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The hydrogeologic situation of the Bad Kissingen spa waters (Lower Frankonia/Bavaria)

Die hydrogeologische Situation der Bad Kissinger Heilwässer (Unterfranken/Bayern)

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1. Introduction

The aim of the present work is to provide an updated scientific analysis of the genesis of the Bad Kissingen spa waters and to evaluate new ground water protection areas based on the results of recent investigations.

Research teams from the Institut für Wasserchemie und Chemische Balneologie ("Institute of Water Chemistry and Chemical Balneology") of the Technische Universität München ("Technical University Munich") investigated the region of W-Unterfranken ("Lower Frankonia"), which borders parts of the State of Hessen ("Hesse") and Thüringen ("Thuringia") for more than 10 years. The studies resulted in numerous publications; several among them deserve particular attention, i. e. "Das Main-Projekt" (The project Main; BAYERISCHES LANDESAMT FÜR WASSERWIRTSCHAFT, 1978), "Das Grundwasser Frankens und angrenzender Gebiete" (The ground water of Frankonia and adjacent regions; P. UDLUFT, 1979) and "Hydrogeologische und hydrochemische Untersuchungen im Bad Kissingen Raum unter besonderer Berücksichtigung der dortigen Heil- und Mineralquellen" (Hydrogeological and hydrochemical investigations in the area of Bad Kissingen with special consideration of the local mineral water wells; N. GEORGOTAS, 1972).

The present study extends beyond the detailed investigations of N. GEORGOTAS (1972) and represents the first attempt to deduce the genesis of the Bad Kissingen wells based on some general structural features and the hydrogeological status of NW-Unterfranken.

Contemporary computer-based mathematical models can contribute significantly to the enrichment of knowledge on the hydrochemistry and hydrodynamics of the wells in Bad Kissingen.

Consideration of the reactions of thermodynamic equilibrium has contributed to the better understanding of the **qualitative** composition of mineral waters and thus, enhanced knowledge of their balneotherapeutic activity and effectiveness.

Since direct observations and measurements in deep ground water zones are practically impossible, model-based computations represent the method of choice for the **quantitative** description of hydrodynamic processes. This method enabled us to determine the physical parameters that significantly influenced the development of the Bad Kissingen wells. Moreover, we obtained results which contribute to the clarification of a frequently raised question regarding the occurrence of **thermal** waters in the Bad Kissingen deep underground.

Hydrochemical and hydrodynamical calculations occupy a preeminent position among the methods employed. They provide valuable information about processes of dissolution, precipitation and intermixing in the underground; at the same time, they enable us to evaluate the effects of several factors, such as density, viscosity, hydrodynamic longitudinal and transversal dispersion on fluid dynamics in the underground.

The results of hydraulic and hydrogeochemical computations provide a general overview of the dynamics of deep ground water from its infiltration up to its appearance at the surface in Bad Kissingen.

One of the main results was the separation of the deep ground water portion from shallow ground waters and the evaluation of the origin of these two water types. The knowlegde of these parameters led to a new delineation of protection areas for the Bad Kissingen well waters. Based on the knowledge of mixing processes of deep and shallow ground water a better understanding of these processes was of great importance.

2. Geological structure of the area of investigation

The area of investigation covers a substantial part of the administrative district of Unterfranken and is located at the intersection of the borders of the states of Hessen, Bayern and Thüringen. Geographically, the area extends W-wards to Rhön, N-wards to the Thüringer Wald and S-wards to the Steigerwald. The southern end corresponds to an imaginary line that connects the towns of Aschaffenburg and Würzburg.

The most prominent feature of the investigated area is the basalt hill Wasserkuppe, 950 m above the sea level, located within the Rhön mountains. The lowest point of the area is within the Main river valley at Aschaffenburg, with an altitude of 160 m. The slopes of Spessart and Rhön consist mainly of triassic sedimentary rocks and tertiary basalts. The landscape of Spessart is dominated by sandstones; the vegetation is represented by beeches, pines and oaks, while the vegetation of Rhön is considerably poorer, i. e. it is basically grassland.

From the slopes of Spessart and Rhön (approximately 600 m high) the terrain declines continuously SE-wards to an altitude of about 400 m. The flat eastern part of the area could be divided (although, with certain oversimplification) into large loess formations and torn-apart Muschelkalk regions. The rivers of Fränkische Saale and Sinn largely collect the superficial waters of the area. At Gemünden they converge into the river Main (Fig. 1).

Figure 1 shows the most important sites witin the zone of investigation. It also points out that Bad Kissingen is situated in the center of one of the most important spa areas in Germany..

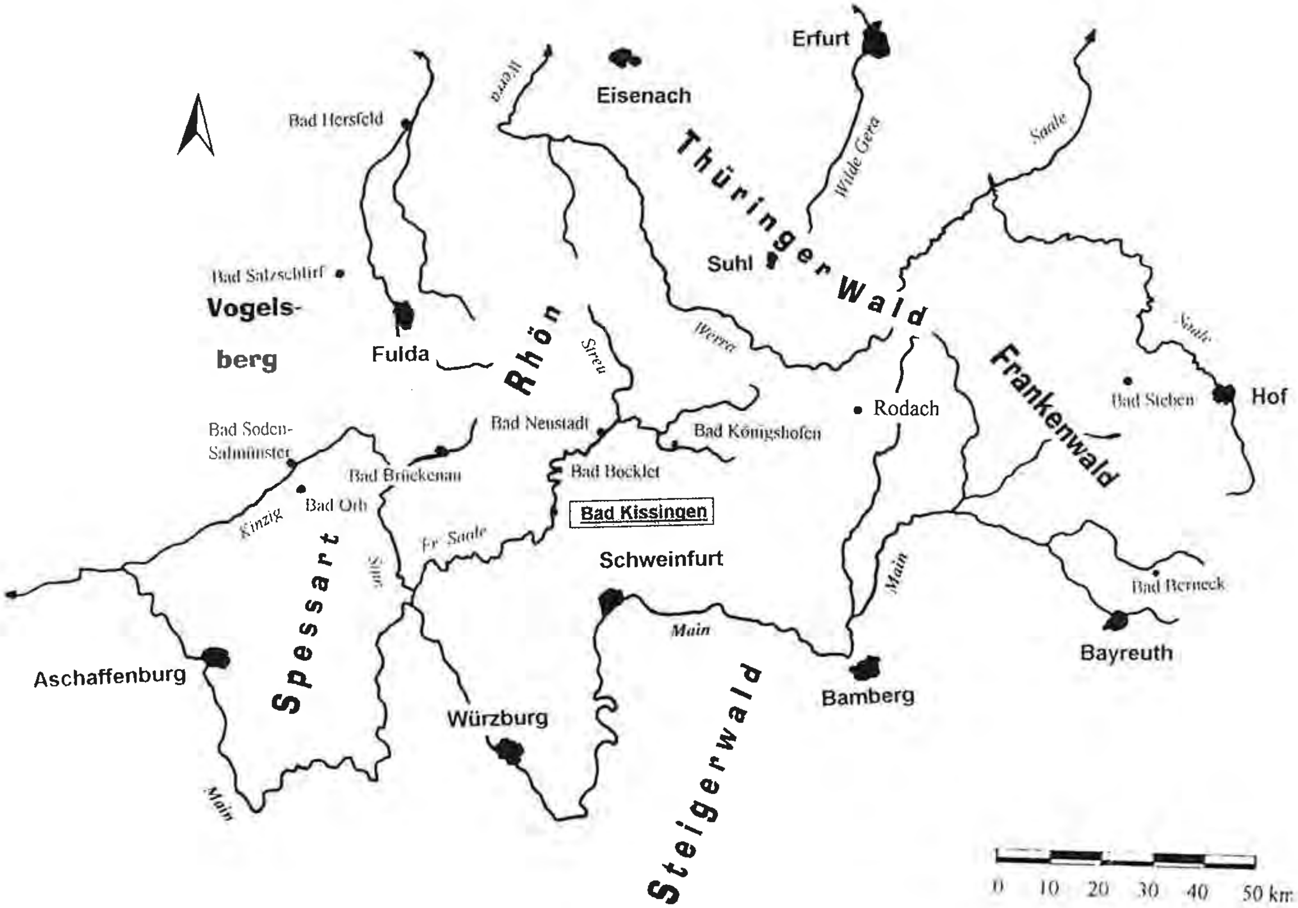

Fig. 1: Area of investigation including the most important sites of the region.
Untersuchungsgebiet mit seinen wichtigsten Lokalitäten.

The deep underground of NW-Unterfranken has been investigated extensively. Publications on this topic also include specialized research covering different geological aspects. Comprehensive geological studies of the area were published by E. RUTTE (1957, 1965, 1981), F. TRUSHEIM (1964) and the BAYERISCHES GEOLOGISCHES LANDESAMT ("BAVARIAN STATE GEOLOGY OFFICE") (1964, 1981).

2.1. Geological formations

2.1.1. Prepermian

Prepermian here refers to all kinds of solid rock that form the crystalline basement. The basement consists of quarzites, micaquarzites, muscovite-plagioclase-gneiss, dolomite marble and orthogneiss. Drillings also revealed granite at Dalherda and Bad Kissingen, mica-schist and feldspargneiss at Bad Brückenau and coarse-crystalline diorite at Volkach (F. TRUSHEIM, 1964, E. RUTTE, 1965). A K/Ar-based age determination in muscovite concentrates, obtained from muscovite-plagioclase-gneiss in Rhön, indicated probable ages of formation of 315 ± 2.8 Ma and 323 ± 2.9 Ma, respectively, corresponding to metamorphosis at the transition from Lower to Upper Carboniferous (F.-P. SCHMIDT et al., 1986). These results fairly overlap those of a similar study of the crystalline basement of Spessart (see W. WEINELT et al., 1985).

2.1.2. Permian

2.1.2.1. Rotliegendes ("Lower Permian")

In the investigated area the Lower Rotliegendes consists mainly of coarse sandy conglomerates and sandstones. Additionally, porphyry, quartz porphyry, tuffs and tuffits are found. The Upper Rotliegendes is dominated by red clay and sand sediments. The Weißliegendes consists of light grey- and white-coloured, mostly fine-grained sands and conglomerates, representing the transition to the Zechstein age. The cementing material of the sedimentary rocks in the Weißliegendes is predominantly carbonate. It is presumed that it originates from sanddunes (U. EMMERT, 1981). In several cases, the transition between Lower and Upper Permian in the hessian-bavarian border area cannot be exactly determined (C. SCHUMACHER, 1985). In the Weißliegendes, non-ferrous metals belonging to the following formations, can be found along with eolian, marine and fluvial compounds.

2.1.2.2. Zechstein ("Zechstein subdivision, Upper Permian")

Zechstein sedimentations begin with Kupferschiefer and Kupferletten, which consist of dark, bitumen- or marl-containing claystone and may include different non-ferrous metal sulfides. Kupferschiefer has been found both in the Spessart-Rhön ridge and in the inner part of the Fränkisches Becken (C. SCHUMACHER & F.-P. SCHMIDT, 1985). In its central part, one observes the disappearance of Zechstein to Werra carbonate and Werra anhydrite down to Werra salts (potassium salts were found in drillings at Mellrichstadt; B. KLARE & B. SCHRÖDER, 1985). At the periphery of the basin, a sedimentation of thin and thick plates of partly cavernous dolomite and limestone, anhydrites and stinkdolomites occurs together with that of terrestrial sedimentary rocks. In some locations, bryozoa reefs have also been found (U. EMMERT, 1981). Zechstein 2 is represented in the entire area by clay anhydrite, while the Zechstein 3 and 4 poorly contributes mainly by clays, letten and anhydrites.

2.1.3. Triassic

2.1.3.1. Buntsandstein ("Bunter, Lower Triassic")

The Lower Buntsandstein appears at the periphery of the Spessart. The stratification of Lower Buntsandstein begins with "Bröckel-" crumbly shale. Alternating layers of claystone and sandstone suggest marine influences on its formation.

The quarzite sandstones begin with the Gelnhausen sequence. They continue up to the Upper Buntsandstein with some interruptions by claystone and pebble interlayers. Sandstones contain mostly iron and manganese and are bound by calcareous or dolomite cement. During the Middle Buntsandstein, long-lasting droughts took place, as evidenced by gypsum and anhydrite evaporites. Increasing marine influences, due to the opening of the Upper-Silesian gate of the Germanic basin, were registered in the Upper Buntsandstein. The varieties range from predominantly clay-containing to salt sedimentations. Sedimentary materials become increasingly sandy toward the periphery of the basin.

The most frequently occurring minerals in the Buntsandstein of Unterfranken are quartz, feldspar, clay minerals, calcite and gypsum. Pseudomorphisms of halite minerals and dolomite are very rare.

2.1.3.2. Muschelkalk ("Muschelkalk series, Middle Triassic")

Wave-limestone ("Wellenkalk") forms a substantial part of Lower Muschelkalk of Rhön up to its SE-borders; several spurs reach Oberfranken ("Upper Frankonia"). The basal basin facies of Lower Muschelkalk is characterized by thick clay layers; at the transition to Middle Muschelkalk they are marl-containing. The peripheral facies of Lower Muschelkalk zone clearly demonstrate the features of fluviatile-marine transitions and vary from sandy to strongly clay-containing.

The basin fillings of the Middle Muschelkalk are of marine origin. Anhydrite and gypsum, with dolomite and clay interlayers, are found reaching up to the area of formation of halite (i. e. the Steigerwald area). Peripheral facies are dominated by sand and clay, interlayered with limestone.

The Upper Muschelkalk is rich in fossils. In the central part of the basin it is represented mainly by the so-called block limestone ("Quaderkalk"). Towards the border of the slope of Keuper formations, the presence of sand- and clay-containing components increases. The periphery of the Muschelkalk sea is characterized by sandy horizones, which are mixed with dolomite interlayers.

2.1.4. Tertiary

During the Oligocene, clay and marl of lacustrine and brackish origin and ligneous coal were sedimentated. Their stratification is frequently interrupted by volcanic material (basalts with ash and volcanic bombs). Age determinations by K/Ar-relations suggested that the tertiarian volcanism of Rhön occurred mainly during the Upper Miocene, however, it probably lasted up to the end of the Early Pliocene. Basalt chimneys and sheets form the relict mountain of large parts of High Rhön.

2.1.5. Quaternary

The large loess- and loess-clay-covers, and several debris accumulations, are of Pleistocene origin, while the soils of the area and several high and low bogs of Rhön were formed during the Holocene.

2.2. Geological-tectonic structure

The geological structure of the surface rocks has been throughly investigated. The author F. TRUSHEIM (1964) compiled the results of several drillings in structural schemes. The data, depicted in fig. 2. are based on the following studies: M. BAUMANN & K.-E. QUENTIN (1987), BAYERISCHES GEOLOGISCHES LANDESAMT (1982), H. GUDDEN & H. SCHMID (1985), P. SCHMITT (1982), F. TRUSHEIM (1964), P. UDLUFT (1969, 1979) and H. VOSSMERBÄUMER (1985). They represent the contemporary thickness and bedding conditions; the tectonic structures were not considered.

The hatched horizontal network in fig. 2 corresponds to altitude above sea level. The figure clearly shows prepermian morphological features in the area investigated. The Fränkisches Becken ("Frankonian Basin") is located in the central part. The deepest part of the basin occurs at the foreland of Steigerwald near Volkach and is estimated to lie at 1100 m below sea level. The filling of the basin is composed mainly of sedimentary rocks of the Rotliegendes and Zechstein. Triassic sedimentations are homogenous and uniformly distributed. They decline flatly SE-wards.

Apart from the Spessart-Rhön ridge ("Spessart-Rhön-Schwelle") and the Steigerwald, several other syn- and anticlines of changing extensions exist, such as the upfold of Thüngersheim, Uffenheim and Steigerwald, and the Grabfeld downfold. The main part of the great quantity of tectonic movements in the investigated area result from leaching salt deposits of the Zechstein formation, thus, leading to collapses of the upper formations into the formed cavities.

2.2.1. Regional-tectonic structures

The main tectonic directions in the area are hercynian (NW–SE) and Rhine-oriented (NNE–SSW); however, divergent secondary influences of Erzgebirge- (NE–SW) and eggic (NNW–SSE) origin also become apparent. Among zones of fault, those of the Heustreu-Hassberg and Kissingen-Hassfurt zone should be emphasized (Fig. 3). The first is approximately 60 km long and extends from the High Rhön in the E, over Heustreu to the Hassberg mountains. The displacement of fault varies between 45 and 240 m. Numerous horsts and grabens were formed in the zones of the fault. They probably resulted from halokinetic changes in the profound underground (E. RUTTE, 1981).

The Kissingen-Hassfurt zone of fault is located some 20 km to the S and runs parallel to that at Heustreu. It commences in the Rhön and roughly follows a line running over Burkardroth, Stralsbach and Bad Kissingen, just north of Schweinfurt, and over Hassfurt to the Steigerwald. The displacement of fault reaches up to 300 m. Apart from the two fault zones described, numerous smaller zones exist, providing a generally complicated picture of syn- and anticlines in Unterfranken (Fig. 3).

2.2.2. Geological-tectonic structures in the area of Bad Kissingen

Several characteristics of the three wells in the park of spa of Bad Kissingen – Rakoczy, Pandur and Max well – are determined largely by the specific geological situation in the 700 to 900 meter wide graben of the Kissingen-Hassfurt zone of fault. Here the Kissingen-Hassfurt zone of fault dislocated Upper Buntsandstein and Muschelkalk from Middle Buntsandstein layers. This process elicits a fine-mesh network of predominantly hercynian fault and joint planes within the city limits of Bad Kissingen.

From the tectonic viewpoint, the park of spa is located in a Buntsandstein-horst, whose flanks consist of Muschelkalk layers. The separation fronts in the Buntsandstein pro-

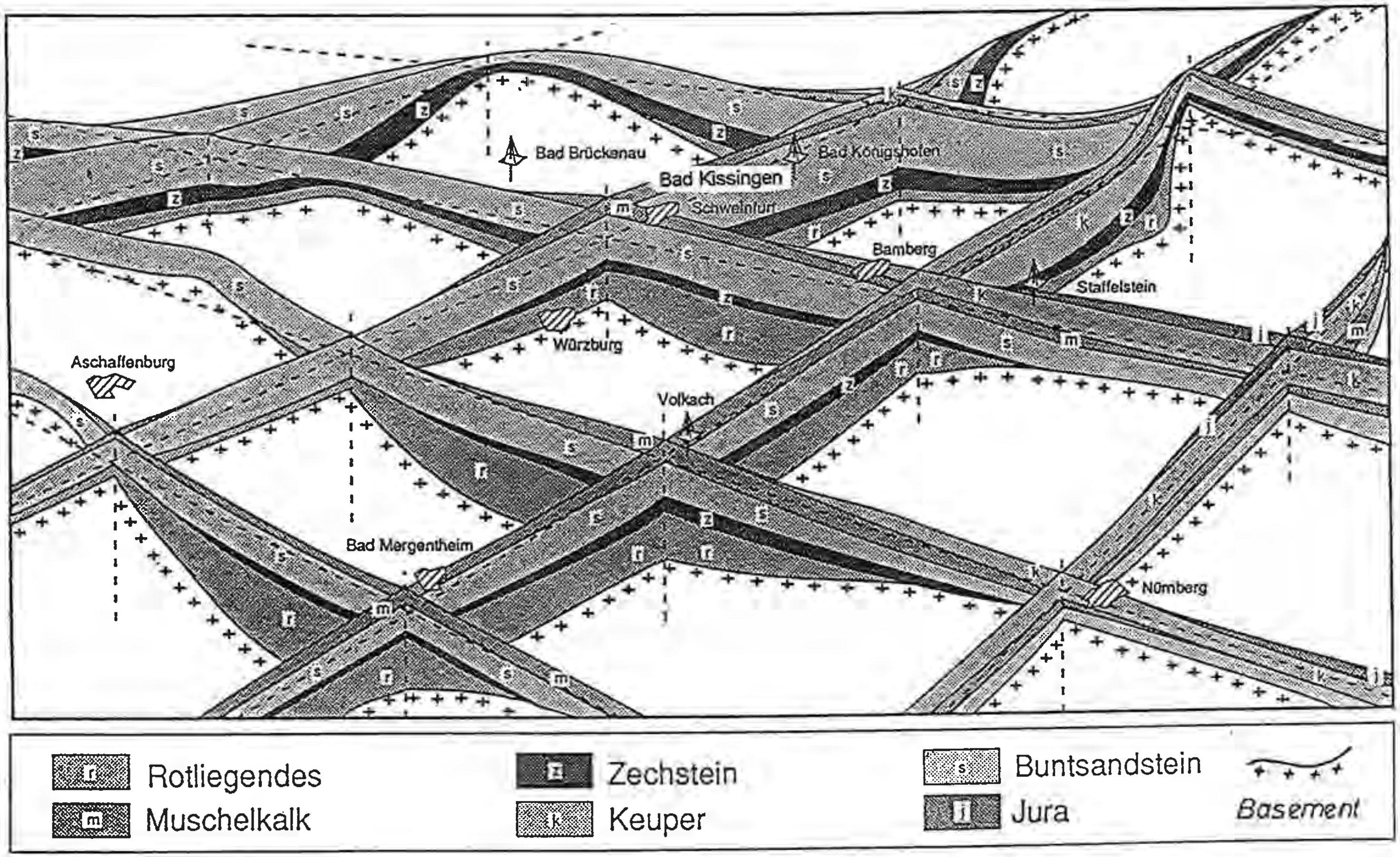

Fig. 2: Geological spatial sections in Unterfranken (size ~1 : 2 500 000; 2.5-fold exaggeration of height).
Geologische Raumschnitte durch Unterfranken (Maßstab ~1 : 2 500 000; 2,5-fach überhöht).

vide the ascent route of highly mineralized ground water. However, quaternary flood plain deposits obstruct its route to the surface and, thus, the deep ground water remains confined. On the other hand, the flood plain deposits mentioned above protect the park of spa springs from anthropogenic impacts.

The geological map of this area (Fig. 4) is based mainly on O. M. Reis & M. Schuster (1914) and on investigations of N. Georgotas (1972), and demonstrates clearly the complexe structure of these mainly hercynian striking faults. NE–SW striking fault planes cross this system secundarily.

Drillings within the park of the spa cleared up the tectonic structure as presented in fig. 5. This tectonic situation and the fractured underground let the mineral waters emerge up to the surface by artesian hydraulic pressure.

The other Bad Kissingen wells, i. e. Schönborn and Luitpold spring as well as the Balthasar-Neumann well in Bad Bocklet, are located outside the Bad Kissingen-Hassfurt fault zone. The Bad Bocklet Balthasar-Neumann well is not a part of the current investigation. However, its protection area is described in chapter 7.

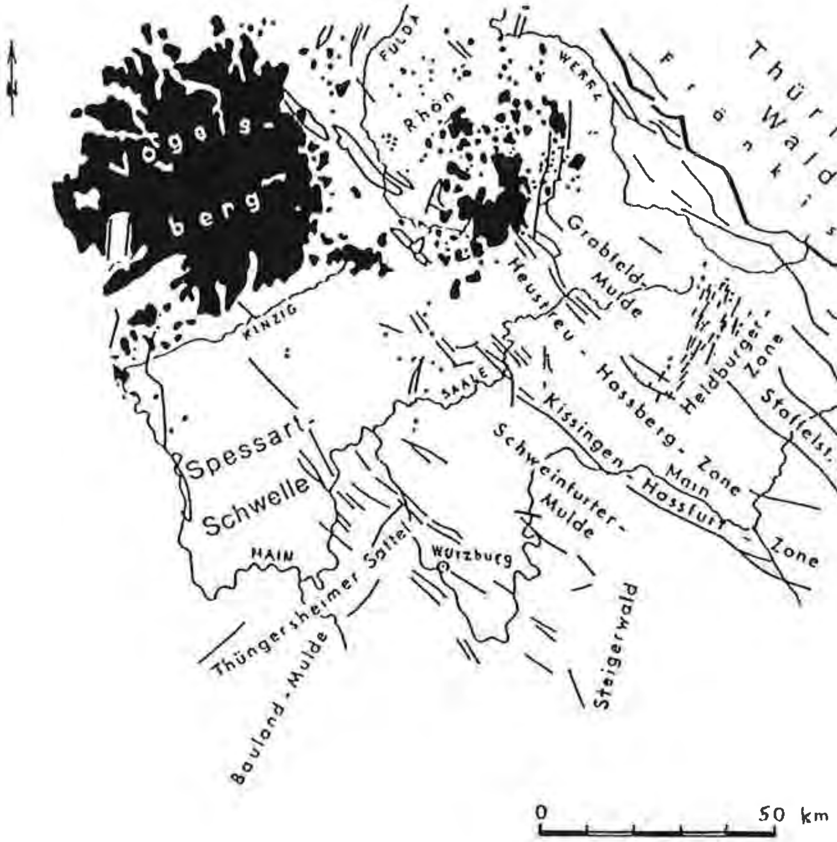

Fig. 3: Map of the tectonic structure (from W. A. Schnitzer, 1978).
Tektonische Strukturkarte (nach W. A. Schnitzer, 1978).

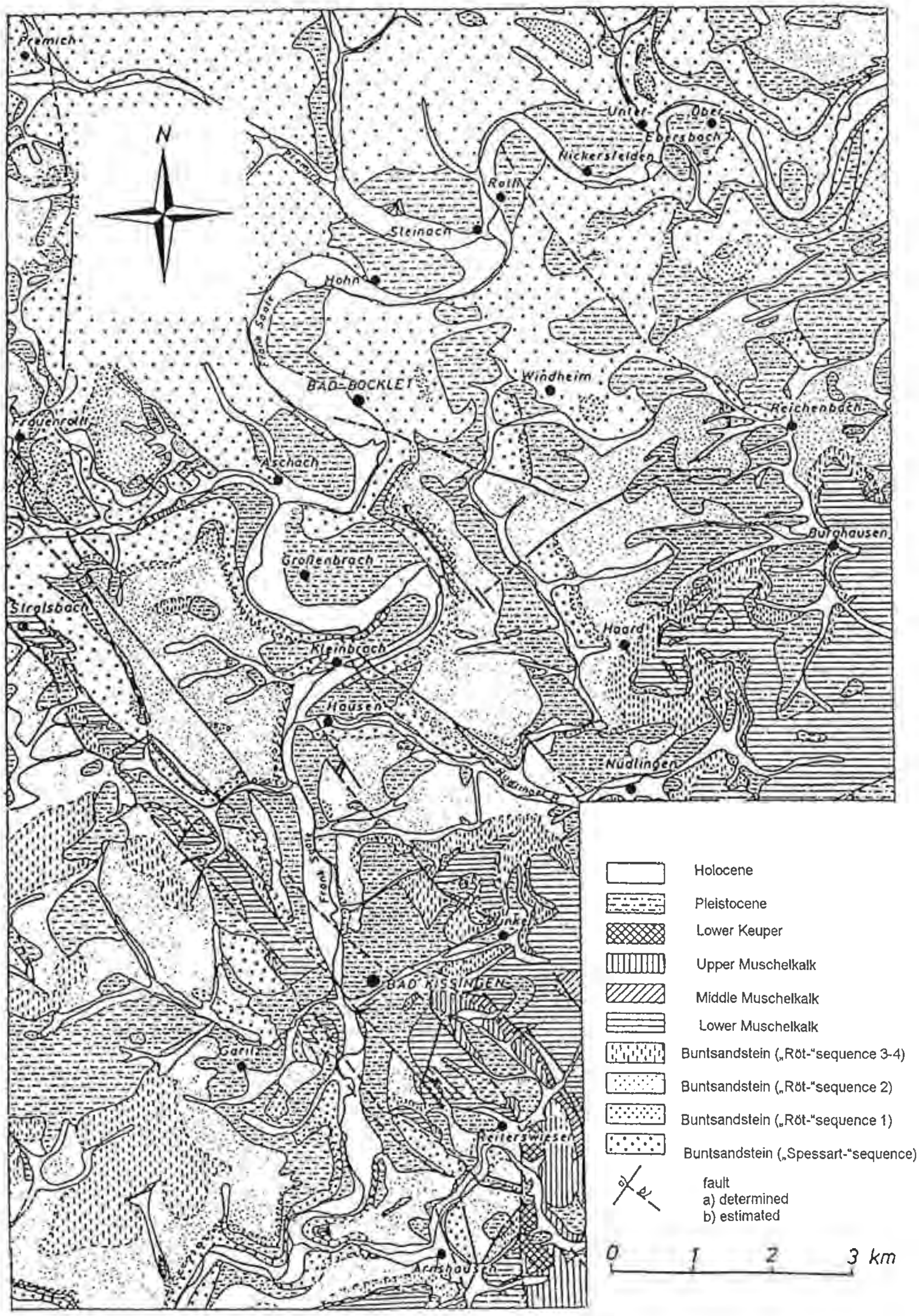

Fig. 4: Geologic and tectonic map of the inner area of investigation.
Geologische und tektonische Karte des inneren Teils des Untersuchungsgebietes.

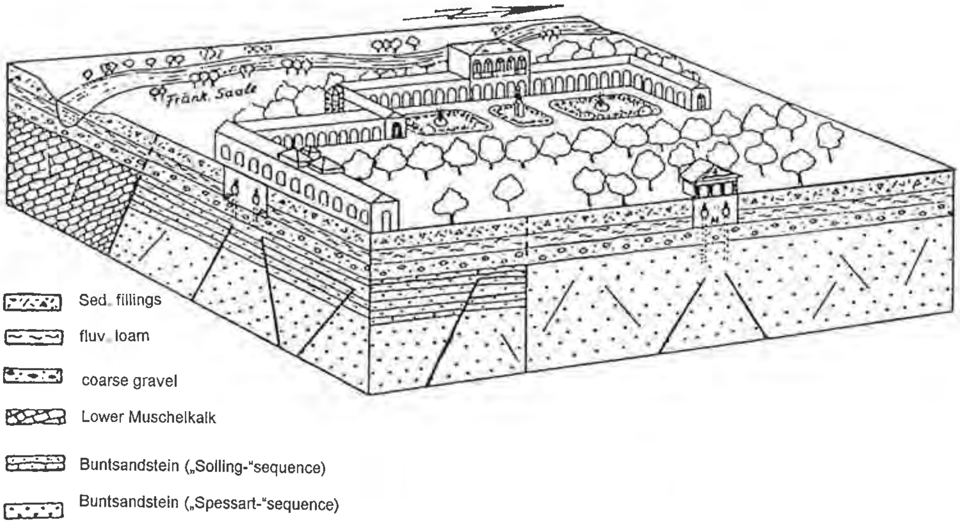

Fig. 5: Bad Kissingen park of the spa as a perspective block.
Kurparkbereich Bad Kissingen als Blockbild.

The Schönborn spring is located, according to M. SCHUSTER (1940), at the intersection of two faults spreading NE and NW, respectively. This drilling penetrated the Buntsandstein formation with a thickness of 464.5 m and ended in the Zechstein formation (Werra series).

However, except the Luitpold spring (in the SW of Kleinbrach), these wells are also connected with faults striking parallel to the Bad Kissingen-Hassfurt fault zone. The Schönborn spring shows a clear connection to NW and NE striking faults in the W of Bad Kissingen (M. SCHUSTER, 1940) and the Balthasar-Neumann spring (Bad Bocklet) gets its deep high mineralized ground water from a WNW–ESE striking fault zone (Fig. 4).

The new drilling of the Luitpold spring is extensively described in chapter 4.3.

3. Hydrogeological overview

3.1. Surface waters

The rivers of Fränkische Saale and Sinn collect the surface waters of large parts of Unterfranken. The river Main, into which they converge, represents the southern border of the investigated area. Comprehensive studies of these rivers were carried out by N. GEORGOTAS & P. UDLUFT (1973, 1978a, 1978b) and P. UDLUFT (1969, 1971). While the river Sinn comprises only the regions of the SE-Rhön and Spessart (Buntsandstein areas), the Fränkische Saale river continues from Grabfeld (Quaternary and Keuper deposits) to Gemünden and alternately traverses Buntsandstein and Muschelkalk domains. The chemistry of the rivers Fränkische Saale and Sinn reflect well the rock composition of their catchment areas (P. UDLUFT, 1971, N. GEORGOTAS & P. UDLUFT, 1973).

3.2. Shallow ground water

The flow of shallow ground water follows the direction of the maximal denivelation of ground water level. Within the first 100 meters of depth, the flow is determined largely by joints and fault planes, but also by karst cavities within the consolidated rocks. This domain comprises a considerable portion of the processes which constitute the interaction between ground water and atmosphere. The waters within this zone are "generally characterized by substantial oxygen saturation, low iron and manganese content and an average temperature which usually corresponds to the mean air temperature of the catchment area" (P. UDLUFT, 1979).

Figure 6 was generated from the appendix of the ground water level map of Bayern 1 : 500 000 (BAYERISCHES LANDESAMT FÜR WASSERWIRTSCHAFT, 1985) and represents, in a simplified form, the surfaces of the corresponding most shallow closed ground water levels. G. EINSELE et al. (1978) determined the maximal circulation depth of shallow ground water in the valley of the Main river (at Erlach/Lohr) to be 80–100 m below ground surface. "Since the output of well drillings does not increase beyond 80 m depth, the permeability of Buntsandstein rocks beyond this depth could be considered negligeable. Thus, a substantial circulation of ground water might end there. Exceptions could occur only in deep and extensive zones of faults."

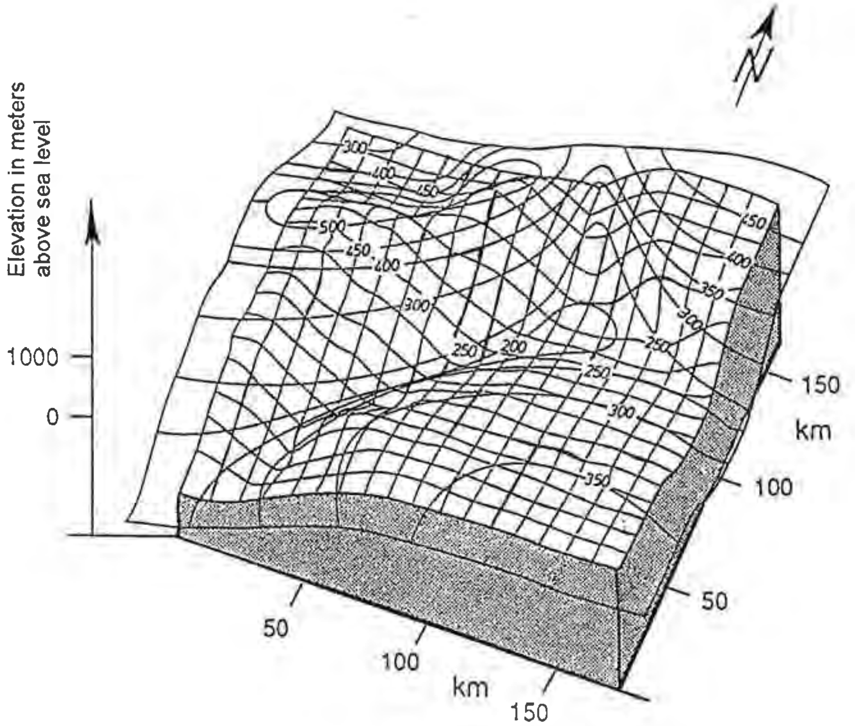

Fig. 6: Contour chart of ground water in Unterfranken (altitudes expressed in meters above sea level). Isolinienplan der Grundwasseroberfläche in Unterfranken (Höhenangaben in Meter über Meeresspiegel).

3.3. Deep ground water

In contrast to that of shallow ground water, the flow velocity of deep ground water is very low. The number of permeable rock apertures decreases with depth and only a few deep, open joints are active in profound zones. The basement may be seen simplyfied as "impermeable".

Flow in deep underground occurs only if the flow system takes an opening or outlet at one or more sites. The direction of flow is determined by the minimal resistance rather than by the maximal denivelation, since the rock matrix is very heterogenous, and tectonic fractures might affect flow direction as well (B. HÖLTING, 1983).

The directions of deep ground water flow in Unterfranken are determined by the morphology of the crystalline basement (P. UDLUFT, 1979). Prepermian may be considered the lowest level of deep ground water flow, and the description of the flow paths are based on this (Fig. 7).

The flow input toward the central part of the "Fränkisches Becken" derives from the ridge flanks, i. e. from the NW, N and NE directions. According to the author

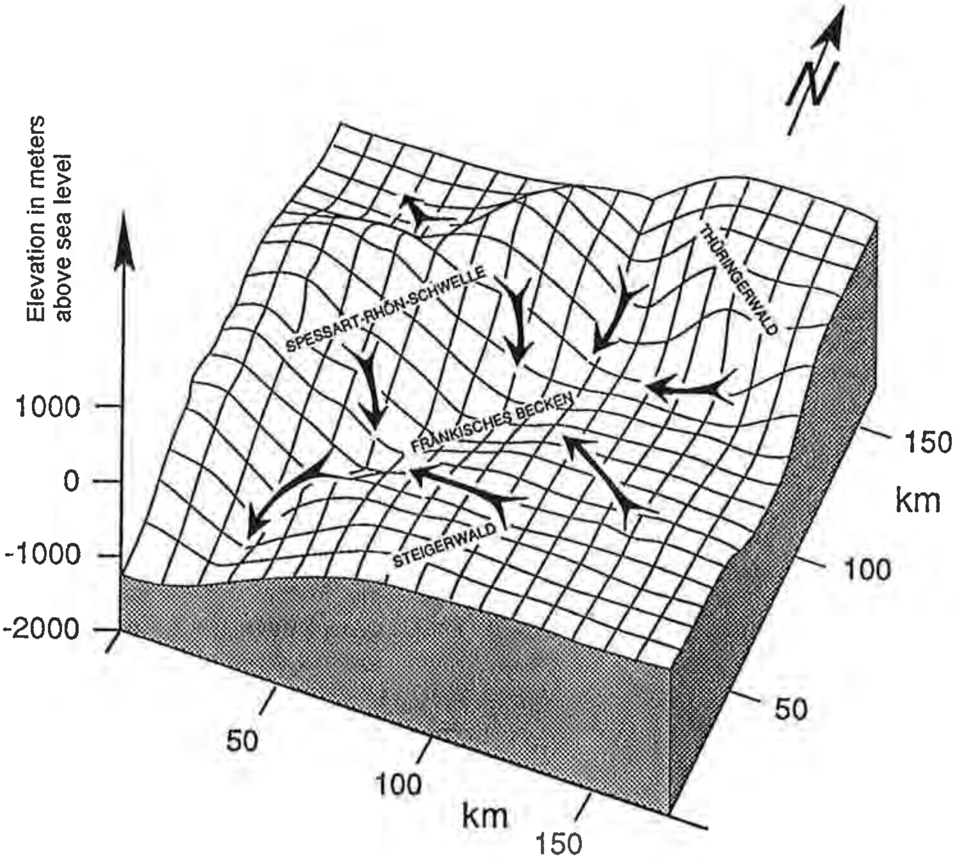

Fig. 7: Flow paths of the deep ground waters in Unterfranken.
Fließwege des Tiefengrundwassers in Unterfranken.

H. KARRENBERG (1981), Rotliegendes sedimentary rocks might provide a hydraulic connection between the Werra through in the N and the Fränkisches Becken in the S. A SW-ward flow direction is supposed in view of corresponding basement denivelation (W. CARLÉ, 1956, 1972). The length of flow paths in Unterfranken might extend from tens to hundreds of kilometers. These waters flow "because of their high density (so-called "Wandersolen") below autochthonous ground water with lower mineral content" (P. UDLUFT, 1979). Figure 7 depicts the basin form of the crystalline basement and the dominant flow directions of deep ground water in the Unterfranken area.

3.3.1. Permeability of joints

Water-permeable joints and faults exert substantial influence, particulary in the quantitative aspect, on the flow of deep ground water in Unterfranken. The joints are formed by tectonic activities or by cooling-induced contraction of the rock associations. Investigations on near surface and underground openings revealed the existence of apertures with widths ranging from a few millimeters to several centimeters. In depths beyond 100 m, the occurence of joints decreases continuously. However, in areas of large-sized faults or lineaments, the fracture zone may extend to substantial depths; hence, water-conducting joints might be present at depths of up to several hundred meters. Figure 3 depicts fault zones and lineament-like faults in Unterfranken. Faults extend mainly from N–NW to S–SE and the direction of flow of deep ground water overlaps fairly with them.

Data on Buntsandstein permeability in Spessart and Rhön have been published by the authors P. UDLUFT (1969 and 1971), G. MATTHESS (1970), DVWK (1983), A. SCHRAFT & D. RAMBOW (1984), and in H. FRISCH (1985). H. FRISCH (1985) determined the general permeability of large sandstone areas in Unterfranken as 3.7×10^{-5} m/s. The average flow-efficient open space volume varied from 0.1–5 %, depending on the corresponding occurrence of joints; however, the actual average presence of cavity volume in internal solid rocks may not exceed 0.1 % (G. MATTHESS & H. MURAWSKI, 1978). Permeability of Rotliegendes in eastern Hessen was estimated as good-to-mediocre by H. KARRENBERG (1981); however, permeability of the deep underground is presumed to be rather poor. The permeability of limestone and dolomite ranges from 10^{-5} to 10^{-3} m/s, while that of sulfate rock ranges between 10^{-5} and 10^{-2} m/s, according to DVWK (1983). The lower values are probably valid for the deep underground of Unterfranken.

3.3.2. Interstitial permeability

Interstitial hydraulic permeability of consolidated rock is considerably lower than that of joints (D. SCHRÄBER et al., 1981). No substantial horizontal differences in interstitial permeability are expected within one and the same facies type. Interstitial storage and flow-effective pore volume in Buntsandstein varies from 0.1–2.5 %. Because of the overburden pressure, pore size decreases downwards. DVWK (1983) pointed out that, at depths beyond 1000 m, pressure-induced quartz melts are intermixed with sandstone and obliterate most of the porosity. Thus, porosity of loose sands in the upper layers (35–40 %) are reduced to 20–30 % in consolidated sandstones, these values corresponding to 5–20 % in sandstone below 1000 m.

Carbonate rock in Unterfranken is dominated by secondary, rather than primary porosity and cavities; however, this does not considerably affect the permeability of deep layers. The effective porosity of limestone and dolomite corresponds to 2–20 %, according to DVWK (1983) and A. PESCHEL (1983).

3.3.3. Water/rock-temperature conditions in the area of Bad Kissingen

Data on temperature conditions in the deep underground of NW-Bayern are scarce. J. Wohlenberg (1982) summarized temperature records and heat flow data in isotherm maps of the Federal Republic of Germany; the curves are also applicable to Bayern (Fig. 8). Similar studies were conducted by V. Cermak (1979), resulting in a curve which represents the average temperature changes in the FRG. Furthermore, investigations of depth-temperature relationships were carried out during drillings of the Luitpold spring (Neu) in Bad Kissingen and in Bad Brückenau.

The data, presented here, originate from the archives of the Institut für Wasserchemie und Chemische Balneologie of the Technische Universität München and from the Dr. Blasy & Mader Ingenieurbüro für Hydrogeologie (pers. comm.; courtesy of Dr. Blasy, 1987).

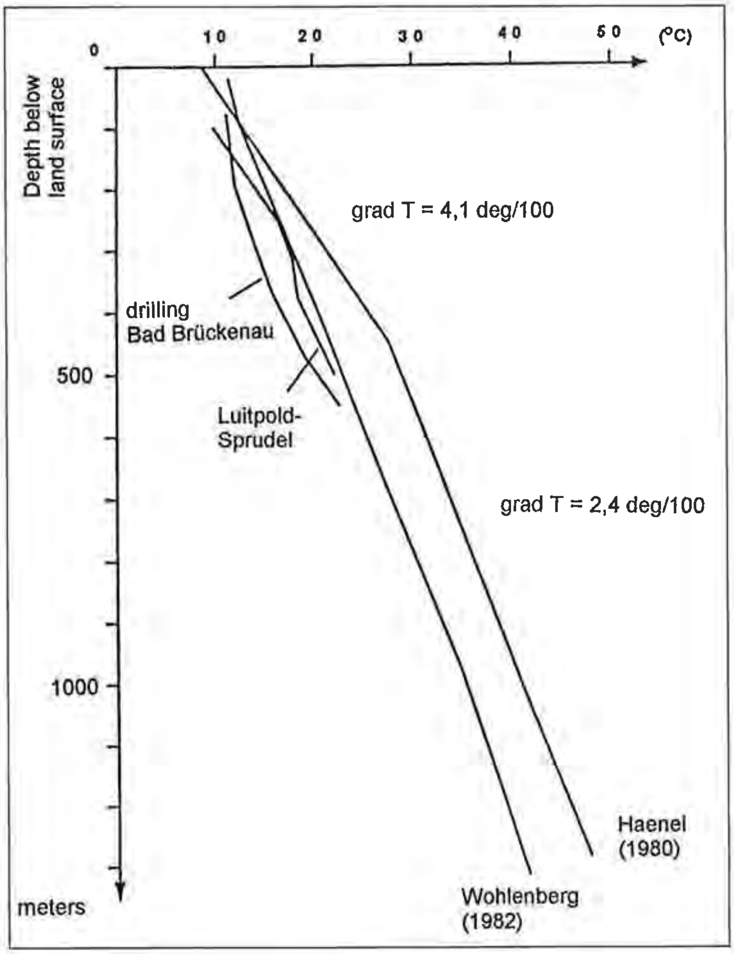

Fig. 8: Depth-temperature-relationship curves in northern Bayern and Unterfranken, and average values for the FRG.
Teufen-Temperatur-Beziehungskurven in Nordbayern und Unterfranken sowie im bundesdeutschen Durchschnitt.

It is evident that the geothermal gradient in Franken is lower than the average for Germany. According to R. Haenel (1980), the temperature gradient in the upper 400–500 m corresponds to 4.1° C/100 m, while at depths beyond 500 m it is 2.4° C/100 m. These data are in accordance with those of J. Wohlenberg (1982); however, the author J. Wohlenberg observed a significant gradient diminution at 300 m depth.

The Luitpold spring (Neu) drilling showed a geothermal gradient of 2.2° C/100 m for the entire upper 500 m. The dominant rock here is sandstone. Its average thermal conductance is with approx. 3.2 W/m deg, somewhat higher than that of several other sedimentary rocks. However, the general thermal conductance is reduced because of the low conductance levels of gases and water in rock cavities or joints; hence, the established temperature gradients appear to be realistic. Deep migration of shallow ground water further contributes to a presumable cooling of aquiferous rocks. J. E. Goldbrunner (1988) provided similar findings for the Austrian "Innviertel" with the infiltration of late pleistocene waters (relatively cold, because of corresponding paleoclimatic conditions) into deep zones which lower the temperature of the underground. Similar relationships may be assumed in Unterfranken too.

Based on the example of Luitpold spring (Neu), with a temperature gradient of 2.2 deg/100 m, we calculated a negative convection heat current density of –0.013 W/m^2 at depths up to 500 m. In accordance with the hydraulic results, described in chapter 4.5., this suggests the existence of a cold transport to the depth, based on the downward flow of ground water that interferes with ascending deep ground water. The conductive heat current density corresponds to 0.07 W/m^2.

In the drilling of Bad Brückenau, a temperature gradient of 2 deg/100 m was found beyond 100 m depth. The convection heat current density was –0.018 W/m^2 (as calculated for depths up to 500 m), while the conductive heat current density corresponded to 0.1 W/m^2. Again, the regeneration of deep ground water by the penetration of shallow ground water should be considered as a determining factor.

Significant differences between N-Bayern and the German average become apparent when absolute temperatures of deep zones are compared. Generally, depth temperatures in Franken are 4–6° C lower than the estimated average for Germany. In Luitpold spring (Neu) this difference reached 7° C. Higher temperatures were registered in the W around Vogelsberg and in the E at Rodach, Colberg and Staffelstein. Hence, the appearance of thermal water in the drilling Schönborn spring in Bad Kissingen should not be considered as an exception. The well provides thermal water with a temperature of 21.2° C, emerging from a depth of more than 500 m. This temperature corresponds well with the temperature conditions of the area.

3.3.4. Quartz temperatures and circulation depths

Circulation depths of springs in Bad Kissingen were determined using SiO_2-geothermometers (Tab. 1). The method is based on the fact that the solubility of SiO_2-phases, such as amorphic SiO_2 or quartz, increases markedly with increasing temperatures. Reversion to a new equilibrium following cooling down occurs with a substantial delay relative to the decrease in water temperature. Changes in pH are not expected to affect the solubility equilibrium of SiO_2, since pH-impacts on this parameter have only been observed at pH-values > 8 (M. Hofmann et al., 1991). The deep ground water of Bad Kissingen is characterized by pH-values of about 7.0. No data are available on SiO_2-concentrations in the Luitpold spring (Neu) well.

Based on the estimated temperature gradient of 0.022 deg/m (see chapter 3.3.3.), these

Tab. 1: Outflow temperatures and quartz temperatures (in °C) and estimated circulation depths (in meter below land surface) of the wells in Bad Kissingen; T_{mes} = measured temperature at outflow.

Austritts- und Quarztemperaturen (in °C) und berechnete Zirkulationstiefen (in m. u. GOK) der Bad Kissinger Quellen und Brunnen; T_{mes} = gemessene Austrittstemperatur.

Bad Kissingen	T_{mes} [°C]	Quartz temperature [°C]	Circulation depth [m. b. l. s.]
Schönborn spring	21.2	5.02	680
Rakoczy spring	12.9	14.8	220
Pandur spring	13.6	19.4	430
Max well	12.3	(0.6)	

data suggest circulation depths of approx. 220 and 430 m for the wells Rakoczy and Pandur, respectively, in Bad Kissingen. The corresponding value for the Schönborn spring is 680 m. The calculated quartz temperature of Max well, however, obviously does not conform with that of the other wells. It should also be noted that, except for the Schönborn spring, quartz temperatures do not indicate real circulation depths, but rather reflect the inflow of cold water of Buntsandstein origin with low concentrations of SiO_2.

4. Hydrogeochemical investigations

Computation models made it feasible to execute complicated calculations within a reasonable time span. The following thermodynamic computations represent an application of this approach. The method permitted the formulation of quantitative statements on the genesis of Bad Kissingen waters, which were beyond our scope a few years ago.

4.1. Dissolved compounds in the waters of Bad Kissingen

Concentrations of the principal compounds in the waters of Bad Kissingen are shown in tab. 2.

The sign Σ will appear frequently in the following text and, as generally accepted in geochemical, chemical and hydrogeological literature, it denotes the sum of the concentrations of all species of a given chemical element. By "sum of concentrations" we refer to the total content of elementary-ionic and complex compounds, involving a given element, which are dissolved in the water.

*Tab. 2: Concentrations of principal compounds and physical-chemical parameters of medicinal waters in Bad Kissingen (concentrations in meq/l, temperature in °C). *): 1 Schönborn spring; 2 Max well; 3 Rakoczy; 4 Pandur; 5 Luitpold spring (Neu).*

*Konzentrationen der Hauptionen und physico-chemische Parameter in den Heilwässern von Bad Kissingen (Konzentrationen in meq/l; Temperatur in °C). *): 1 Schönborn spring; 2 Max well; 3 Rakoczy; 4 Pandur; 5 Luitpold-Sprudel (Neu).*

No.*)	pH	Temp.	ΣNa	ΣK	ΣCa	ΣMg	ΣCl	ΣS	HCO_3^-	CO_2°
1	6.4	21.2	160.4	3.2	37.6	19.1	155.3	35.2	35.2	34.2
2	5.7	12.3	79.6	1.7	21.3	12.3	81.5	14.6	16.4	63
3	5.8	12.9	105.3	2.3	26.9	17.0	113.5	18.8	21.7	69.3
4	5.7	13.6	118.7	2.4	29.7	17.7	129.3	20.0	22.9	72.8
5	6.3	16.9	62.6	1.9	34.0	15.0	47.0	28.6	40.0	85.5

The analytical data were adopted from the studies of K.-E. QUENTIN (1970) and P. UDLUFT (1979), and from the archive of the Institut für Wasserchemie und Chemische Balneologie of the Technische Universität München.

According to P. UDLUFT (1979), the waters in the wells of Bad Kissingen should be considered as allochthonous and autochthonous mixed waters emerging from the Buntsandstein and Zechstein aquifers. This thesis was confirmed by statistical comparisons, with numerous sample investigations, of deep ground waters from several Unterfranken areas (M. HOFMANN, 1990). The dominant components were found to be sodium, chloride and carbonic acid in differing concentrations.

4.2. Thermodynamic computations of Bad Kissingen waters

The term molality denotes the actual electrolyte or ionic concentration, while activity indicates the effective concentration of the corresponding compound. Activity (a_1) and molality (m_1) are directly related, as shown by equation (1):

$$a_1 = m_1 \cdot \gamma_1, \tag{1}$$

where γ_1 = activity coefficient.

Depending on the strength of the electrolyte and its ionic strength, the activity of a given compound differs, more or less, from its concentration. The effective concentration (activity) of electrolytes or ions is inversely proportional to the degree of total mineralization. In contrast, the activity may exceed the concentration when complexed and uncharged compounds occur in waters with high mineral concentrations.

Using the hydrogeochemical computation model PHREEQE (D. L. PARKHURST et al., 1980), we investigated the complex-forming affinity and the activity of the principal compounds in Bad Kissingen mineral water. Additionally, we calculated the saturation ratios for several dissolved minerals.

4.2.1. Complex-forming affinity of principal compounds

The results of the computations are provided as the concentration and activity of the compounds in their thermodynamically-determined distribution in the aqueous solution.

The concentration and activity values shown in tab. 3 were calculated for the principal compounds of Bad Kissingen well waters.

Generally, the ratio of complexed vs elementary dissolved compounds increases with increasing mineralization (ionic strength). In the spa wells Rakoczy, Pandur and Max well, 84 % of calcium appear in its elementary ionic form (as Ca^{2+}) and 16 % exist as dissolved complexes; Schönborn spring and Luitpold spring (Neu) show a somewhat enhanced presence of complexed calcium (77 % elementary and 23 % as complexed). The complex-forming affinities of magnesium and calcium are very similar. The wells in the park of spa contain 82 % of Mg^{2+} and 18 % of dissolved Mg-containing complexes, while the corresponding values for Schönborn and Luitpold spring (Neu) are 74 and 26 % respectively. When compared to the principal compounds mentioned above, sodium, potassium and chloride appear as typical strong electrolytes, characterized by a clear trend of formation of a comprehensive hydrate shell. Thus, in all wells, 96–98 % of sodium, potassium and chloride exist as elementary ions, and only a modest percentage is present in a complexed form. Sulfur in Bad Kissingen wells shows a well-expressed tendency to form complexes. The wells in the park of spa contain approximately 68 %

Tab. 3: Concentrations and activities in Bad Kissingen medicinal waters (mmol/l).
Konzentrationen und Aktivitäten der Hauptinhaltsstoffe (mmol/l) in den Heilwässern von Bad Kissingen.

Species	Rakoczy		Pandur		Max well		Schönborn spring		Luitpold spring (Neu)	
	Concentr.	Activity	Concentr.	Activity	Concentr.	Activity	Concentr.	Activity	Concentr.	Activity
Ca^{2+}	11.7	3.99	11.8	3.92	6.92	2.67	14.8	4.50	6.80	2.46
Mg^{2+}	5.28	1.91	6.56	2.31	4.88	1.97	7.37	2.41	5.88	2.24
Na^+	105.9	80.0	118.9	89.1	65.8	51.3	158.4	116.1	82.8	63.5
K^+	2.31	1.68	2.65	1.90	1.66	1.26	3.21	2.23	1.65	1.22
Cl^-	10.8	80.6	124.0	89.1	67.2	51.1	157.4	109.4	55.6	41.3
SO_4^{2-}	6.33	1.99	7.08	2.14	4.41	1.62	11.58	3.11	5.99	2.03
HCO_3^-	29.7	22.5	34.6	26.0	19.3	15.1	39.7	29.1	59.5	45.9
$H_2CO_3^\circ$	63.9	66.5	62.5	65.4	42.6	43.7	26.0	27.6	69.5	71.8
$CaHCO_3^+$	0.85	0.65	0.97	0.73	0.36	0.28	1.63	1.21	1.04	0.80
$CaSO_4^\circ$	1.40	1.46	1.47	1.54	0.77	0.79	2.60	2.76	0.89	0.91
$MgHCO_3^+$	0.62	0.47	0.87	0.65	0.41	0.32	1.08	0.80	1.45	1.11
$MgSO_4^\circ$	0.59	0.61	0.76	0.79	0.50	0.51	1.22	1.29	0.71	0.73
$NaHCO_3^\circ$	0.95	0.99	1.21	1.27	0.41	0.42	1.79	1.90	1.54	1.59
$NaSO_4^-$	0.97	0.73	1.17	0.88	0.49	0.38	2.39	1.76	0.77	0.59
KSO_4^-	0.026	0.020	0.033	0.025	0.016	0.012	0.063	0.047	0.019	0.015

SO_4^{2-}, 15 % $CaSO_4^\circ$, 7 % $MgSO_4^\circ$ and 10 % $NaSO_4^-$; 65 % of the total sulfur in Schönborn spring is represented by SO_4^{2-}, 15 % by $CaSO_4^\circ$, 7 % by $MgSO_4^\circ$ and 13 % by $NaSO_4^-$; the values for Luitpold spring (Neu) are 72 % SO_4^{2-}, 10.5 % $CaSO_4^\circ$, 8.5 % $MgSO_4^\circ$ and 9 % $NaSO_4^-$.

Carbon-containing compounds in Bad Kissingen water show a clear prevalence of hydrocarbonate ions (HCO_3^-) and non-dissociated carbonic acid ($H_2CO_3^\circ$); the actual proportion of each depends strongly on the corresponding pH-value. J. D. HEM (1988) additionally described a dependence of the ratio $HCO_3^-/H_2CO_3^\circ$ on the temperature and ionic strength. $CaHCO_3^+$, $MgHCO_3^+$ and $NaHCO_3^\circ$ in Bad Kissingen wells together account for about 1.5 % of the total carbon content of the water.

When compared to that of deep ground water in Unterfranken, the percentage of elementary ions and complexed species in the Bad Kissingen wells fits within the mid-range (M. HOFMANN, 1990). With respect to the mineral content of other wells in Unterfranken, the presence of complexed ions in water of Buntsandstein origin (i. e. Bad Brückenau) is usually considerably lower, but increases significantly in water with a substantial proportion originating in Zechstein (i. e. Bad Neustadt).

4.2.2. Concentration, activity and activity coefficient

The activity coefficient γ_1 of ionic-dissolved species in waters is usually close to 1, except for water with a high mineral content. Hence, according to equation (1), the activity of dissolved compounds should be somewhat less than their concentration. Activity coefficient of compounds in complexed form, which are characterized by neutral external charge, may be slightly higher than 1 and thus, activity may exceed concentration (Tab. 3).

Strong electrolytes, such as Na^+, K^+, Cl^-, HCO_3^-, $CaHCO_3^+$, $MgHCO_3^+$, $NaCO_3^-$ and KSO_4^-, are characterized by higher activity coefficients than those of weak electrolytes like Ca^{2+}, Mg^{2+}, CO_3^{2-} or SO_4^{2-}. This is due to the lower charge/radius ratio of stronger electrolytes and by the formation of a hydratic shell around the ion. Thus, the activity of weak electrolytes is mostly considerably lower than their concentration. Activity coefficients of calcium range from 0.30 to 0.38, while these of stronger electrolytes, such as sodium, are between 0.73 and 0.78. The activity of non-charged complexes, such as $H_2CO_3^\circ$, $CaSO_4^\circ$, $MgSO_4^\circ$ and $NaHCO_3^\circ$ slightly exceeds the concentration, with activity coefficients ranging here between 1.02 and 1.06.

Comparisons of activity coefficients of dissolved compounds in the water of Bad Kissingen wells with those of other wells and springs in the surrounding area showed that the activity coefficient of the former resides somewhere between those of typical low-mineralized Buntsandstein waters and Zechstein waters which have a higher mineral content.

4.2.3. Chemical equilibrium of principal compounds, as related to their mineral phases

The saturation index (SI) exhibits the presence or absence of equilibrium between the aqueous solvent and the solubilized mineral phases. This parameter results from the corresponding ionic activity product (IAP) and the temperature-dependent equilibrium constant K_t.

$$SI = \log \frac{IAP}{K_t}. \tag{2}$$

An equilibrium is characterized here by SI values of 0 ± 0.3; saturation index below –0.3 represents under-, and above 0.3 oversaturation.

Table 4 depicts the saturation index of Bad Kissingen wells versus predominant mineral phases in the Unterfranken formations, as calculated using the hydrogeochemical computation model PHREEQE.

The waters of the Rakoczy, Pandur and Luitpold spring (Neu) wells are in equilibrium with the calcite mineral phase; Max well is slightly calcite-undersaturated, while Schönborn spring is slightly oversaturated. The findings suggest ample calcite reserves in the underground. Oversaturation of Schönborn spring might result from CO_2 escape (see also chapter 4.2.4.). As already shown by the calculation of quartz temperatures (see chapter 3.3.4.), a process of water mixing takes place in the emergence zone within the Buntsandstein layers. This assumption is valid for all park of spa wells and for the Luitpold spring (Neu). Intermixing of water of Buntsandstein origin with deep

Tab. 4: Ionic activity product (IAP), temperature-corrected solubility constant (K_t) and saturation index (SI) of the Bad Kissingen medicinal waters.
Ionenaktivitätsprodukt (IAP), temperatur-korrigierte Löslichkeitskonstante (K_t) und Sättigungsindex (SI) der Bad Kissinger Heilwässer.

Phase	**Rakoczy**		
	log IAP	logK_t	SI
Calcite	–8.53	–8.42	–0.11
Dolomite	–17.38	–16.76	–0.61
Gypsum	–5.10	–4.60	–0.50
Halite	–2.19	1.55	–3.74

Phase	**Pandur**		
	log IAP	logK_t	I
Calcite	–8.40	–8.41	0.01
Dolomite	–17.04	–16.76	–0.28
Gypsum	–5.08	–4.60	–0.48
Halite	–2.10	1.55	–3.65

Phase	**Max well**		
	log IAP	logK_t	SI
Calcite	–8.87	–8.41	–0.46
Dolomite	–17.87	–16.73	–1.14
Gypsum	–5.36	–4.60	–0.76
Halite	–2.58	1.55	–4.13

Phase	**Schönborn spring**		
	log IAP	logK_t	SI
Calcite	–7.85	–8.45	0.60
Dolomite	–15.97	16.94	0.97
Gypsum	–4.86	–4.60	–0.26
Halite	–1.90	1.57	–3.47

Phase	**Luitpold spring (Neu)**		
	log IAP	logK_t	SI
Calcite	–8.16	–8.41	0.26
Dolomite	–16.35	–16.75	0.40
Gypsum	–5.30	–4.60	–0.70
Halite	–2.58	1.55	–4.13

ground water from the Zechstein aquifer do not affect calcite saturation here. Undersaturation, such as in Max well, results from the inflow of shallow ground water that is poorly saturated with calcite.

With respect to dolomite, Bad Kissingen wells appear to be both under- and oversaturated. Only water from the Pandur well is in solution equilibrium relating to dolomite. Rakoczy and Max well are slightly undersaturated, suggesting the possibility for inflow of dolomite-undersaturated water of Buntsandstein origin. The undersaturation of Max well is more pronounced than that of the Rakoczy well; thus, an additional influx of shallow ground water must be the case in Max well (see also tab. 4). Oversaturation of dolomite in Schönborn and Luitpold spring (Neu) could be due to release of CO_2 during emergence to the surface, in similarity with the situation previously described for calcite.

Solubility and mineral phase supply are major factors affecting gypsum saturation. All Bad Kissingen wells are undersaturated in respect to gypsum; this fact suggests a limited supply in the underground. An additional component of gypsum undersaturation is the influx of water of Buntsandstein origin with low gypsum saturation.

As with the gypsum saturation conditions, all Bad Kissingen wells are undersaturated in respect to halite. Due to the high solubility of salt in water on the one hand and scarce underground salt supplies on the other, all Bad Kissingen wells contain considerably less NaCl than the anticipated maximal soluble concentration.

4.2.4. Partial pressure of CO_2

The partial pressure of CO_2 and the **HENRY-constant** determine the content of water solubilized CO_2.

$$pCO_2 = K_H \cdot [CO_2], \tag{3}$$

where K_H = HENRY-constant for CO_2.

Table 5 shows the partial pressures of CO_2 in the Bad Kissingen wells and springs.

The CO_2-concentrations in Bad Kissingen wells point to post-volcanic CO_2-production. The profound underground of the still active volcanic part of Rhön is presumed to be the site of CO_2-exhalation. Regional investigations of deep ground waters in Unterfranken revealed that CO_2-content abates with increasing remoteness from Rhön volcanism (M. HOFMANN, 1990). Bad Kissingen is located about 25 km distant from Rhön volcanism; thus, a lower partial pressure of CO_2 would be expected. The calculated CO_2-pressures in the underground of Bad Kissingen suggest the existence of a direct communication to Rhön volcanism by deep-reaching joints, through which dissolved CO_2 proceeds to the area of Bad Kissingen.

Tab. 5: Partial pressure of CO_2 in the Bad Kissingen wells and springs.
CO_2-Partialdruck in den Bad Kissinger Brunnen und Quellen.

Bad Kissingen wells and springs	partial pressure CO_2 [atm]
Rakoczy	1.399
Pandur	1.374
Max well	0.883
Schönborn spring	0.735
Luitpold spring (Neu)	1.486

4.3. Thermodynamic computations of an unidimensional depth profile Luitpold spring (Neu) – Bad Kissingen

Redrilling of the Luitpold spring (Neu), which is located closely to Bad Kissingen, was carried out in 1986. This drilling pierced 480 m of Buntsandstein- and 100 m of Zechstein-formations (Fig. 9).

The Buntsandstein consists of sandstone, interlayered with clay stratas and contains solitary anhydrite and gypsum sequences in its depth portion. The Zechstein is composed mainly of clay and clay schists, interrupted by gypsum-, dolomite-, anhydrite- and limestone-layers (M. BAUMANN & K.-E. QUENTIN, 1987).

Water samples were collected from several drilling depths and the dissolved compounds were analyzed. The results are summarized in tab. 6.

Analysis of the data revealed that a water mixture, originating from the Zechstein basin facies and Buntsandstein, is already detectable at a depth of 100 m. Mineralization increases with advancing depth penetration; a sudden sharp increase occurs between 216 and 300 m.

Tab. 6: Results of the analysis of Luitpold spring (Neu) in mg/l (penetration depth in meter: casing between 100 and 50 m; casing between 150 and 50 m; 216 m with packer at 155.5 m; 300 m with packer at 155.5 m; 581 m/1 with a pump at 353 m; 581 m/2 with a pump at 570 m).
Ergebnisse der chemischen Analyse aus der Bohrung Luitpold-Sprudel (Neu) in mg/l (Bohrteufe in Meter: zw. 100 und 50 m verrohrt, zw. 150 und 50 m verrohrt; 216 m mit Packer bei 155,5 m; 300 m mit Packer bei 155,5 m; 401 m mit Packer bei 160 m; 581 m/1 mit Pumpe bei 353 m; 581 m/2 mit Pumpe bei 570 m).

Penetr. depth[m]	pH	Temp. [°C]	ΣNa	ΣK	ΣCa	ΣMg	ΣCl	ΣS	HCO_3^-	CO_2
100	5.95	13.0	441.5	37	234	113	578	243	1051	1540
150	5.85	13.3	415	38	244	121	530	274	1006	2020
216	6.0	13.2	363	53	115	63	344.5	245	1050	2000
300	6.02	14.4	872	62	424	135	1044	633	1574	3520
401	6.03	15.3	1175	65	551.1	146	1322	760	1915	4430
581/1	6.22	16.8	1770	70	433	187	1719	935	2644	3200
581/2	6.29	16.9	1440	75.4	681.4	182.3	1666	915	2440	3762

4.3.1. Saturation conditions within the profile

We calculated the states of saturation of Luitpold spring (Neu) water with calcite, dolomite, gypsum and halite at different depths. These results are presented in fig. 9.

The saturation index curve parallels that of electrical conductivity shape of these curves suggests that ground waters in the investigated profile may be placed into two categories. The yields, as estimated by pumping sessions, suggest the existence of a horizon of low permeability at a depth of approximately 220 m. Alternating layers of clay and sandstone act as a separator between the two ground water-bearing levels.

Water with a significantly higher degree of mineralization emerges from depths beyond 300 m. Increasing mineral content is associated with an increase of saturation index and, at the final depth, saturation equilibrium is established in respect to calcite, dolomite and gypsum. With respect to halite, the water is clearly undersaturated within the whole profile investigated.

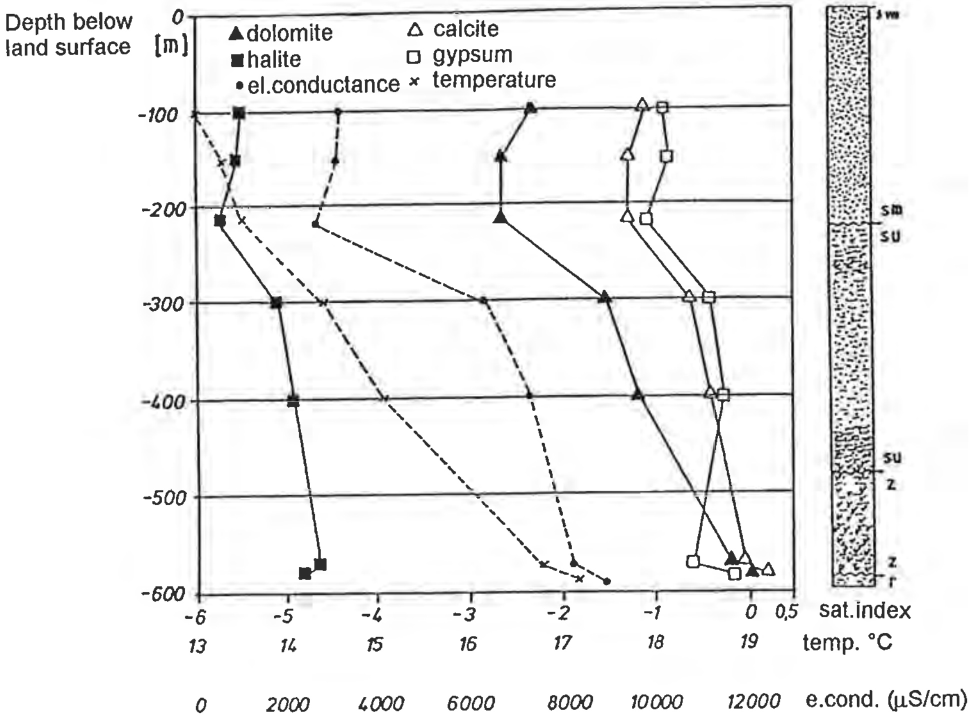

Fig. 9: Saturation conditions with different mineral phases at different depths.
Sättigungsverlauf gegenüber verschiedenen Mineralphasen in verschiedenen Tiefen.

4.3.2. Thermodynamic computations of the genesis of Luitpold spring (Neu)

The drilling profile and the results of hydrochemical investigations suggest that a hydraulic-geological-related stratification of the water may exist in Luitpold spring (Neu). The main subtype is located above the impermeable layers at a depth of approximately 220 m.

This allochthonous mixed water is diluted during its flow path and also locally by shallow ground water. The water found beyond 300 m is also of mixed character; however, no dilution by shallow ground water occurs.

Based on these hydraulic considerations, a three-step simulation of the genesis of deep ground water in Luitpold spring (Neu) was carried out, using the computation program PHREEQE. This permitted quantification of hydrochemical processes and thermodynamic parameters related to the genesis of the water.

The computation was based on an analysis of shallow ground water originating from the Middle Buntsandstein (sm) of Spessart (N. GEORGOTAS & P. UDLUFT, 1978b). The column (sm) in tab. 7 represents the data of this analysis. Carbon dioxide partial pressure and temperature were employed as additional parameters in thermodynamic calculations. The pH-values of computation-related waters were determined anew by model calculations.

The first step involved equilibration of water of Buntsandstein origin with dolomite and gypsum at a partial pressure of CO_2 of 1050 hPa and temperature of 14° C.

Tab. 7: Simulation of the genesis of Luitpold spring (Neu) (deep ground water).
Simulation der Genese des Luitpold-Sprudels (Neu) (tiefes Grundwasser).

Analysis	(sm)	L1	L2	L3	Luitpold-spring (Neu)
		1st step saturation to gypsum & dolomite	2nd step 92,8% L1 7,2 zr mixed	3rd step ion exchange Ca+Mg→Na	
P_{CO2}	–	0.015	0.086	0.18	–
Temperature (°C)	7.5	14.0	14.72	17.0	16.9
pH	5.6	6.1	6.15	6.0	6.3
ΣCa (meq/l)	0.2	22.2	25.8	17.9	17.1
ΣMg (meq/l)	0.04	7.44	9.48	7.72	7.56
ΣNa (meq/l)	0.2	0.17	44.5	63.9	63.2
ΣK (meq/l)	0.05	0.05	1.32	1.32	1.94
ΣCl (meq/l)	0.3	0.25	46.26	46.3	47.4
ΣS (meq/l)	0.2	14.7	17.7	17.7	14.4
HCO_3^- (meq/l)	0.02	27.5	31.6	32.2	35.4
$H_2CO_3^\circ$ (meq/l)	0.15	47.1	44.7	62.2	63.2

This resulted in an increase of ΣCa-, ΣMg-, ΣS- and ΣC-contents to levels resembling those of water originating from peripheral Zechstein facies (i. e. Siebener spring, Bad Brückenau, P. Udluft, 1969).

The second step simulated the penetration of the so-called "peripheral Zechstein facies" water into the Zechstein basin. These autochthonous ground water types were mixed according to hydraulic preconditions (see chapter 3.3.). We used the chloride content of the primary solution (**L1**) and of the Luitpold spring (Neu) as a measure of the mixing ratio of the two components. The calculated mixing ratio involved 92.8 % of the primary solution and 7.2 % of water from the Zechstein basin (**zr**, as emerging for example at Bad Neustadt; M. Hofmann, 1990). The corresponding calculated pCO_2 was 1235 hPa, the mixing temperature was 14.72° C and the resulting pH was 6.15. It is obvious that after step 2 the values for ΣCa-, ΣMg- and ΣNa-contents do not overlap with those of Luitpold spring (Neu). This fact suggests the possibility of cation exchange.

The adjustment of ΣCa-, ΣMg- and ΣNa-contents was carried out in **the third step.** During the simulated ion exchange, 7.9 meq/l of ΣCa and 1.76 meq/l of ΣMg were attracted by the exchanging medium, while 19.4 meq/l of ΣNa were delivered to the solution. The accessory conditions corresponded to pCO_2 of 1533 hPa and temperature of 17° C.

The final calculated values correspond well with those of water from the Luitpold spring (Neu). Only the ΣS-content of the simulated solution was higher but this could be released from the system as H_2S.

The hydrochemical processes considered in this study appear very close to the real conditions, as evaluated previously. Both the accessory parameters of the simulation and the amounts of principal compounds exchanged, correspond to values suggested for the Bad Kissingen area by N. Georgotas (1972) and M. Hofmann (1990).

5. Hydrodynamics

This part of the study considers the relative importance of several physical-hydrodynamic processes in the genesis of Bad Kissingen waters. These investigations could both explain the problem of the site of regeneration of emerging deep ground water in Bad Kissingen and describe the factors responsible for the motion of ground water.

5.1. Principles of model computations

The model proposed by W. E. Sanford & L. F. Konikow (1985) allows a simulation of ground water flow in association with the transport of chemically conservative compounds. The program is particularly appropriate for calculations of hydrodynamic processes involved in the genesis of Bad Kissingen water because of its applicability in cases of density-dependent flow with simultaneous consideration of diffusion and dispersion processes. However, the fulfillment of three important requirements is a prerequisite for the application of this model:

(1) **The flow must be reduceable to a two-dimensional case and one of the coordinate axes must be parallel to gravity (z-axis).**
(2) **The transported chemical compounds must be conservative, i. e. they should not participate in any reaction during their motion.**
(3) **The density and viscosity of the fluid should depend only on the concentration of the dissolved compounds, but not on underground temperature.**

The case of a stationary flow was employed for the computation of hydraulic conditions, i. e. the applied parameters were considered as independent of the temporal dimension.

Flow conditions were determined using the transport of chloride ions as a measure. The distribution of chlorides in the drilling Georgi spring (P. Udluft, 1979) in Bad

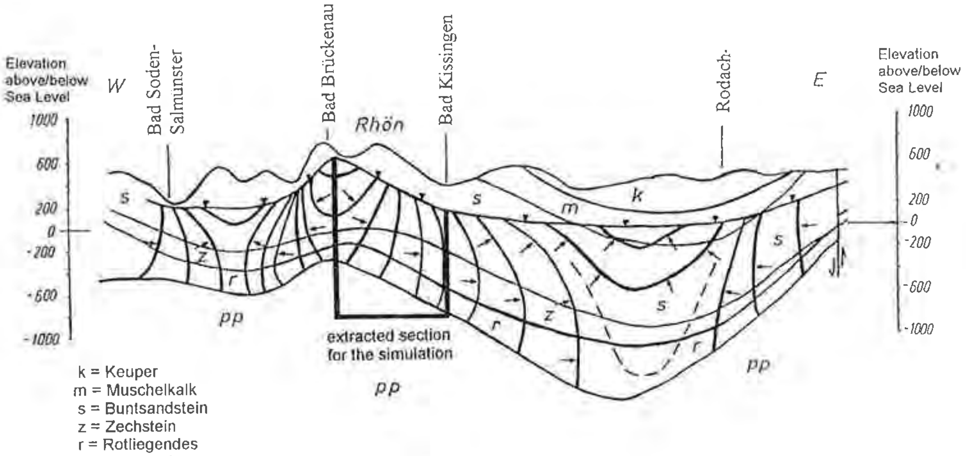

Fig. 10: Location plan of the investigated area, geological stratification (after P. Udluft, 1979) and grid net.
Lage des untersuchten Gebiets (Profilschnitt), seine geologischen Einheiten (nach P. Udluft, 1979) und Gitternetz.

Tab. 8: Input parameters for the simulation of chloride distribution at the SE-periphery of the Spessart-Rhön ridge.
Eingabeparameter zur Simulation der Chloridverteilung auf der SE-Flanke der Spessart-Rhön-Schwelle.

Absolute permeability	5.5 bis 0.1×10^{-7} m^2
Ratio of horizontal/vertical permeability	0.75
Effective porosity	0.12
Initial pressure conditions at the upper simulation line	3.12 bis 0.7×10^6 Pa
Initial chloride concentration	10–8000 mg/l
Longitudinal dispersivity	30.5 m
Ratio of longitudinal/transversal dispersivity	0.2
Molecular diffusion coefficient	0.031 cm^2/s
Grid bar distance (X axis)	1000 m
Grid bar distance (Z axis)	50 m
Total simulation time	35000 a
Convergence criterion	0.000001

Brückenau (W-NW-side) and in Luitpold spring (Neu) in Bad Kissingen (E-SE-side) was used for calibration of the system. The calculated area between Bad Brückenau and Bad Kissingen comprises 14.4 km² and was divided into smaller areas by a horizontal (1000 m bars) and vertical (50 m bars) grid. In fig. 12 and 19, the prepermian basement represents the relatively impermeable underground. The stratification of other geological formations is depicted in fig. 10.

The calibration experiment generated the input parameters (Tab. 8).

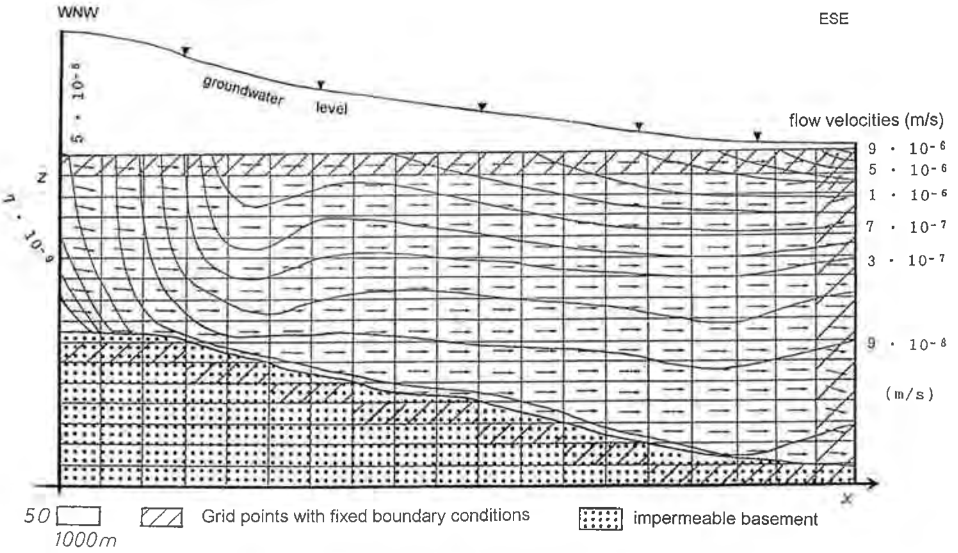

Fig. 11: Flow velocities and directions (see text).
Strömungsgeschwindigkeiten und Fließrichtungen (Erläuterungen im Text).

Prepermian was assumed impermeable. The E-SE-border was defined as a constant-flux boundary, while the W-NW-border was set as a watershed (no-flow boundary). Figure 11 depicts the flow velocities at the grid nodes (contour lines); the arrows indicate the flow directions. In the W-NW-periphery, flow velocities are minimal and decline little with progressing depth. The highest flow velocities were evaluated at the upper edge of the E-SE-boundary; they abate with increasing depth.

A short estimation of the flow velocities leads to a deep ground water age of the Bad Kissingen of approx. 20 000 years; this also indicates that the waters were infiltrated during the last glacial age of Würm. This corresponds well to the results evaluated for the ground water temperatures in chapter 3.3.4.

5.2. Development of the present chloride distribution pattern in the underground of Bad Kissingen

Our intention was to mimic the events which led to the contemporary distribution of chlorides in the wider underground of Bad Kissingen. Flow directions are indicated by arrows in fig. 11. Our starting point was a hypothetical chloride distribution pattern, which could result from the solubilization of Zechstein salts (Fig. 12). The highest chloride concentrations are located within the early salt deposits of the Zechstein. Figures 13 to 18 show the changes in chloride distribution patterns over a time-span of 720 years. The data presented in the figures are "separated" by periods of 120 years each. The situation after 35 000 years is depicted in fig. 19. At the end of the simulation period a steady final condition, closely resembling the present status was established.

A considerable portion of the chlorides migrate downwards as after as short a period as 120 years, while another portion expands upwards (mainly due to diffusion!). At the W-NW-side of the simulation area (Bad Brückenau) chloride-sparse ground water penetrates into E–SE (Bad Kissingen) in a downward direction. As a result, dense chloride-rich deep ground water migrates E-SE-wards to the underground of Bad Kissingen, forming an additional diffuse mixing zone (range from 20–100 mg/l Cl^-.

With advancing time, it becomes evident that chloride broadens at the Bad Kissingen side. Horizontal stratification of low- to high-chloride-containing ground water (from top to bottom) becomes increasingly apparent. Within the following time periods chloride migrates in an E-SE-direction and their concentration decreases. Similary, the mixing zone between low-mineralized and salt-bearing ground water declines stepwise and, at the end of the simulation period a homogenous increase of chloride con-

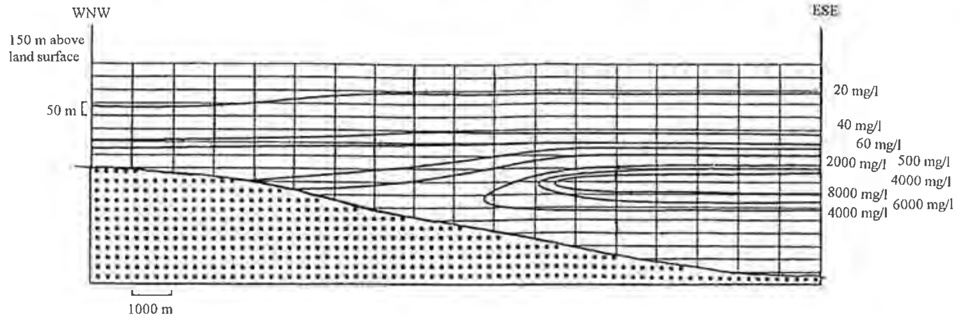

Fig. 12: Chloride distribution after 0 years (initial INPUT); profile 20-fold enlarged.
Chloridverteilung nach 0 Jahren (Anfangszustand); Profil 20-fach überhöht.

centrations is established in both horizontal (from W–NW to E–SE) and vertical directions.

A comparison of the chloride distribution patterns after 480 (Fig. 16) and 35 000 years (Fig. 19) reveals that the changes within this period are rather irrelevant and the conditions after 35 000 years may be considered as more or less stable. Only the concentrations are steadily reduced since, according to the mathematical input parameters, no additional chloride supply was provided. The positions of the 500 and 1000 mg/l concentration lines are characterized by their striking stability.

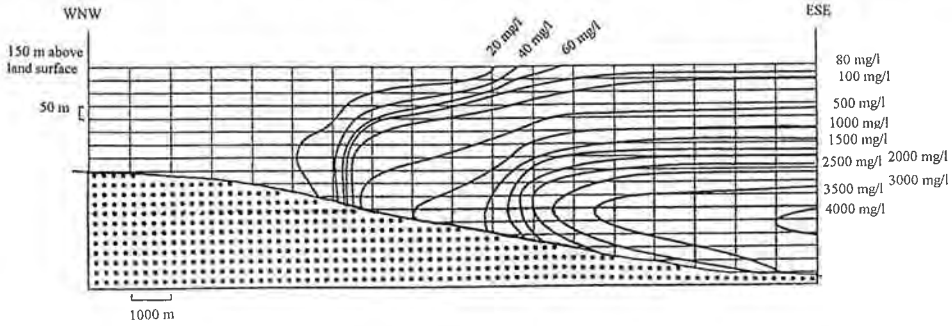

Fig. 13: Chloride distribution after 120 years; profile 20-fold enlarged.
Chloridverteilung nach 120 Jahren; Profil 20-fach überhöht.

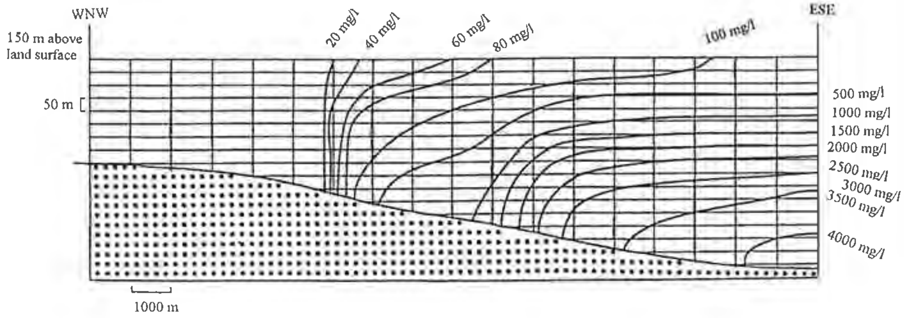

Fig. 14: Chloride distribution after 240 years; profile 20-fold enlarged.
Chloridverteilung nach 240 Jahren; Profil 20-fach überhöht.

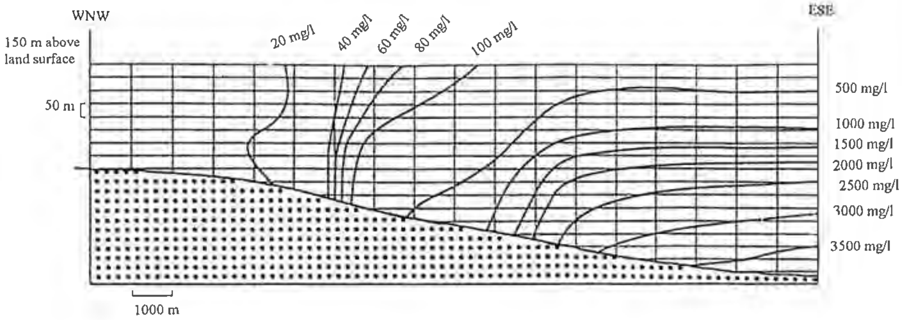

Fig. 15: Chloride distribution after 360 years; profile 20-fold enlarged.
Chloridverteilung nach 360 Jahren; Profil 20-fach überhöht.

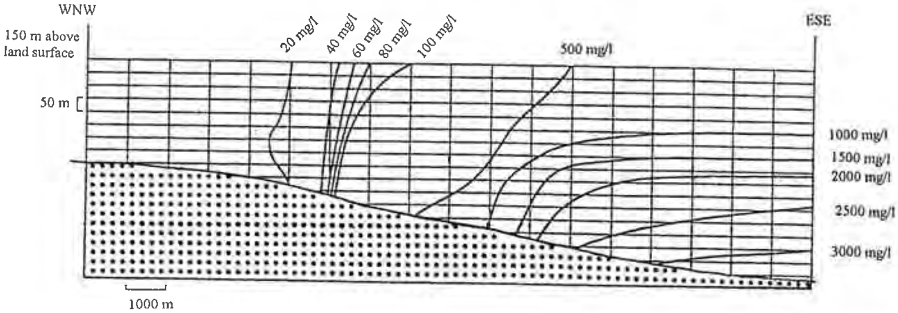

Fig. 16: Chloride distribution after 480 years; profile 20-fold enlarged.
Chloridverteilung nach 480 Jahren; Profil 20-fach überhöht.

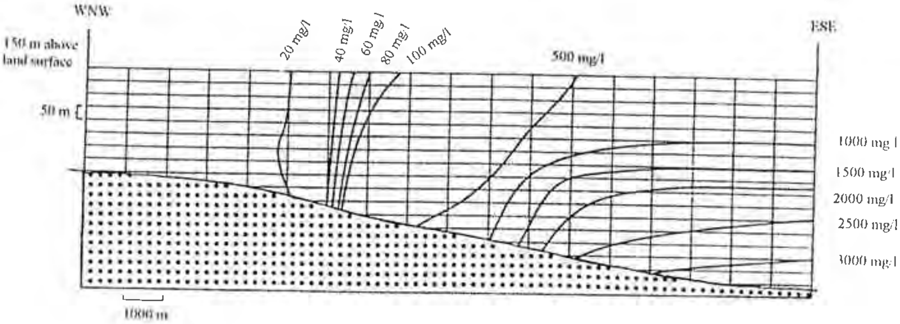

Fig. 17: Chloride distribution after 600 years; profile 20-fold enlarged.
Chloridverteilung nach 600 Jahren; Profil 20-fach überhöht.

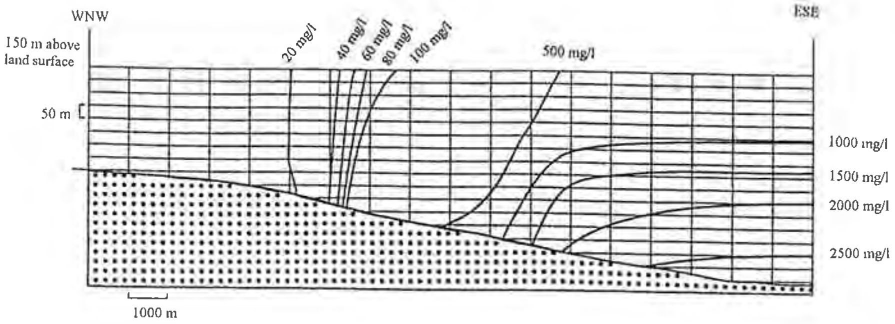

Fig. 18: Chloride distribution after 720 years; profile 20-fold enlarged.
Chloridverteilung nach 720 Jahren; Profil 20-fach überhöht.

5.3. Contemporary chloride distribution pattern in the underground of Bad Kissingen

The chloride distribution at the SE edge of the Spessart-Rhön ridge is presented in fig. 19 in a form intended to depict a situation free of anthropogenic impacts (i. e. withdrawal from wells).

The left edge of the simulation area (Georgi spring in Bad Brückenau) is characterized by low chloride content, resembling that of Buntsandstein- or peripheral-Zechstein-emerging water (10–18 mg/l). However, as mentioned by P. UDLUFT (1969) and N. GEORGOTAS & P. UDLUFT (1978c), the chloride content of Georgi spring increases since drilling (initially, 3 mg/l, presently, approx. 1 g/l). In contrast, the Siebener spring in its vicinity is characterized by a permanently low chloride content. This fact illustrates how sensitively chloride distribution may react to different water withdrawal rates, drilling position and CO_2-content.

The E-SE-side of the profile (drilling Luitpold spring (Neu) in Bad Kissingen) is characterized by a different phenomenon. Due to diffusion and gravity-induced differentiation, a chloride stratification occurs here, ranging from 650 mg/l Cl^- in the vicinity of ground water level to 2100 mg/l Cl^- at the bottom of the basin.

The situation closely resembles the contents observed in the drilling of Luitpold spring (Neu) (see chapter 4.5.), when phenomena such as gas-lift are not taken into account. Artesian, ascending chloride-rich deep ground waters are known to exist in the area of Bad Kissingen and Bad Bocklet. Their hydrostatic pressure suggests a considerable flow potential (see chapter 5.4.5.), but also the existence of gas-lift effects (see chapter 5.3.1.).

The chloride distribution in ground water may be explained by circulation of the relatively deep ground water, associated with a high diffusion within the slow-flowing water. B. HÖLTING (1983) describes comparable conditions in the Hessisches Becken which borders the area in the W: "once the Zechstein series are reached, the water levels (usually salt-containing) escalate abruptly, above the surface of the terrain in valleys, or a few meters below it in higher located regions. The (salt-containing) Zechstein water must be more confined and its hydraulic potential significantly exceed those of overlaying stratifications."

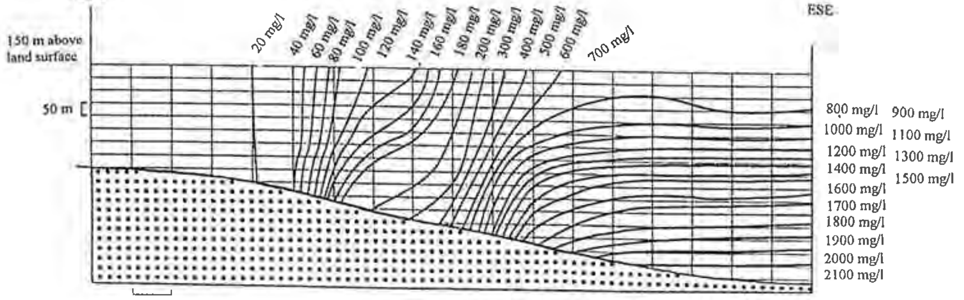

Fig. 19: Chloride distribution after 35 000 years; profile 20-fold enlarged.
Chloridverteilung nach 35 000 Jahren; Profil 20-fach überhöht.

In the zone located immediately below the terrain surface, mixing with shallow low-mineralized ground water may be presumed. Thus, in this zone where a substantially larger turnover of ground water takes place, the existence of a clear-cut boundary between chloride-containing and almost chloride-free ground water should be anticipated. The wells Rakoczy and Pandur in Bad Kissingen, in which high sodium chloride concentrations are observed at low depths, are partially sheltered from this effect by alluvial covers. However, as previously mentioned, influx of shallow ground water occurs in Max well. In the wells Schönborn and Luitpold spring (Neu), ground water emerges from more profoundly situated sources and, in similarity with the Rakoczy and Pandur wells, only typical Buntsandstein and Zechstein ground water can be distinguished in the mixture.

The situation depicted in fig. 19 results from the computation of a stationary process, and interfering factors such as gas-lift or ground water turnover in fault planes and joints have been largely neglected. The calculated chloride distribution is based on pressure conditions and hydrodynamic dispersion after 35 000 years. The calculations showed that under slow-flow conditions the effect of dispersion was negligible (in contrast to diffusion processes). The steady-state densities range from 0.99 kg/cm^3 in the W-NW-part of the investigated area to 1.02 kg/cm^3 at a depth of 1000 m at the E-SE-edge of the simulation area. The calculated viscosities range between 0.001 Pa s in the W-NW-part and 0.00155 Pa s at the bottom of the E-SE-part.

6. Synopsis of hydraulic and hydrogeochemical results

The aim of the investigation was to explore the overall aspects of the genesis of Bad Kissingen waters and to quantify mixing ratios as well as possible influences of superficial impacts. For this purpose, we determined several hydrochemical characteristics of Bad Kissingen water using thermodynamic calculations, and conducted quantitative investigations of hydrochemical processes in the underground. Further, we carried out measurements of hydrodynamic parameters which characterize the flow conditions in the deep underground and affect Bad Kissingen water qualitatively and quantitatively.

As a result of the paleogeographical development of the area, conglomerates occur above the crystalline prepermian basement in the Rotliegendes deposits and limestone, dolomite, anhydrite and gypsum are found in peripheral Zechstein; the halite deposits of the Zechstein formation within the basin are mostly outwashed (F. TRUSHEIM, 1964). Clay minerals, quartz and feldspar occur in the Buntsandstein. The soluble mineral fractions among the listed types determine the hydrogeochemical properties of deep ground water.

The flow of deep ground water in Unterfranken is determined largely by the morphology of the crystalline basement. The Fränkisches Becken is considered as a collector of the water influx from the peripheral zones. Water of high density flows into the basin from the N and mixes in its central region with deep ground water of low mineral content emerging from the Spessart-Rhön ridge. The outflow from the Fränkisches Becken occurs in a SW-direction (W. CARLÉ, 1956), probably toward the Oberrheingraben structure ("Upper Rhine graben") (P. UDLUFT, 1979). Within the described flow system, Bad Kissingen is situated in the foreland of the Spessart-Rhön ridge, which inclines NW-wards.

The flow of shallow ground water occurs through fractured and jointed Buntsandstein aquifers in NW-Unterfranken, karstic Muschelkalk in middle Unterfranken and porous, partly fractured Keuper sediments in the region of its eastern boundary.

The circulation depth of shallow ground water ranges from approx. 100 m in areas with steep ground water level declines (i. e. a SE-slope of Spessart) to approx. 250 m in flatly ground water where the main portion of circulating water takes place at depths up to 60 m in the Rhön-Spessart area and up to 150 m below the surface in the Bad Kissingen area. Beyond these depths at the beginning of the deep ground water zone, the flow could be considered stationary.

Substantial portions of the deep ground water flowing toward Bad Kissingen takes place through rock apertures of tectonic origin (joints, fractures, and faults); their hydraulic efficiency extends to depths of more than 1000 m. The periphery of the Fränkisches Becken is dominated by deep ground waters of low mineral content, while in the central part of the basin (Bad Kissingen) with advancing flattening of the ground water level, high mineralized ground water is found at lower depth.

Density differences cause a stratification within the deep ground water system. At the SE-slope of the Spessart-Rhön ridge, a mixing zone of fresh and saline water is formed; it expands toward Bad Kissingen and is located close below the surface level. In close proximity to the surface, a zone of quantitatively high ground water regeneration occur; here, ascending deep ground waters with high mineral content are diluted by shallow ground water.

This mixing process is associated with a partial loss of some characteristic hydrochemical properties of the ground water. Considering quantitative relationships, it seems that at depths between 150 and 500 m, approximately 97 % of the water is of autochthonous origin while 3 % emerge from a part of the Hessisches Becken ("Hessian basin"), entering from the N. A small amount of highly mineralized water may also result from salt deposits in the nearer underground. Regeneration by water of Buntsandstein origin abates with increasing depth and thus, approximately 10 % could be considered to be of northern origin. Hydraulic computations and the directions of the main joints, fractures, and faults suggest that the SE-periphery of the Spessart-Rhön ridge should be considered as the principal site of origin of the deep ground water which flows toward the Bad Kissingen area.

Density differences of ground water in the Bad Kissingen area largely result from different sodium chloride contents. The highest concentrations are found immediately above the basement of the Fränkisches Becken. The presence of Ca-, Mg-, C- and S-containing species increases progressively with depth. Autochthonous water of Buntsandstein origin has, on the other hand, a low level of mineralization. Higher mineral contents result mostly from the influence of Zechstein layers, and increased NaCl-content suggests an influx of Zechstein water from the N toward Bad Kissingen (Bad Neustadt, Mellrichstadt, Bad Königshofen, drilling Heustreu).

The wells of Bad Kissingen deliver water which could be considered a mixture of autochthonous deep ground water of Buntsandstein and Zechstein origin. Before emerging in Bad Kissingen, one part of the water of Buntsandstein origin travels through layers of Zechstein periphery and Zechstein basin facies. At the points of transition between geological facies, a thermodynamic equilibrium between the deep ground water and the corresponding rock is established; during this process dolomite, gypsum and, partially, salt is dissolved, and calcite precipitates (M. HOFMANN, 1991). Further, an ion exchange between sodium and calcium or magnesium takes place. During emergence of deep ground water in the deep joints and fractures in the Bad Kissingen area, a mixing with inflowing water of Buntsandstein origin occurs once again.

7. Protection of the Bad Kissingen spa waters

The great importance of the Bad Kissingen wells requires a clear and concise protection plan to keep out any qualitative and quantitative contamination. Hygienical influences on the well waters should be suspended by qualitative protection areas which are marked in fig. 20 with roman cipher codes (I, II etc.). In contrast to that, the zones of chemical protection areas, which should protect the individual chemical characteristics of the wells are marked with arabian letters like A, B, etc. These zones correspond with the German guidelines of protection areas for drinking water and represent the new concept of protection areas for the Bad Kissingen/Bad Bocklet wells.

Mainly based on the investigations of N. GEORGOTAS (1972) which are included in this study, these recommendations were used to design modern protection areas separating three different zones to obtain the best possible protection of the Bad Kissingen wells in respect to quantity and quality. The appearance of the mineral waters and their relation to the geological structure of the underground are explained in detail further in this study.

The highly mineralized deep ground waters originating from the Zechstein formations emerge in a deep joint system up to the surface. They get their emergence energy mainly from the lifting power of degassing carbon dioxide and also from their potential hydraulic energy. The Bad Kissingen well waters and also the Balthasar-Neumann spring (Bad Bocklet) get their high mineralized ground water from allochthonous origin in the N and W of their location, the Schönborn spring may get a small amount of its sodium and chloride content also from autochthonous origin in the deep underground and by deep water circulation. A quantitative estimation of mixing processes can be made by their different chloride contents as shown in chapter 4.3.2. where low mineralized Buntsandstein waters dilute deep mineralized ground waters of the Zechstein aquifer. Basing in the idea that the dominant amount in the Bad Kissingen spa waters is of low mineralized shallow ground water the hydraulic flow system should be explained in detail.

Taking into consideration all hydraulic and hydrochemical results the following protection areas can be designed. Generally speaking, the deep ground waters do not need any protection because of their low flow velocities and deep circulation depths; the main risks can be seen in a contamination of shallow ground waters within the Buntsandstein.

The following proposed protection areas are determined by an agreement of best possible protection and smallest possible space dimension. Strictly viewed, the protection area should extend approximately to Bad Brückenau nearly 20 km in the WNW of Bad Kissingen (see chapter 4.3. and 5.3.).

The protection area concept proposes only three different zones according to the guidelines for protecting drinking waters: an extended zone (zone C), a narrow zone (zone B), and an inner zone (zone A) are recommended.

The extended protection zone (zone C)

For delimiting this zone, mostly tectonical, morphological and hydrological characteristics were considered. Their E- and SW-limits correspond mainly with tectonical fault lines, outside of these displacement lines no influences by anthropogenic excavations can be foreseen. For fixing the N- and W-limits mainly morphologic criterias were taken into consideration. In respect to the geological structure, the western part of the Fränkische Saale represents itself in quite a different way than its corresponding part in the E. While in the E mainly less fractured sandstones and clay (Upper Buntsandstein)

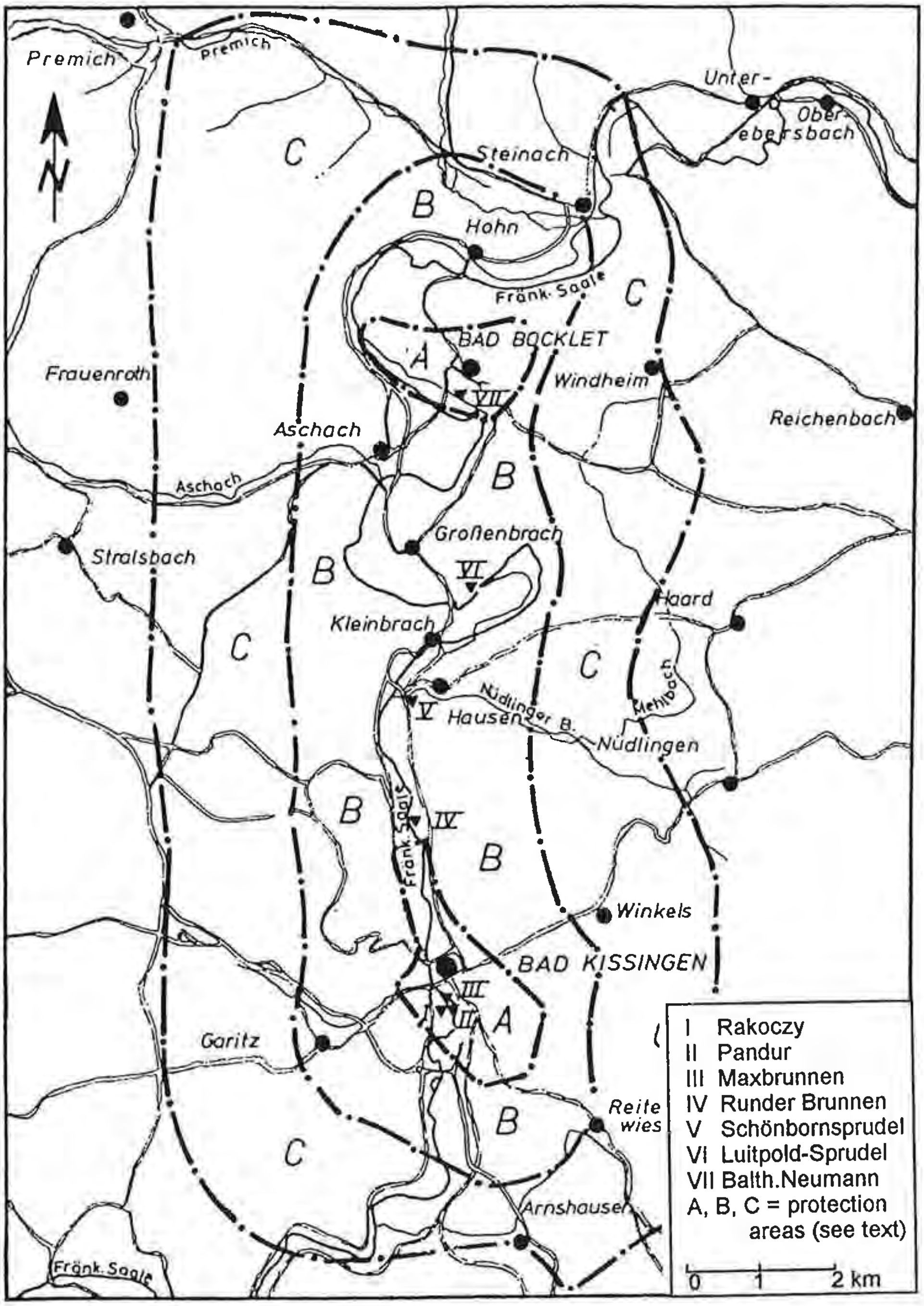

Fig. 20: Protection areas for the Bad Kissingen and Bad Bocklet wells and springs.
Wasserschutzgebiete der Bad Kissinger und Bad Bockleter Brunnen und Quellen.

dominate and protect the underground from undesired influences, the W represents a much more jointed and fractured structure consisting of sandstones (Middle Buntsandstein) and less covered by protective layers close to the surface. For this reason, the western part of zone C takes a larger extension than on the eastern zone.

Within this area anthropogenic disturbances are harmless and can be allowed to depths up to 40 m below the overflow of the wells. Drillings up to 80 m below spill-over should be allowed only with official permission. Deeper drillings more than 80 m should not be permitted. In case of carbon dioxide escaping during any activity, all further excavations or drillings should be stopped and refilled.

The narrow zone (zone B)

This area encloses the flood river plain of Fränkische Saale and the flanks of hill surrounding this plain. Because of missing or insufficient soil covers at the hillsides, any deep disturbance which opens up consolidated rocks over greater parts should be avoided. These openings may contaminate the underground and ground water. Drillings or excavations seem to be harmless if they do not penetrate the alluvial deposits; activities in deeper part can be permitted only after consulting an authorized office, institute or person. Drillings for water exploitation should be permitted only in exceptional cases.

The inner zone (zone A)

Within zone B, inner protection zones for the Bad Kissingen park of the spa wells and the Bad Bocklet well were marked. For the Schönborn and Luitpold spring no zone A was proposed, because of the kind of bore support, penetration depth and geological conditions seemed to be sufficient to protect these wells. The drawing of these limits results from pumping tests carried out by N. GEORGOTAS (1972).

Zone A of the Bad Kissingen park of spa wells encloses greater parts of the urban Bad Kissingen city. Within the flood plain of the Fränkische Saale river, the protection area extends some hundred meters upstream to the N of Bad Kissingen to ensure no water contamination will happen. Outside the valley to the W and E, the extension of the protection area corresponds exactly with the tectonical lines of the inner Bad Kissingen fault zone; to the S the limits were drawn only approx. 200 m downstream taking into consideration that the main direction of flow leads to the S, and no contamination could be expected from this side.

At the flanks of hill, within this zone, no excavations deeper than 3 m should be permitted without official instructions. The deep and strong jointed and fractured Buntsandstein and karstic Muschelkalk underground, including the slight thickness of the clay covers surrounding the wells, demands special protection instructions. The hillside seepage water leads mostly to the quaternary gravel layers in the valley. However, these waters are connected with the emerging deep ground waters; because of that any anthropogenic activity may lead to contaminations of the ground water and therefore to a possible damage of the Bad Kissingen mineral waters. The inner part of the flood plain near the wells seems to be protected sufficiently by meadow loam of the Fränkische Saale river. This alluvial soil layers also keep the emerging carbon dioxide from escaping. Every action which will destroy these layers should be prohibited; the conservation of these layers is of the greatest importance for protecting the Bad Kissingen wells.

The observance of all guidelines mentioned above is recommended unconditionally, especially in case of the shallow foundation of the drillings within the park of the spa.

In respect to the **protection zone (zone A) of Balthasar-Neumann well in Bad Bocklet** the same restrictions made above for the Bad Kissingen park of spa wells are valid. The Bad Bocklet well takes a much greater penetration depth and seems to be better protected, however restrictions will be necessary here to keep carbon dioxide from escaping.

New drillings, done in 1994 and 1995, on the border of zone A and B at the E-side of the Fränkische Saale river showed up that the salt water uplift is very closely related to the fractures and deep joints. Outside the central, tectonically altered part only low mineralized Buntsandstein water is found (P. UDLUFT, pers. comm.).

Summary

Knowledge of the processes involved in the facial establishment of geological formations is an indispensable requirement for hydrogeochemical model computations. While Buntsandstein consists predominantly of monotonous silt- and sandstone-sequences, Zechstein is found in gypsum and anhydrite series and, locally, in salt facies too.

Knowledge of the directions of deeply extending fault zones is of crucial importance; the hercynian direction deserves particular attention. Structural features of significant importance include the Fränkisches Becken and its peripheral elevations, i. e. the Spessart-Rhön ridge and Steigerwald.

Apart from knowledge of the distribution of geological formations, evaluation of the factors which influence the water balance also proved necessary. The publications of P. UDLUFT (1979), the MAIN-Projekt (BAYERISCHES LANDESAMT FÜR WASSERWIRTSCHAFT, 1978), K.-E. QUENTIN (1970), M. BAUMANN & K.-E. QUENTIN (1987) and the archive of the Institut für Wasserchemie und Chemische Balneologie of the Technische Universität München served as references for this purpose. Surface flows and shallow ground water conditions were reviewed only briefly in the analysis of hydrogeological conditions, but more attention was paid to hydraulic parameters like joint intensity, porosity and rock permeability which largely determine the conditions of deep ground water flow.

Underground temperature conditions were evaluated using four temperature-logs. It was found that the temperature gradient in Bad Kissingen and the surrounding area is slightly lower than the established average in Germany.

The silica content was employed as a geothermometer for the determination of dissolution temperatures of Bad Kissingen water and its circulation depths. Calculations confirmed the existence of a low temperature gradient in the thick Buntsandstein layers and suggest that a mixing between emerging deep ground water and water of Buntsandstein origin takes place. A short estimation of the flow velocities led to a deep ground water age to approx. 20 000 years which corresponds to the glacial period of Würm.

Further, we determined the distribution of elementary and complexed forms of water-dissolved species in Bad Kissingen water. Calcium, magnesium and sulfur exposed a clear trend toward formation of complex molecules. In contrast, strong electrolytes such as sodium, potassium and chloride, are dissolved almost entirely as elementary ions of Na^+, K^+ and Cl^-.

The activity and the corresponding activity coefficients of the dissolved compounds were deduced from their concentrations. We found that activity coefficients of externally charged complexes were, in part, substantially less than 1, while activity coefficients of uncharged complexes were slightly greater than 1. Deviation of activity from the

corresponding concentration depends on ionic strength and the ratio between ionic radius and valency of the participating elements.

Genesis of deep ground water in the Bad Kissingen well Luitpold spring (Neu) was simulated using a hydrogeochemical model strategy. The Luitpold spring (Neu) drilling pierces a Buntsandstein-Zechstein profile of the Fränkisches Becken. The analysis of water samples from different depths showed increasing ionic strength and NaCl-concentrations with progressing depth. In parallel, an increase in the proportion of large molecular complexes was observed. Calculations of solution saturation with increasing depth revealed that undersaturation of the phases calcite, dolomite, gypsum and halite occurs in shallow water, while an equilibrium for calcite, dolomite and gypsum is established at the final depth in Zechstein. Salt saturation of the water is always poor.

Unexpectedly high concentrations of CO_2 were measured in Bad Kissingen water. Since the probable CO_2-exhalation source is relatively remote, the probability of direct communication with the volcanic zone of the Rhön is suggested. It could consist of water-conducting faults, similar to those of the Kissingen-Hassfurt fault zone.

Hydraulic calculations allowed the quantitative characterization of numerous parameters which portray the flow conditions in the influx area of Bad Kissingen. We found that circulation depths are determined essentially by the incline of ground water levels. Density differences exert only negligible effects. Release of carbon dioxide in the underground of Bad Kissingen generates a reduction of water density, enabling deep ground water to emerge to the terrain surface (the so-called gas-lift effect).

Using the computation model of W. E. SANFORD & L. F. KONIKOW (1985), we determined the distribution of chloride in deep ground water between Bad Kissingen and Bad Brückenau. The experiment showed that the thickness of the mixing zone is considerably lower at the slope of the Spessart-Rhön ridge than in Bad Kissingen underground where it extends almost up to the surface. This diffusion was suggested as the main cause for this phenomenon, while hydrodynamic, longitudinal and transversal dispersion seem to be of negligible importance. The effects of viscosity and density were also evaluated. Interaction of these factors results in the ascent of deep ground water with high mineral content at the base of the Spessart-Rhön ridge (Bad Kissingen), while at the top of the ridge a broad displacement zone is formed.

The hydraulic and hydrogeochemical results fit well into the following overall scheme: the ground water traverses a Zechstein aquifer on its way between the Buntsandstein formation area (Spessart-Rhön ridge) and the emergence point (Bad Kissingen). Every transition elicits a new chemical-thermodynamic situation resulting in a new solution equilibrium between the ground water and the actual rock contacted. Further, mixing processes and ion exchange occur which are directly related to gravity-dependent stratification, the localization of fresh/salty water boundary, and the depth of circulation within the ground water system.

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Zusammenfassung

Aufbauend auf den zahlreichen Veröffentlichungen zur Geologie und Hydrogeologie des nordwestlichen Unterfrankens beginnt die Arbeit mit einer Beschreibung der mineralogischen Zusammensetzung der Schichten und der geologisch-strukturellen Verhältnisse im Untersuchungsgebiet. Hierbei werden die Heilwasservorkommen Bad Kissingens großräumig und im Detail erläutert. Um die Genese dieser Heilquellen besser verstehen zu können, wurde besonders darauf Wert gelegt, die Charakteristika des gesamten „Einzugsgebietes“, wie die chemische Zusammensetzung der geologischen Formationen, die Durchlässigkeiten der Schichtglieder und die Temperaturverhältnisse im Untergrund zu erkennen und zu beschreiben. Nur alle diese Komponenten zusammen lassen die besonderen balneologischen Eigenschaften der Bad Kissinger Heilwässer so entstehen, wie sie heute vorgefunden werden. Der Mineralbestand der Schichten, die den Chemismus der Heilwässer entscheidend beeinflussen, kann in Bezug auf die Genese der Heilquellen von den physikalischen bzw. hydraulischen Verhältnissen, wie z. B. die sich ergebenden Verdünnungseffekte oder Mischungsverhältnisse, nicht getrennt betrachtet werden. Hierin ist ein großer Verdienst dieser Arbeit zu sehen, da hierdurch quantitativ Aussagen über das Zusammenwirken der äußerst komplexen Vorgänge gemacht werden können.

Im Gegensatz zu den hydrodynamischen Bedingungen in oberflächennahen Lockergesteinshorizonten bewegt sich das tiefe Grundwasser nicht in Gesteinsporen, sondern vorwiegend auf geologisch-strukturell vorgegebenen, offenen Trennflächen (Kluft- und Störungsflächen). Bedingt durch die paläogeographische Entwicklung des Gebietes weisen diese Trennflächen hauptsächlich eine herzynische (NW–SE) Richtung auf. Demnach liegt es nahe, die Neubildung des Bad Kissinger Grundwassers im NW von Bad Kissingen an der SE-Flanke der „Spessart-Rhön-Schwelle“ zu suchen. Die Mineralstoffzusammensetzung (erhöhte NaCl-Gehalte, erhöhte CO_2-Gehalte, thermodynamisches Gleichgewicht mit Calcit und Dolomit) der Bad Kissinger Heilwässer weist weiterhin auf eine Passage des tiefen Grundwassers durch Zechstein-Formationen (Calcit, Dolomit und z. T. Gips) bzw. auf eine Zumischung NaCl-reicher Tiefengrundwässer (aus den Steinsalzlagern im N von Bad Kissingen) hin. Zusätzlich verursachen eine Kohlendioxid-Entgasung („Gas-Lift“) und der hohe hydrostatische Druck auf das Tiefengrundwasser im Untergrund Bad Kissingens, daß tiefes Grundwasser bis zur Geländeoberfläche „aus eigener Kraft“ aufsteigt. Die Quantifizierung aller hier wirkenden physikalischen Parameter und ihre Auswirkungen auf den Chemismus der Heilwässer ist Ziel und Ergebnis dieser Arbeit.

Im Detail stellt sich die Situation aufgrund der hier vorliegenden Untersuchungen jedoch wesentlich differenzierter dar. Auf der Basis einer Literaturstudie wurden zahlreiche Angaben zur Gebirgsdurchlässigkeit der permischen (Zechstein) und mesozoischen Schichten (Buntsandstein und Muschelkalk) gesammelt und bewertet. Hierbei zeigte sich, daß die relativ hohe Durchlässigkeit des Gebirges im oberflächennahen Bereich zur Tiefe hin deutlich abnimmt, da der hohe Gebirgs-Auflastdruck sowohl Poren- als auch Trennflächen z. T. schließt. Nur tiefreichende Störungen erhöhen hier die ansonsten geringe hydraulische Wasserwegsamkeit. Weiterhin lassen unterschiedliche Temperaturverhältnisse einerseits charakteristische SiO_2-Gehalte in den Bad Kissinger Heilwässern entstehen, andererseits wurden hier aus den gemessenen SiO_2-Gehalten unterschiedliche Zirkulationstiefen ermittelt, die bereits ein recht differenziertes Bild der Genese der verschiedenen Bad Kissinger Heilquellen entwerfen lassen.

Die hydrogeochemischen Berechnungen zielen besonders auf eine moderne, thermodynamische Beschreibung der Bad Kissinger Heilwässer ab. Die hier veröffentlichten Daten zur Konzentration und Aktivität sowie die unterschiedliche chemische Zusammensetzung an Wasserinhaltsstoffen können insbesondere bezüglich ihrer balneologischen Wirkung gedeutet werden und bieten ein weites Feld neuer medizinischer Untersuchungen. Während bei einer Wasseranalyse im allgemeinen lediglich Summenkonzentrationen an Haupt- und Spureninhaltsstoffen gemessen werden, so ergeben sich aufgrund der hier für die Bad Kissinger Heilwässer durchgeführten Berechnungen eine Vielzahl an gelösten Komplex-Molekülen. Insbesondere bei zunehmender Mineralisation, aber auch bei unterschiedlichen Temperatur- und Druckbedingungen ergeben sich abweichende Werte für die Konzentration und Aktivität der Inhaltsstoffe sowie verschiedene Werte in Bezug auf die Form (unkomplexiert/komplexiert) der Spezies. Inwieweit sich die hier beschriebenen Zusammensetzungen der Heilwässer auf die Beurteilung ihrer balneotherapeutischen Wirkung auswirken, mußte hier jedoch offenbleiben und an fachkundige Adressen weitergegeben werden.

Eine erste Zusammenfassung der hydrogeochemischen und hydrodynamischen Verhältnisse im Untergrund Bad Kissingens stellen die Berechnungen zur Genese des Luitpold-Sprudels (Neu) dar. Hier werden hydrochemisch-thermodynamisch die Vorgänge simuliert, die den Luitpold-Sprudel (Neu) vom Punkt ihrer Neubildung bis nach Bad Kissingen entstehen lassen. Mit Hilfe verschiedener Steuerungsmechanismen, die als hydrochemische Randbedingungen (pH-Wert, CO_2-Partialdruck) in die Berechnung eingehen, zeigte sich, daß die Genese des Luitpold-Sprudels und somit unter ähnlichen Randbedingungen auch die anderen Bad Kissinger Heilwässer, vereinfacht in drei Teilschritte unterteilt werden kann: erstens eine chemische Gleichgewichtseinstellung des Ausgangswassers aus dem Buntsandstein der Rhön mit den Mineralphasen Calcit und Dolomit, zweitens eine Zumischung NaCl-reichen Tiefengrundwassers aus den Steinsalzlagern im N von Bad Kissingen und drittens ein Ionenaustausch von Ca- und Mg-Ionen mit Na-Ionen im Untergrund von Bad Kissingen.

Entgegen früheren Annahmen hat sich beispielhaft aus den Untersuchungen am Luitpold-Sprudel gezeigt, daß der Anteil an Tiefengrundwasser deutlich überschätzt wurde. Vielmehr muß auch an den anderen Bad Kissinger Heilwässern mit einem überwiegenden Anteil an oberflächennahem Grundwasser (ca. 90 %) gerechnet werden und nur etwa 10 % sind als Tiefengrundwasser zu bezeichnen. Dies hat zur Folge, daß für einen nachhaltigen Bestand der Heilquellen ein wirksamer Schutz gefordert werden mußte, der durch eine Ausweisung von Schutzgebieten erreicht werden soll.

Ein weiterhin äußerst komplexes Berechnungsverfahren stellt die Ermittlung der Strömungsbedingungen im Untergrund Bad Kissingens dar. Dabei wurden nicht nur die hydraulischen Kenngrößen wie Durchlässigkeit, Porosität und Mächtigkeit der geologischen Formationen, sondern auch die Dichte („Salzgehalt"), Viskosität und Dispersivität des durchströmenden Mediums berücksichtigt. Zur Eichung (d. h. zur Wahl der Größenverhältnisse) der Eingabeparameter im Modell wurden die hydrogeologischen Situationen am SE-Rand der Spessart-Rhön-Schwelle (hier Bad Brückenau) und bei Bad Kissingen herangezogen. Im folgenden wurde anschaulich dargestellt, wie sich die Verteilung der Chloridionen (Chlorid kann in guter Näherung als chemisch-konservativer Markierungsstoff betrachtet werden und bleibt überwiegend als Chlorid-Ion (Cl^-) in Lösung) bis zur heutigen Situation im Untergrund von Bad Kissingen entwickelt hat und welche Zeiträume hierfür nötig sind, um eine solche Entwicklung geschehen zu lassen. In einem Profilschnitt wird weiterhin gezeigt, welche Strömungsgeschwindigkeiten auftreten, und wie sie von den jeweiligen hydrostatischen Druckverhältnissen im Untergrund abhängen.

In einer Art Synthese werden die berechneten Faktoren und Parameter nochmals zusammengefaßt und ihre Auswirkungen auf die Genese der Bad Kissinger Heilwässer beschrieben. Die zahlreichen

Ergebnisse und physikalisch-geochemischen Prozesse zeigen somit nicht nur neue Wege geologischer Untersuchungen auf, sondern erhellen das ansonsten vielzusehr vernachlässigte Gebiet des Tiefengrundwasserbereiches. Die Arbeit macht dabei nicht nur deutlich, daß hydrochemische und hydrodynamische Prozesse nur zusammen betrachtet werden können, sondern daß sich Bad Kissingen in bevorzugter Lage für eine Erschließung von Heilwasser befindet. Die detaillierten und modernen Untersuchungen sind jedoch nur möglich gewesen, weil der unterfränkische Raum bereits durch zahlreiche Voruntersuchungen gut bekannt ist.

Alle alten und neuen Ergebnisse und Kenntnisse zur hydrogeolischen Situation im Raum Bad Kissingen zusammenfassend entstand ein neues Schutzkonzept der Heilquellen/-brunnen. Insbesondere der hohe Anteil oberflächennahen Grundwassers und die detaillierten Kenntnisse zur Hydrodynamik des Untersuchungsgebietes fanden hierbei ihren Eingang. Auf diese Weise konnten drei Schutzgebietszonen ausgewiesen werden, die vorwiegend die Qualität der Heilwässer sicherstellen sollen.