad Labem area, located in the SW part of the hydrogeological structure, pelitic material becomes more important and only the bottom aquifer is present. The bottom aquifer is composed of Peruce–Korycany Sandstone (Cenomanian) and Bílá Hora Sandstone (Lower Turonian) and its thickness ranges from 30 to 70 m. Further to the west, the thickness of the aquifer decreases to 10 m and then to zero at the contact with the Teplice Rhyolite.

In the Děčín area there is less pelitic material compared to the Ústí nad Labem region. In Děčín, the bottom Cenomanian aquifer is also present, but the principal aquifer is composed of the Jizera Formation (Middle Turonian, Malkovský et al., 1974). These aquifers are separated by the Bílá Hora Marlstone Aquitard. The Turonian Aquifer is in a large part of the Benešov–Ústí hydrogeological system overlain by a thick aquitard formed by the Teplice Strata (Upper Turonian) and the Březno Strata (Coniacian). Above the aquitard there is an occurrence of Merboltice Strata (Santonian) and Březno Strata, psammitic rocks, which form the Upper Cretaceous Aquifer.

In the Cenozoic period Cretaceous sediments between Ustí nad Labem and Teplice were covered by the continental freshwater sediments of the Most Basin (Oligocene–Miocene) and simultaneously significant volcanic activity occurred. Both the development of Cenozoic sedimentary basins and intensive volcanic activity are related to the formation of the continental Ohře/Eger Rift. The most intense volcanic activity took place in the Ústí nad Labem region, where volcanic rocks penetrated through the basement and BCB sedimentary fill.

The Cenozoic alkaline basaltic volcanism in the area covers a relatively long time period, with pre-rift series formed between 95 and 51 Ma, and more important rift series between 42 and 0.1 Ma (Ulrych et al., 1999). Formation of shallow lakes and marshes in the area of intensive volcanic activity locally led to increased mineralization of surface waters. A conceptual model of the Na–SO_4–Cl type of brines present in the deep zone of the Eger Rift was suggested by Paces and Smejkal (2004). The model includes: (a) penetration of magmatic S and Cl volatiles from a deep magmatic source into the Tertiary playa lakes, increase of SO_4^{2-} and Cl^- concentrations by evaporation; (b) infiltration of concentrated solutions into deep zone via fractures and precipitation of salts

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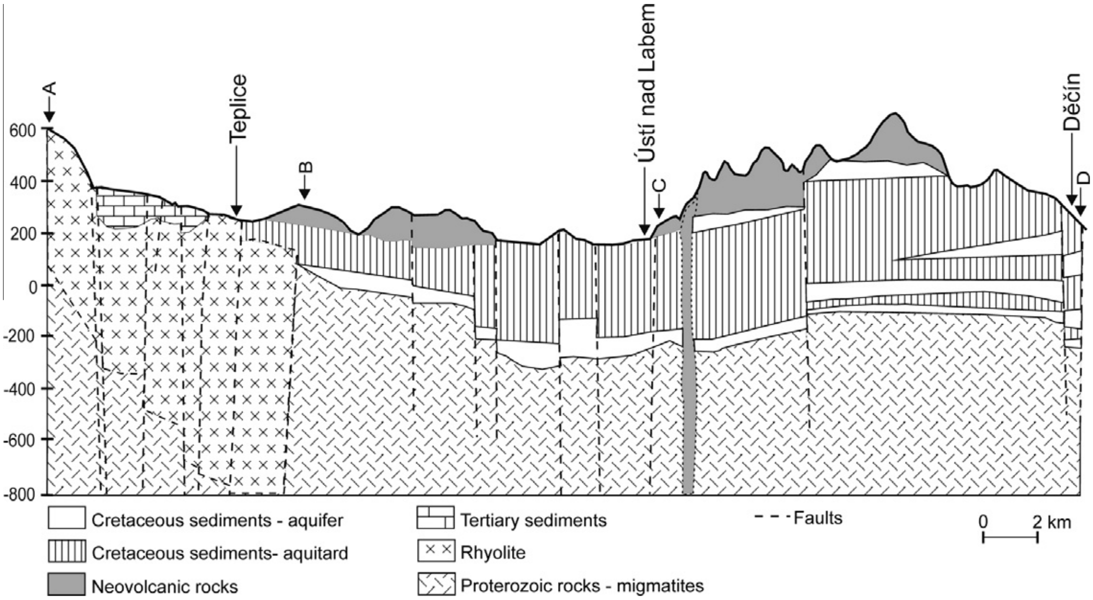

Fig. 2. Cross section of geological units and principal aquifers (after Hazdrová et al., 1964).

such as Na_2SO_4 and NaCl; and (c) reversal of flow direction after the formation of the rift graben and gradual dissolution of salts by meteoric waters. Saline playa lakes are well documented in the western part of the Ohře/Eger Rift (Šmejkal, 1978), while the more eastly-located Most Basin experienced strong mineralization of water only in some shallower peripheral parts (Mach et al., 1999). Sodium–SO_4–Cl brines have been documented in the western part of the rift zone, but also in the eastern rift.

With respect to the above mentioned Cenozoic rifting there has been significant tectonics in the whole study area, which has a strong impact on flow pattern and the upper mantle CO_2 input (Weinlich et al., 1999; Herčík et al., 2003; Pačes et al., 2008). Vertical movements on some faults had amplitudes of up to several hundred meters. Some faults act as hydrogeological barriers, but others connect different aquifers.

General present-day groundwater flow direction within the sediments of the western part of the BCB is from NE to SW, following the direction of sediment transport, Herčík et al. (2003, Fig. 1). At the border with Germany close to the Lužice Fault there is a principal recharge zone. In the SW groundwater discharges into Labe (Elbe) River and is pumped from wells in Děčín and Ústí nad Labem. However, it is assumed that thermal waters in Ústí nad Labem also have a recharge zone in the eastern part of the Erzgebirge Mts. and groundwater recharged in this zone could enter the Cenomanian Aquifer via deep tectonic zones (Herčík et al., 2003).

Teplice Spa is underlain by a rhyolite body of Permian–Carboniferous age, which is a part of the Altenberg Caldera. During the Cenozoic rifting the rhyolite body was tectonically disturbed by a set of faults of mostly E–W to WSW–ENE direction and partly covered by sediments of the Most Basin. The thermal waters in Teplice Spa are linked to tectonic structures within the rhyolite body and are supposed to be recharged at the higher elevated Erzgebirge Mts ridge. Although the rhyolite aquifer is connected to the sediments of the Most Basin, there is no evidence so far for hydraulic communication between aquifers of the BCB and rhyolite.

4. Chemical and isotopic composition of studied groundwaters

4.1. Water chemistry and trace elements

Water chemistry data are presented in Table 1 and groundwater samples are plotted in the Piper diagram (Fig. 3), where principal groundwater groups are marked. Thermal waters in Děčín are of Ca–HCO_3 type, just one well, DC-1, is of Ca–SO_4–HCO_3 type. Total dissolved solids (TDS) are about 160 mg/L. In Ústí nad Labem there is a group of wells with groundwater of the Na–HCO_3 type and relatively high concentrations of Cl (about 130 mg/L) and F (about 10 mg/L) (Fig. 3). The probable source of F is in granitic bodies related to the Altenberg Caldera, rich in light elements such as Li and F. Fluorine contents in these granites are high, from 0.5 to 1 wt.% (Breiter et al., 2007). Values of TDS for wells of Na–HCO_3–Cl–SO_4 groundwater type are about 1500 mg/L. This group is represented by wells ML-2, UL-ZOO-1, and HB-2. In contrast, two wells in Ústí nad Labem, ULK-1 and TH-10, have about a half of the TDS of other wells, concentration of Cl is an order of magnitude lower (14 mg/L), but concentration of F is still high, about 6 mg/L. Their groundwater chemistry type is different, they are of Na–Ca–HCO_3–SO_4 type. Temperature and pH values in wells in Děčín and Ústí nad Labem are similar, with respective values of about 30 °C and 7.5.

Wells in Teplice have groundwater of Na–HCO_3 and Na–SO_4–HCO_3 types. The Na–HCO_3 is represented by the Pravřídlo well with much lower SO_4^{2-} concentrations than in well TP-28. The Pravřídlo well is only 51 m deep and is located in a tectonic zone, however well TP-28 is 972.5 m deep. Concentrations of F are about 7 mg/L, just as in Ústí nad Labem, but temperatures in Teplice wells are approximately 10 °C higher, reaching more than 40 °C.

Well SK-10C, located relatively close to the Lužice Fault recharge zone (Fig. 1), represents a typical Cretaceous groundwater of Ca–HCO_3 type with TDS of 160 mg/L. The SK-12C well, located far from the recharge zone (Fig. 1), has different groundwater chemistry, with groundwater of Na–Ca–HCO_3 type, TDS of 260 mg/L, F of 1 mg/L and K of 7.6 mg/L. Wells in Děčín have respective concentrations of F and K of only 0.1 mg/L and 1.3 mg/L.

4.2. δD and $\delta^{18}O$

Isotopic data are presented in Table 2. Values of δD are in the range from −67.9‰ to −81.5‰. Values of $\delta^{18}O$ are in the range from −9.71‰ to −11.43‰. All points fall on the Global Meteoric Water Line (GMWL), indicating no significant evaporation during recharge and lack of higher temperature water–rock interaction (Fig. 4). It is worth mentioning the position of the wells in Ústí

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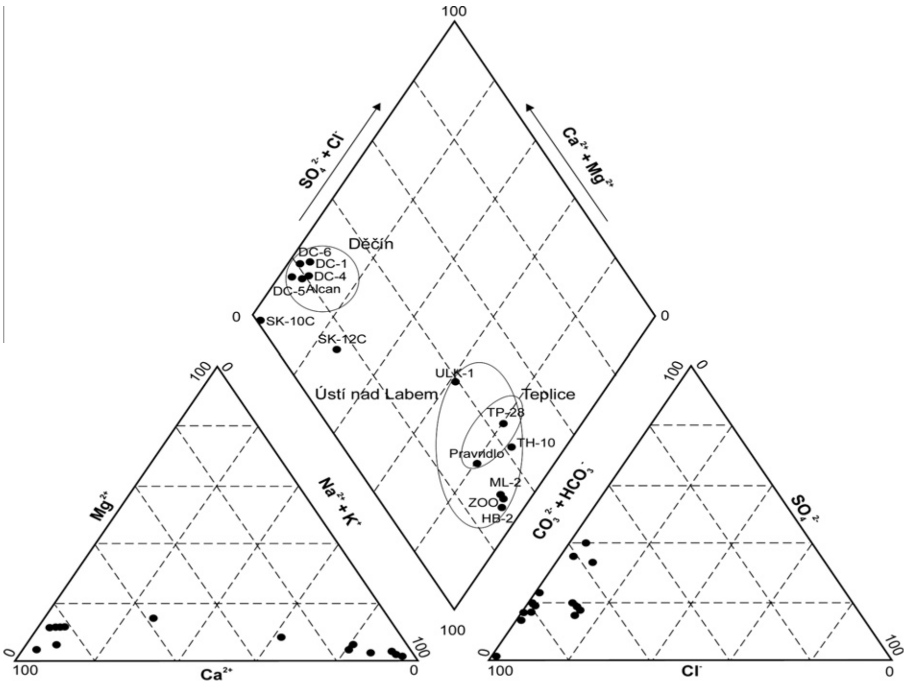

Fig. 3. Piper diagram of water chemistry.

Table 2
Isotopic data.

Sample	$\delta^{18}O$ (‰ vs. VSMOW) ±0.1	$\delta^{2}H$ (‰ vs. VSMOW) ±1.5	$\delta^{34}S$ (‰ vs. CDT) ±0.15	$\delta^{18}O–SO_4$ (‰ vs. SMOW) ±0.3	$^{87}Sr/^{86}Sr$ ±0.00003	$\delta^{13}C$ (‰ vs. PDB) ±0.1	^{14}C (pmc)	^{3}H (TU)
SK-10C	−9.7	−67	–	–	0.70971	−13.78	52.6	–
SK-12C	−11.4	−82	−19.7	11.9	0.70880	−8	1.2	bdl
DC-4	−11.1	−79	−24.9	11.1	–	–	–	–
TP-28	−9.8	−69	1.39	10.5	–	−6.48	14.6	–
Pravřídlo	−9.9	−69	1.78	10.4	0.71860	−5.36	10.5	2.17 ± 0.28
UL-ZOO-1	−10.5	−73	10.2	8.1	0.71012	−3.68	0.3	bdl
HB-2	−10.6	−75	7.2	11.7	–	–	–	bdl
ML-2	−10.7	−75	3.5	7.1	–	−3.66	0.7	–
ULK-1	−10.6	−75	−17.7	4.5	–	−6.72	5.7	bdl
TH-10	−10.7	−75	−17.1	4.9	–	−6.39	4.1	0.22 ± 0.36

bdl – Below detection limit.

nad Labem such as UL-ZOO-1 and HB-2 is on the GMWL, almost in the middle between wells SK-12C (δ^2H −82‰ and $\delta^{18}O$ −11.4‰) and DC-4 in Děčín (δ^2H −79‰ and $\delta^{18}O$ −11.1‰) and wells Pravřídlo (δ^2H −69‰ and $\delta^{18}O$ −9.9‰) and TP-28 (δ^2H −69‰ and $\delta^{18}O$ −9.8‰) in Teplice (Table 2). The samples from Ústí nad Labem seem to be a mixture of an old groundwater component with negative isotopic values and also a component of isotopically enriched modern groundwater. The isotopically depleted groundwater component could be either related to the presence of some proportion of pre-Holocene water, which infiltrated during the Upper Pleistocene under cooler climatic conditions, or the presence of water infiltrating under recent climate, but at higher elevations. Precipitation on the slopes of the Erzgebirge Mts. was studied for 3 years (1984–1986) by Buzek et al. (1991), who found at the rift valley (240 m asl) average precipitation $\delta^{18}O$ values of −8.4‰ (V-SMOW), while at the range of Erzgebirge Mts. (700–800 m asl) precipitation averaged below −11.0‰ (SMOW). However, enriched isotopic values at Pravřídlo well indicate relatively low altitude recharge and altitude-dependent values would more probably be expected for the higher elevated recharge area located close to the Lužice Fault in the NE.

4.3. Carbon isotopes and tritium

Activities of ^{14}C(DIC) are generally very low (<15 pmc), except for the SK-10C well located close to the recharge zone with a value of 52.6 pmc. Samples with very low ^{14}C(DIC) activities have strongly enriched $\delta^{13}C$(DIC) values (Table 2, Fig. 5). Common values of $\delta^{13}C$(DIC) in waters saturated by soil CO_2 are from −16‰ to −20‰ PDB (Clark and Fritz, 1997). The carbonates in sediments of the BCB, which can be one of the sources of C in groundwater, are mostly impure limestone and marlstones. Carbon isotope composition of these rocks was studied by Uličný et al. (1993), who found $\delta^{13}C$ values in the range 0.5‰ to 3.4‰ (V-PDB). Voigt and Hilbrecht (1997) found $\delta^{13}C$ values between 1.7‰ and 4.6‰ (V-PDB) in carbonates in the German part of the BCB. Pivec et al. (1998) found in Cretaceous marlstones in the contact-metamorphosed aureole of Tertiary magmatic rocks $\delta^{13}C$ values between 0‰ and +2‰, while the locally abundant carbonate veinlets in Tertiary magmatic rocks themselves had $\delta^{13}C$ values between 0‰ and −5‰ (V-PDB) (Kopecký et al., 1987).

Groundwaters sampled in this project have values of $\delta^{13}C$ from −3.6‰ to −8.0‰, i.e. there is a strong enrichment in the heavier C

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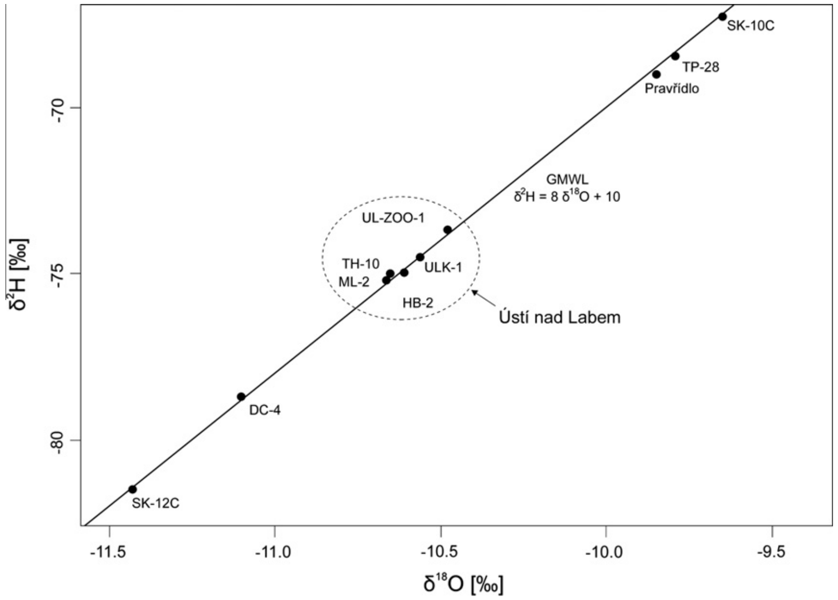

Fig. 4. Graph of $\delta^{18}O$ vs. δD.

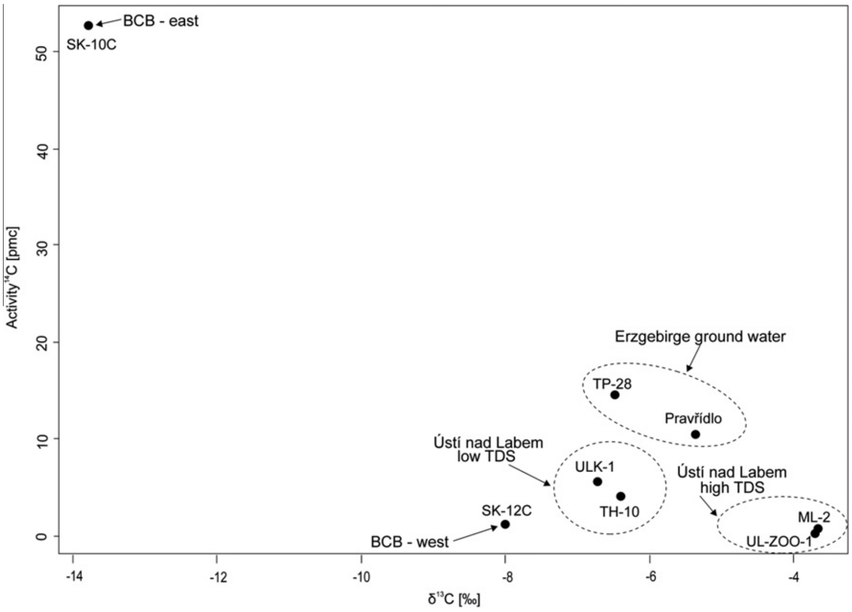

Fig. 5. Graph ^{14}C(DIC) activity vs. $\delta^{13}C$(DIC).

isotope relative to the range of soil-derived CO_2, presumably caused by endogenous CO_2 input. All samples except SK-12C and SK-10C belong to this category. Groundwaters in northwestern Bohemia with endogenous CO_2 input have $\delta^{13}C$(DIC) values -4 ± 2‰ VPDB (Weinlich et al., 1999; Noseck et al., 2009). The lowest ^{14}C(DIC) activity (less than 1 pmc) is in high TDS groundwater from wells UL-ZOO-1 and ML-2, which also have enriched values of $\delta^{13}C$, about -3‰ (Fig. 5). In contrast, low TDS wells in Ústí nad Labem have an order of magnitude higher ^{14}C activity values (about 5 pmc) and more depleted $\delta^{13}C$ values (about -6‰). The SK-12C well has low ^{14}C(DIC) activity and relatively negative $\delta^{13}C$(DIC) values.

Results of ^{3}H measurements indicate a lack of mixing with younger groundwaters except for samples from TH-10 and Pravřídlo with detectable values of ^{3}H (Table 2).

4.4. $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$

Determination of both $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values is a useful approach to estimate origin of aqueous SO_4^{2-}, and its further history in a groundwater (reviewed by Seal, 2003; Bottrel, 2007; Hubbard et al., 2009). Both O and S isotope ratios were determined in aqueous SO_4^{2-} of 10 wells, with highly variable $\delta^{34}S(SO_4^{2-})$ values (-24.9‰ to +10.2‰ V-CDT), and less variable $\delta^{18}O(SO_4^{2-})$ values (+4.5‰ to +11.9‰ V-SMOW; Table 2). These variable isotope data indicate at least three different sources of aqueous SO_4^{2-} in the thermal waters of Děčín – Ústí nad Labem – Teplice area. If SO_4 reduction had taken place, samples with lowest SO_4^{2-}concentrations would have very enriched $\delta^{34}S(SO_4)$ values (Clark and Fritz, 1997), but this is not observed (Fig. 6). The $\delta^{34}S(SO_4)$ values should, therefore, fingerprint the S sources.

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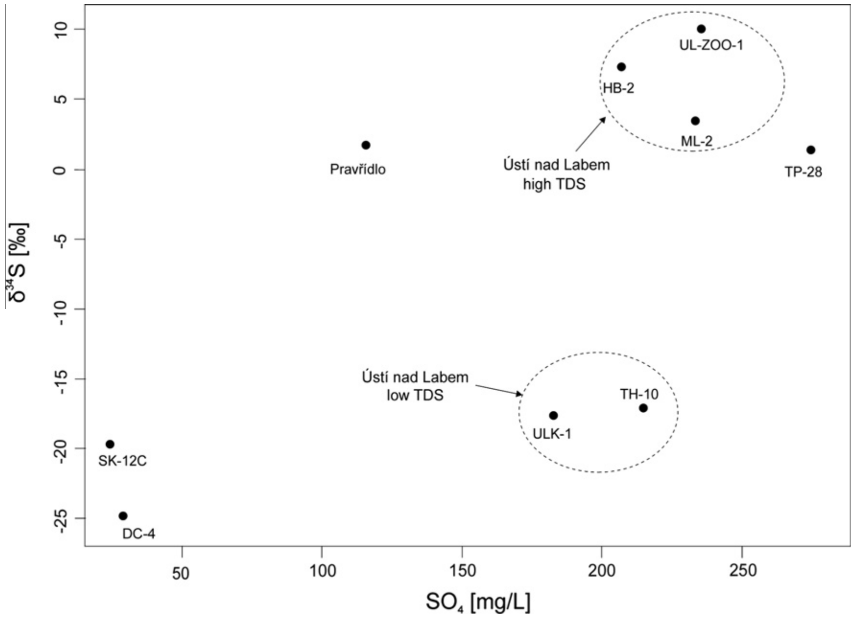

Fig. 6. Graph delta $^{34}S(SO_4)$ vs. SO_4 concentration.

Possible S sources show highly variable, and partly overlapping, $\delta^{34}S$ values. The sulfidic minerals in crystalline rocks and ore deposits of the Krušné Hory crystalline basement usually show $\delta^{34}S$ values in the range between −5‰ and +5‰ (Šmejkal et al., 1974; Mach et al., 1999). There are scarce data for S isotopic composition of sulfates in the Carboniferous–Permian sediments. Skoček et al. (1977) presented $\delta^{34}S$ values of seven gypsum samples from the Lower Permian in the range from +6.2‰ to +10.2‰ (CDT).

Cretaceous sediments of the BCB, which contain the studied groundwaters, are locally rich in sulfidic minerals, which are characterized by extremely variable $\delta^{34}S$ values (Šmejkal et al., 1974; Vavřín et al., 1975). Basal freshwater Cenomanian sediments contain bacteriogenic pyrite with generally negative $\delta^{34}S$ values (average for the measured data of −18.9‰), marine Cenomanian pyrites average at −12.2‰, and those of Lower Turonian average at −1.2‰ (V-CDT). In the bottom Cenomanian aquifer of the BCB located NE from the study area, the aqueous SO_4 was completely reduced, due to the high organic matter content in the aquifer matrix (see SK-10C). However, in case of insufficient availability of Fe in groundwater, the groundwater downstream can contain significant amounts of H_2S with generally negative $\delta^{34}S$ values. Another important S source can be sediments of the Tertiary Most Basin with a S-rich lignite seam. The $\delta^{34}S$ values of the coal (dominated usually by sulfidic S) again show a wide range, from +15.45‰ to −17.42‰ (average +1.64‰). The coal seems to exhibit a vertical upward trend of decreasing $\delta^{34}S$ values (Mach et al., 1999).

The $\delta^{18}O(SO_4^{2-})$ values of sulfidogenic aqueous SO_4 are controlled by mechanisms of oxidation of the source sulfides (pH and O_2 fugacity, different rates of O isotope exchange in SO_3^{2-}(water) and SO_3^{2-}(water), Hubbard et al., 2009). Dissolution of sulfate minerals fingerprints both the S and O isotope data of the source.

In the $\delta^{34}S(SO_4^{2-})$ vs. $\delta^{18}O(SO_4^{2-})$ plot (Fig. 7), the data for water from studied wells show three distinct fields. Wells TH-10 and ULK-1 are characterized by low $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values and moderate SO_4^{2-} concentrations. Here the aqueous SO_4^{2-} seems to be a result of oxidation of sulfidic minerals in Cenomanian sediments under oxidizing conditions with availability of Fe^{3+}. This is also supported by the fact that one of these wells has detectable ^3H.

Wells SK-12C and DC-4 in the Děčín area show extremely low $\delta^{34}S(SO_4^{2-})$ values, but higher $\delta^{18}O(SO_4^{2-})$ values. Groundwaters from both wells have very low SO_4^{2-} concentrations. Here the most probable interpretation is either oxidation of H_2S or decomposition of sulfides in reducing, Fe^{2+} dominated environments, followed by O isotope exchange between SO_3^{2-} and water.

The third group is the most interesting and has the highest SO_4^{2-} concentrations (Teplice Pravřídlo and TP-28; Ústí nad Labem ZOO-1, HB-2, ML-2). The $\delta^{34}S(SO_4^{2-})$ are relatively high (between 1.4‰ and 10.2‰) and $\delta^{18}O(SO_4^{2-})$ values are also high (between 7.1‰ and 11.7‰). Because of high SO_4^{2-} concentrations these samples most probably do not contain residual SO_4^{2-} influenced by bacterial SO_4 reduction. The source can be either a brine, which infiltrated deep into the tectonically disturbed basement of the Eger Rift, a brine or gypsum present in Carboniferous/Permian sediments locally underlying the BCB, or oxidation of sulfidic minerals in any of the potential sources listed above (except of freshwater Cenomanian), followed by prolonged evolution of the SO_4^{2-} during the very long residence time of groundwater in the aquifers.

Groundwaters with aqueous $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values in this range were clearly present in the study area for very long periods of geological time. Ulrych et al. (2007) studied barite crystals, which were deposited by thermal water in rock cracks in the study area (both from Teplice and Děčín). These barite crystals have $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values in the same range as the studied groundwaters (Fig. 7). Duration of activity of the Pravřídlo spring in Teplice was estimated by Čadek and Malkovský (1982) to be at least 0.5 Ma.

After a catastrophic groundwater outbreak in the Döllinger coal mine located in the Tertiary sediments in 1879, the thermal water level started to decline rapidly in the Teplice Spa. Simultaneously with this outbreak, the chemistry of the water started to change, with increasing SO_4^{2-} concentrations. Fig. 7 documents stable isotope evolution of the Pravřídlo spring between 1980 and the present. This probably also indicates that the group of studied wells with high SO_4^{2-} concentrations and both high $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values does not depend on a single S source, and is again a result of mixing of several SO_4 components.

4.5. Strontium isotopes

The $^{87}Sr/^{86}Sr$ isotope ratio for well UL-ZOO-1 in Ústí nad Labem, 0.710117, located between the ratio 0.708803 for old Cretaceous

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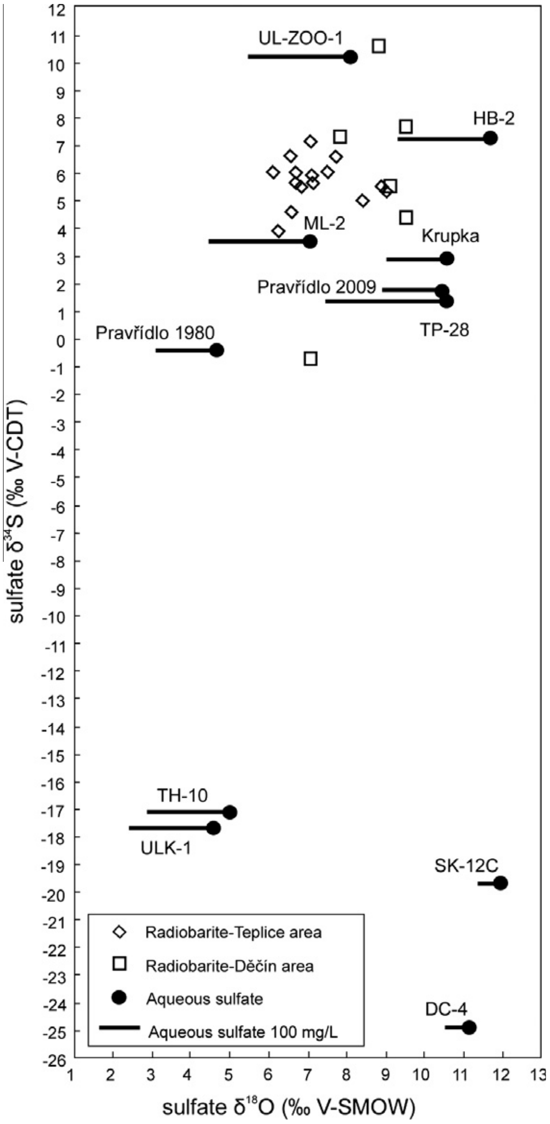

Fig. 7. Sulfur and O isotope data for aqueous sulfates in studied wells. The line segment lengths indicate SO_4 concentration in water. Historical data from the Pravřídlo source in Teplice are after Šmejkal (1979) and Šmejkal et al. (1981). The data show significant evolution of isotopic composition of aqueous SO_4 and are probably related to present-day deeper artificial capture of the Pravřídlo. Data for barite crystals on walls of cracks in rocks are after Ulrych et al. (2007).

groundwater Těchlovice well SK-12C and Pravřídlo well 0.718598 indicates a potential contribution of Erzgebirge Mts. (crystalline basement) groundwater from Rb-rich crystalline rocks to thermal water in Ústí nad Labem. In contrast, the ratio of 0.70912 for well SK-10C is close to the value for well SK-12C, representing the BCB groundwater (Table 2).

5. Multivariate statistics

Results of Principal Component Analysis (PCA) are presented in Fig. 8. The method reduces the original variables to only a few important variables, called principal components (PCs), which can be linked to geochemical processes (Davies, 2002). Principal component 1 (PC1) explains 97.13% of variability in the data set and highly positive loadings for HCO_3, Na, and intermediate positive loadings for electrical conductivity (EC), SO_4 and Cl; and represents high mineralization Na–HCO_3–Cl–SO_4 groundwater type with high SO_4 and Cl concentrations. Shift of samples to the right indicates their evolution towards the high mineralization groundwater type in Ústí nad Labem. Principal component 2 (PC2), which is less well defined, explains 1.98% of variability in the data set and has high positive loading for HCO_3, and intermediate negative loadings for SO_4, Ca and Na. In total, the first two components together explain 99.11% of the variability in the data set. Most wells representing typical groundwater of Ca–HCO_3 type from the Cretaceous Aquifer are clustered together on the left, but there are three outliers far to the right with high PC1 loadings: ML-2, HB-2, and UL-ZOO wells. These wells in Ústí nad Labem have high TDS values, groundwater of Na–HCO_3 type and significant concentrations of SO_4 and Cl. Also other wells in Ústí nad Labem, ULK-1 and TH-10, are shifted to the right. It is worth noting that wells in Teplice Pravřídlo and TP-28 are located between samples from Ústí nad Labem and typical Cretaceous Aquifer wells.

6. Speciation modeling

Results of speciation modeling are presented in Table 3. Concentrations of C expressed as total CO_2 are much lower at the Děčín site (wells from Alcan to DC-6) than at the Ústí nad Labem site (wells from UL-ZOO-1 to TH-10). Respective ranges are from 2.85 mmol/L to 3.6 mmol/L at Děčín and from 6.9 mmol/L to 23.9 mmol/L at Ústí nad Labem. In Ústí nad Labem, high TDS groundwaters (wells UL-ZOO-1, MI-2 and HB-2) have about three times higher total CO_2 concentrations than low TDS groundwaters from wells ULK-1 and HB-2 (Table 3). Similarly, calculated $\log P_{CO2}$ values at Děčín are much lower than those from Ústí nad Labem,

Table 3
Selected results of speciation modeling, total CO_2 is in mmol/L.

Well/parameter	$(CO_2)_{total}$	$\log P_{CO2}$	$SI_{calcite}$	$SI_{dolomite}$	SI_{gypsum}	$SI_{fluorite}$	SI_{quartz}	$SI_{SiO2(a)}$
Alcan	2.85	−2.03	−0.41	−1.59	−2.25	−2.02	n.a.	n.a.
DC-1	2.99	−1.80	−0.52	−1.75	−2.09	−3.14	**0.24**	−0.99
DC-4	3.31	−1.50	−0.79	−2.55	−2.18	−2.87	**0.24**	−0.97
DC-5	2.9	−1.90	−0.42	−1.55	−2.25	−3.04	n.a.	n.a.
DC-6	3.6	−1.43	−0.82	−2.32	−2.18	−3.15	**0.23**	−0.98
UL-ZOO-1	22.0	−1.26	0.00	−0.23	−1.91	**0.36**	**0.35**	−0.94
Ml-2	21.3	−1.03	−0.10	−0.30	−1.90	**0.30**	n.a.	n.a.
HB-2	23.9	−0.88	−0.37	−0.98	−2.08	**0.36**	**0.31**	−0.92
ULK-1	7.81	−1.35	−0.12	−0.64	−1.47	**0.38**	**0.03**	−1.18
TH-10	6.9	−1.32	−0.87	−2.00	−1.85	−0.03	**0.27**	−0.98
Pravřídlo	9.72	−1.34	**0.06**	−0.22	−1.90	**0.16**	**0.57**	−0.57
TP-28	10.6	−1.41	**0.13**	−0.05	−1.66	−0.03	**0.60**	−0.53
SK-10C	2.3	−2.21	−0.74	−2.99	−3.66	−3.54	**0.01**	−1.36
SK-12C	2.8	−2.19	−0.21	−0.89	−2.43	−1.22	**0.27**	−0.97

Bold – supersaturation.
n.a. – Not available.

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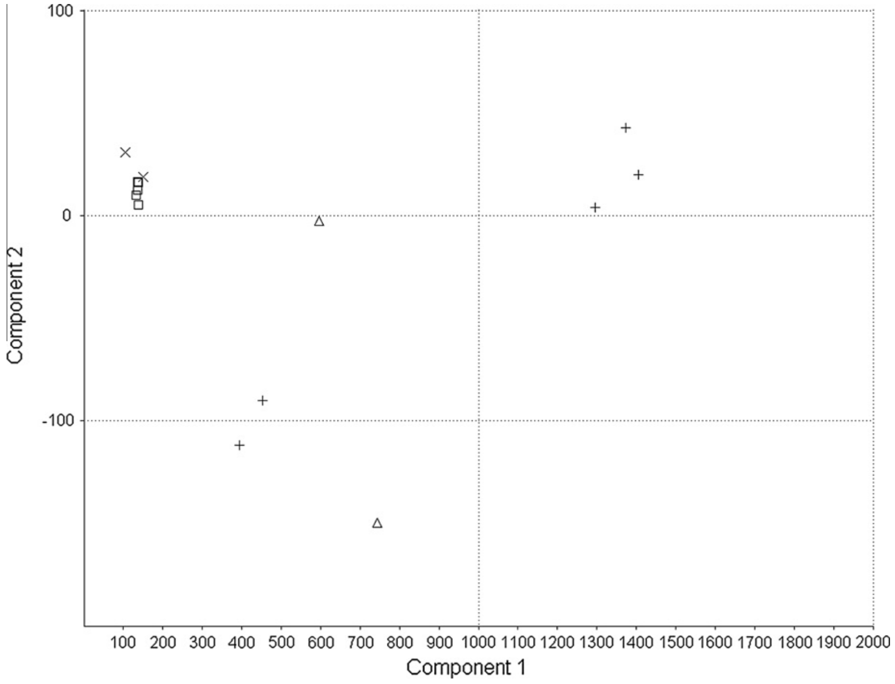

Fig. 8. Results of Principal Component Analysis (PCA), cross-Ústí nad Labem, square-Děčín, triangle-Teplice, X-Cretaceous Basin.

with respective ranges from −2.03 to −1.43 and from −1.35 to −0.88. Values for thermal waters in Teplice (wells Pravřídlo and TP-28) are in between, but they are closer to the values for wells in Ústí nad Labem. Well SK-10C, representing a typical Bohemian Cretaceous Formation groundwater close to recharge zone at Lužice Fault, and well SK-12C, representing groundwater from the same formation, but far from the recharge zone, have total CO_2 and $\log P_{CO2}$ values similar to wells in Děčín. Most samples are undersaturated with respect to calcite and dolomite, except for samples from wells Pravřídlo and TP-28 in Teplice. In Ústí nad Labem, supersaturation is reached with respect to fluorite, CaF_2, as a consequence of high F^- concentrations. In contrast, groundwater samples from all wells are undersaturated with respect to gypsum, indicating conservative behavior of SO_4 under the assumption that SO_4 reduction does not take place. Almost all wells are supersaturated with respect to quartz and undersaturated with respect to amorphous silica.

7. Discussion

The presented data suggest that groundwater at Ústí nad Labem, which is different from groundwater in Děčín, is produced by the mixing of old BCB formation groundwater represented by well SK-12C, and the Erzgebirge Mts crystalline basement groundwater, with additional processes such as the input of endogenous CO_2. Evidence for such evolution includes: (1) the position of groundwater in Ústí nad Labem almost in the middle between SK-12C well and Pravřídlo well in the δD and $\delta^{18}O$ graph (Fig. 4), (2) the high concentrations of typical mountain water species such as F and Li in Ústí nad Labem groundwater, (3) the values of $^{87}Sr/^{86}Sr$ ratios, which in Ústí nad Labem are close to values typical for the Erzgebirge Mts. (Table 2), (4) the extremely high concentrations of total CO_2 and high $\log P_{CO2}$ values in Ústí nad Labem (Table 3), (5) the position of groundwater samples in multivariate statistics result plots (PCA in Fig. 8), and (6) the evolution of groundwater from the Ca–HCO_3 end-member towards the Na–HCO_3 end-member in Ústí nad Labem.

However, the difference between high TDS and low TDS groundwater wells in Ústí nad Labem cannot be explained only by simple mixing. Both types of groundwater have components of BCB and Erzgebirge Mts groundwaters as indicated by δD and $\delta^{18}O$ isotopes and F and Li concentrations, but their TDS, groundwater types, DIC concentrations and C isotope values are different. High TDS groundwaters have enriched $\delta^{13}C$ values (about −3‰) and close to 0 pmc ^{14}C activities. This is in a good agreement with endogeneous CO_2 $\delta^{13}C$ values of about −2.7‰ (Weinlich et al., 1999) and its zero ^{14}C activity. In contrast, low TDS groundwaters have more depleted $\delta^{13}C$ values (about −6‰) and ^{14}C activities about 5 pmc (Table 2).

There are two principal processes responsible for the formation of Na–HCO_3 groundwater type from Ca–HCO_3 groundwater type (Toran and Saunders, 1999; Sracek and Hirata, 2002): (1) cation exchange coupled to dissolution of carbonates such as calcite, and (2) hydrolysis of silicates such as plagioclase. Process (1) can be expressed as (Sracek and Hirata, 2002)

$$\mathrm{CaCO_3 + CO_2 + H_2O + Na_2{-}X = 2Na^+ + 2HCO_3^- + Ca{-}X} \qquad (1)$$

This process generates a Na–HCO_3 groundwater type and both alkalinity and total concentration of C increase. Process (2) is expressed as

$$\mathrm{NaAlSi_3O_8 + CO_2 + 5.5H_2O = Na^+ + 0.5Al_2Si_2O_5(OH)_4 + 2H_4SiO_4^0 + HCO_3^-} \qquad (2)$$

Compared to process (1), there is no production of C assuming a closed system, i.e. no external sources of CO_2 and total concentration of C does not change. Also, the values of $\delta^{13}C(DIC)$ change in the process of carbonate dissolution, but not in the process of silicate hydrolysis. Both processes may operate simultaneously in the same aquifer. For example, in the Guarani Aquifer System in Brazil dissolution of silicates takes place in unconfined and shallow confined zones and cation exchange with calcite dissolution in a deep confined zone, where the calcite pool in the solid phase has not been depleted (Gastmans et al., 2010).

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To test potential evolutionary scenarios, inverse geochemical modeling was performed using groundwater from the Pravřídlo well and SK-12C well as Initial well 1 and Initial well 2, respectively, for mixing and groundwater from well UL-ZOO as the Final well. This well was chosen as an end-member with a maximum input of endogenous CO_2. This type of modeling is used to deduce geochemical reactions between hydraulically connected points, but frequently results are non-unique and less probable scenarios have to be eliminated (Sracek et al., 2004). In this study, the purpose of the modeling was to evaluate potential geochemical reactions with emphasis on inorganic C sources. The program used was NETPATH (Plummer et al., 1994), which also includes isotopic fractionation. The initial C isotope composition was $\delta^{13}C(\text{calcite}) = 0‰$ (Clark and Fritz, 1997) and $\delta^{13}C(CO_2\ \text{gas}) = -2.7‰$ (Weinlich et al., 1999). Both calcite and CO_2 gas were assumed to be radiocarbon-free. Input of C from organic matter was not considered in modeling because there is a strong enrichment in $\delta^{13}C$ in well UL-ZOO-1 in Ústí nad Labem, indicating a negligible C input from organic matter with depleted $\delta^{13}C$ values of about −25.0‰. A single value of $\delta^{34}S(SO_4)$ equal to +6.4‰, reported for thenardite, Na_2SO_4, by Paces and Smejkal (2004) was used in modeling.

7.1. Model 1

In this model, no silicates were included. Constraints were: Na, Ca, C, S and Cl. Phases were calcite, gypsum (dissolution), $CO_2(g)$ (in-gassing), halite (dissolution), and Ca/Na-exchange. The model mixes a 0.54 fraction of groundwater from Pravřídlo with a 0.46 fraction of water from well SK-12C (Table 4). Inputs of calcite and endogenous CO_2 gas are 7.03 mmol/L and 7.86 mmol/L, respectively. Sodium is provided by release of 9.02 mmol/L from Ca/Na-exchange and by dissolution of 3.24 mmol/L of NaCl balanced with the input of Cl^-. The input of SO_4^{2-} from dissolution of gypsum is 1.71 mmol/L. There is a fairly good agreement for the calculated $\delta^{13}C(DIC)$ value, which is slightly lower than the observed value (−2.77 compared to −3.68‰, see Table 5). Calculated $^{14}C(DIC)$ activity is higher than the measured one, 2.66 compared to 0.3 pmc, giving an age of groundwater of 18.05 ka. However, this is an apparent age, resulting from mixing of very old Cretaceous groundwater and much younger groundwater from the Erzgebirge Mts.

7.2. Model 2

In this model, constraints were the same as in Model 1, however Si was added in Constraints and Al was assumed to be retained in the solid phase. Additional phases compared to Model 1 were albite and kaolinite, but calcite was still included. The mixing ratio of the initial groundwaters was the same, as were the amounts of halite and gypsum. The amount of endogenous $CO_2(g)$ was roughly double, reaching 16.88 mmol/L because there was no C input from calcite, just a small amount of calcite precipitated. Large amounts of albite dissolved and kaolinite precipitated, with respective values 18.05 mmol/L and 27.18 mmol/L (Table 4). No cation exchange was necessary because all Na was provided by dissolution of albite and partly from halite. There was a perfect match for $\delta^{13}C(DIC)$ values (Table 5) and calculated $^{14}C(DIC)$ activity was slightly higher than in Model 1, giving an apparent age of 16.73 ka.

7.3. Model 3

In this model, constraints were the same as in Model 2, but calcite was dropped from phases. The input of endogenous $CO_2(g)$ is slightly lower than in Model 2, reaching 14.89 mmol/L and a part of the Na, 1.99 mmol/L, is provided by Ca/Na-exchanger. Respective amounts of dissolved albite and precipitated kaolinite, 14.07 mmol/L and 21.2 mmol/L, are large, but lower than in Model 2 (Table 4). Amounts of dissolved halite and gypsum are again fixed by Cl^- and SO_4^{2-} inputs. This model results in a perfect match for $\delta^{13}C(DIC)$ (Table 5) and in the same $^{14}C(DIC)$ activity as in Model 1, giving an apparent age of 18.05 ka.

7.4. Model 4

Constraints in this model were the same as in Model 3, but gypsum was replaced by thenardite, Na_2SO_4, as a potential source of SO_4^{2-} (Paces and Smejkal, 2004). Results are similar to model 3, i.e. the amounts of dissolved albite and precipitated kaolinite are almost the same (Table 4). The amount of dissolved thenardite is the same as the amount of dissolved gypsum because they are fixed by the difference in SO_4^{2-} concentration. The same applies to halite because it is fixed by the difference in Cl^- concentration. A small amount of Ca/Na cation exchange is needed. Again, the match for $\delta^{13}C(DIC)$ is perfect and resulting apparent age of groundwater is 18.14 ka. Fractionation of $\delta^{34}S(SO_4)$ was modeled only in this run and the result was relatively satisfactory (Table 5).

In summary, both types of models, i.e. based on dissolution of carbonates/cation exchange and based on dissolution of silicates, can explain the evolution of the chemistry of high TDS groundwater equally well. All models require an input of endogenous CO_2. This is consistent with the isotopic composition of CO_2 and other gases (Weinlich et al., 1999) and by a good correlation between

Table 4
Transfer of phases in inverse geochemical models, mass transfer coefficients in mmol/L, + dissolution, − precipitation.

Model/phase	Initial 1 (Pravří-dlo)	Initial 2 (SK-12C)	Calcite	$CO_2(g)$	Ca/Na-exchange	Gypsum	Halite	Albite	Kaolinite	Thenardite
Model 1	0.54	0.46	+7.03	+7.86	+9.02	+1.71	+3.24	–	–	–
Model 2	0.54	0.46	−1.99	+16.88	–	+1.71	+3.24	+18.05	−27.18	–
Model 3	0.54	0.46	–	+14.89	+1.99	+1.71	+3.24	+14.07	−21.2	–
Model 4	0.54	0.46	–	+14.66	+0.29	–	+3.24	+14.07	+21.2	1.71

Table 5
Comparison of calculated and observed isotopic values for well UL-ZOO-1.

Model/ parameter	$\delta^{13}C(DIC)$ calculated (‰)	$\delta^{13}C(DIC)$ observed (‰)	$^{14}C(DIC)$ calculated (pmc)	$^{14}C(DIC)$ observed (pmc)	$\delta^{34}S(SO_4)$ calculated (‰)	$\delta^{34}S(SO_4)$ observed (‰)	Apparent age (ka)
Model 1	−2.77	−3.68	2.66	0.3	–	–	18.05
Model 2	−3.64	−3.68	2.70	0.3	–	–	16.73
Model 3	−3.66	−3.68	2.66	0.3	–	–	18.05
Model 4	−3.67	−3.68	2.68	0.3	4.11	10.2	18.14

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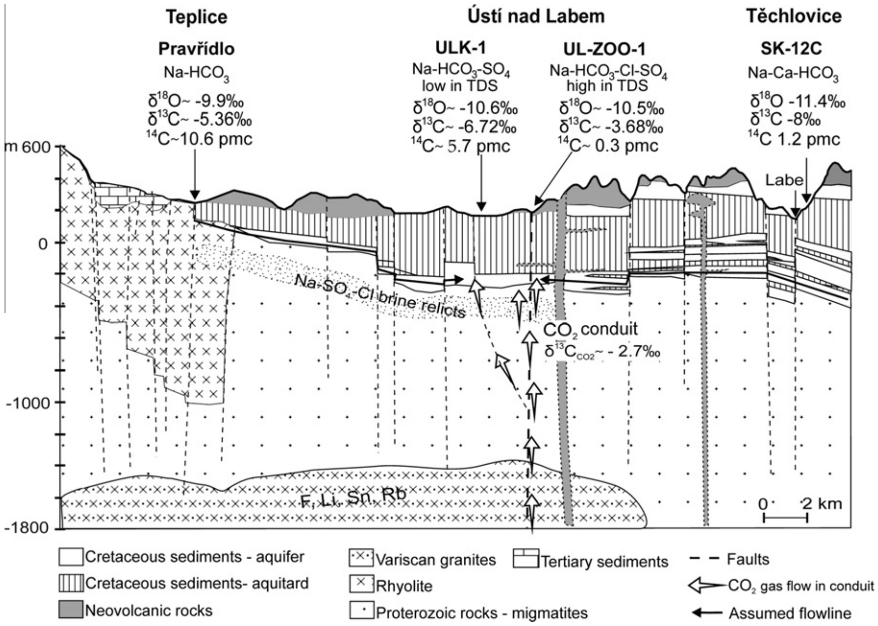

Fig. 9. Conceptual model of the origin of thermal waters in Ústí nad Labem.

the concentrations of free CO_2 gas and mantle-derived He (Paces and Smejkal, 2004) in the Eger River rift zone. Models based on the dissolution of silicates are slightly superior to those based on the dissolution of carbonates in terms of a better match for δ^{13}C(DIC) data. Similar performance of both types of model can be explained by similar δ^{13}C and ^{14}C values in endogenous CO_2 and carbonates (around −2.0‰ and 0 pmc, respectively). Discrepancy between measured and calculated δ^{34}S(SO$_4$) values in well UL-ZOO-1 are probably caused by multiple sources of SO_4^{2-}. All models require a source of SO_4^{2-} and Cl^- represented by gypsum or thenardite and halite in the models. The source of the Cl^- seems to be relict deep Na–SO$_4$–Cl brine in the rift zone, which was in northwestern Bohemia postulated by Pačes (1962, 1974), Šmejkal (1978), Šmejkal and Pačes (1992) and Dvořák (1998) and found by Markovič (1979). As suggested by Paces and Smejkal (2004), the brine was formed in the Miocene playa lake and infiltrated via fractures to the zone close to magmatic source. Minerals such as Na_2SO_4 and NaCl precipitated in fractures are currently dissolving and contributing SO_4^{2-} and Cl^- to groundwater. The presence of such brine in deep crystalline basement in the study area is supported by the occurrence of high TDS groundwater in Bílina SW of Ústí nad Labem (Fig. 1). The groundwater in Bílina is of Na–HCO$_3$–Cl–SO$_4$ type, has a higher value of TDS than the well UL-ZOO-1 (7.62 mg/L compared to 1.66 mg/L), higher concentrations of SO_4^{2-} and Cl^- and the concentration of Li reaches 3.98 mg/L (Table 1).

A conceptual model of the formation of thermal waters in Ústí nad Labem is in Fig. 9. Old BCB groundwater from the NE, represented by well SK-12C, and more recent Erzgebirge Mts. groundwater represented by thermal water at Teplice Spa in the west are mixed. Then endogenous CO_2 enters the mixture of groundwaters via localized preferential CO_2 transport zones, causing dissolution of carbonates coupled to cation exchange and/or hydrolysis of silicates. Dissolution of NaCl and Na_2SO_4 originating from infiltrated residual Tertiary brine provides Cl^- and SO_4^{2-}. Resulting high TDS groundwater, represented by well UL-ZOO-1, is of Na–HCO$_3$–Cl–SO$_4$ type and has an enriched δ^{13}C(DIC) value and close to zero activity of ^{14}C(DIC). In contrast, low TDS, Na–Ca–HCO$_3$–SO$_4$ type groundwaters, represented by well ULK-1, are located out of CO_2 emanation centers and, thus, the CO_2 input and resulting mineral dissolution rates are limited. Limited endogenous CO_2 input is also consistent with their different δ^{13}C(DIC) and ^{14}C(DIC) fingerprints.

The localized character of CO_2 emanations, previously suggested by Hynie (1949), is consistent with findings of Weise et al. (2001), who postulated transport of CO_2 along channel-like conduits on the basis of very fast CO_2 transport induced by the earthquake swarms in the western part of the Eger Rift.

8. Conclusions

Hydrogeochemical and isotopic data were used to determine the origin of thermal waters at Ústí nad Labem and surrounding areas in the northeastern part of the Eger Rift. The two types of thermal waters in Ústí nad Labem, Na–HCO$_3$–Cl–SO$_4$ type, high in TDS, and Na–Ca–HCO$_3$–SO$_4$ type, low in TDS, are very different from the thermal water in Děčín, Ca–HCO$_3$ type with low TDS, in spite of similar groundwater temperatures and similar estimated circulation depths. Thermal water in Děčín matches the composition of a typical groundwater from the aquifers of the Bohemian Cretaceous Basin, represented by the SK-10C well located close to the recharge zone near the Lužice Fault. Based on δD and δ^{18}O values, ^{87}Sr/^{86}Sr ratios and significant concentrations of F and Li, the thermal waters in Ústí nad Labem are a mixture of the old BCB groundwater, represented by SK-12C well and groundwater from the Erzgebirge Mts. with a contribution of fossil brines. There is a strong increase in total dissolved C in Ústí nad Labem high TDS groundwaters, suggesting a large input of endogenous CO_2. This is in a good agreement with enriched δ^{13}C(DIC) values and close to zero ^{14}C(DIC) activities. In low mineralization groundwaters the values of δ^{13}C(DIC) are more negative and ^{14}C(DIC) are more positive, as expected in the case of limited endogeneous CO_2 input. The difference between high and low TDS wells in Ústí nad Labem is caused by the location of the former in the localized channel-like conduits linked to deep-seated faults. The large endogenous CO_2 input results in fast dissolution rates of minerals and very high concentrations of dissolved inorganic C.

Inverse geochemical modeling provided several possible scenarios of the origin of high TDS thermal water in the Ústí nad Labem area. In all models, mixing of the BCB water with Erzgebirge

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Mts. water and endogenous CO_2 input were included. Additional processes were cation exchange coupled with dissolution of carbonates and hydrolysis of silicates such as albite. The source of SO_4^{2-} and Cl^- seems to be linked to the relicts of brine originating in a Cenozoic lake, which infiltrated to the deep zone of the rift.

All models were able to reproduce thermal water chemistry in well UL-ZOO-1 in Ústí nad Labem, but the model with hydrolysis of silicates gave a better match for $\delta^{13}C(DIC)$ and required a higher endogenous CO_2 input than cation exchange/dissolution of the carbonates model. The impossibility of discriminating between the models is a consequence of similar $\delta^{13}C(DIC)$ and $^{14}C(DIC)$ values for carbonates and endogenous CO_2 (around −2.0‰ and 0 pmc, respectively). The results confirm the initial hypothesis about the input of endogenous CO_2 and clearly show problems related to the modeling of geochemical evolution in complex conditions with multiple C sources.

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