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# Hydrochemical properties of deep carbonate aquifers, SW-German Molasse Basin

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# ABSTRACT

The Upper Jurassic (Malm) limestone and the middle Triassic Muschelkalk limestone are the major thermal aquifers in the southwest German alpine foreland. The aquifers are of interest for production of geothermal energy and for balneological purposes. The hydrochemical properties of the two aquifers differ in several aspects. The total amounts of dissolved solids (TDS) are much higher within the Upper Muschelkalk aquifer than within the Upper Jurassic. Water composition data reflect the origin and hydrochemical evolution of deep water. Rocks and their minerals control the chemical signature of the water. With increasing depth, the total of dissolved solids increases. In both aquifers, the water evolve to a NaCl-dominated fluid regardless of the aquifer rock. The salinity of the aquifers has different sources. In the case of the Upper Muschelkalk it is linked to deep circulation-systems, while the hydrochemical properties in the Upper Jurassic developed due to changing overburden and hydraulic potential.

# **1. INTRODUCTION**

The deep Upper Jurassic carbonates are the most important reservoir rocks for hydrothermal energy use in Southern Germany. Especially in the Munich area of Bavaria (Germany), several geothermal power plants and district heating systems were installed since 2007. In Baden-Württemberg (SW-Germany), the Upper Jurassic thermal aquifer is of shallower depth (Fig.1), therefore colder and the thermal water is rather used for balneological purposes including heating of nearby buildings.

Far less well-known than the Upper Jurassic is the Upper Muschelkalk aquifer. First scanty hydraulic and hydrochemical results are given in Bertleff et al. (1988). New hydraulic investigation results are presented in Stober (2013).

This paper compiles several hundred checked, validated hydrochemical data of two carbonate aquifers in the Molasse basin of SW-Germany. The presented data derive from deep wells in the depths range from several hundred meters to 3500 m.

# 2. GEOLOGICAL FRAMEWORK CONDITIONS OF THE SW-GERMAN MOLASSES BASIN

Geologically, the investigation area is located in the southwestern part of the German Molasse basin, in the federal state Baden-Württemberg. The course of the river Danube and the Upper Jurassic of the Swabian Alb form the northwest border. The eastern border of the investigation area follows the river Iller and the southwestern border is linked to the lake Constance (Fig. 1).

The investigation area is part of the so-called Molasse basin, a foreland basin of the Alps that formed during the Cenozoic Oligocene and Miocene as result of the flexure of the European plate under the weight of the orogenic wedge of the Alps (Geyer & Gwinner 2011). The basis of these Molasse sediments – at least in the investigation area – is formed by the Upper Jurassic dipping from the outcrops at the Swabian Alb in southeastern direction below the Cenozoic sediments. Below the Jurassic, follow the Triassic series (Fig. 1, 2). Our investigations are focused on the Upper Jurassic and the Triassic Upper Muschelkalk, two carbonate aquifers, both dipping gently in southeastern direction below the Cenozoic Molasse sediments reaching a depth of more than 3,000 m at the boundary to the alpine orogeny (Bertleff 1986).

Reservoir quality of the **Upper Jurassic** varies strongly, depending on sedimentary facies, diagenesis, dolomitisation, karstification, and tectonic situation. The Swabian facies, located in the middle and northwestern part of the investigation area, developed in a shelf environment with reef facies in the northwest and basin facies in the central part. The reef facies in the northwest has generally a higher hydraulic conductivity (> $10^{-4}$  m/s) than the thinner bedded, banked basin facies in the central part of the investigation area. Farther in the southeast the Swabian facies of the Upper Jurassic changes into the Helvetian facies, characterized by darker, very tight limestone (Meyer & Schmidt-Kaler 1996).

The deeper laying **Upper Muschelkalk** aquifer (Middle Triassic) is a fractured and karstified limestone aquifer, with fractured dolomites. Karstification and fractures are preferentially in the upper part the so-called Trigonodusdolomit. Generally, the thickness of the total Muschelkalk is decreasing in the investigation area in ESE-direction.

Between the two carbonate aquifers extends the 60 - 130 m thick lithostratigraphic unit of the Keuper, consisting of dolostones, shales, claystones and evaporates, followed by the Lower and Middle Jurassic series of 20 - 50 m and 120-180 m thickness resp. Especially the Lower Jurassic is composed of very tight clay and marlstones. Thus, the hydraulic potentials of the Upper Jurassic and the Upper Muschelkalk aquifer are uncoupled from each other, showing very different flow directions and differences in hydraulic head of up to 300 m (Stober 2013). Obviously, there should be no hydraulic interaction between the two carbonate aquifers.



Figure 1: Location of the investigation area in the SW-German Molasse basin, showing the location of the cross section (Fig. 2)



Figure 2: Geological cross section through the Molasse basin showing the Upper Jurassic and the Upper Muschelkalk aquifer. In the Upper Jurassic the different facies are illustrated: reef and basin carbonates of the Swabian facies and the Helvetian facies (modified after Jodocy & Stober 2009).

## 3. HYDROCHEMICAL PROPERTIES OF THE UPPER JURASSIC UND THE UPPER MUSCHELKALK AQUIFER

Generally the total of dissolved solids (TDS) in the Upper Muschelkalk waters are much higher than those in the Upper Jurassic, which often show drinking water quality up to depths of 1200 m b.s.. Below 1300 m depth TDS in the Upper Jurassic is increasing significantly, reaching values of more than 10 g/kg in about 2000 m depth. Contrarily, TDS in the Upper Muschelkalk reaches already in 1300 m depth about 10 g/kg and in the 2000 m about 65 g/kg.

Figures 3a and 3b show the main constituents of the Upper Jurassic and Upper Muschelkalk waters in a so-called Schoeller diagram with the concentration on the vertical axes. The composition of fluids at shallow depth (Upper Jurassic < 1300 m;

Upper Muschelkalk < 900 m) having low TDS-values is strongly controlled by the minerals of the reservoir rock (Fig. 3a, 3b):

- Upper Jurassic aquifer: Ca-HCO<sub>3</sub> water, related to fractured, karstified limestone (calcite, dolomite, quartz, clay minerals)
- Upper Muschelkalk aquifer: Ca-SO<sub>4</sub>-HCO<sub>3</sub> water, due to the fractured, karstified limestone, with thin marly clay layers
  and dolomite, containing sulfate-rich strata underneath the aquifer, rarely within the aquifer.

The thermal waters in the Upper Jurassic with low NaCl-concentrations show in the majority of cases increasing calciumwith coexistent decreasing magnesium-concentrations (Fig. 5a), probably caused by dolomitisation of calcite. During this process, by which dolomite is formed, magnesium ions of the fluid replace calcium ions in the calcite. Therefore, the calcium-concentration in the fluid is increasing while magnesium is decreasing. This process does not affect HCO<sub>3</sub> in the water (Fig. 3a). Geyer & Gwinner (2011) observed in bore-cores and cutting material an increase in dolomite in SEdirection. Calculations, using the computer-program PHREEQE (Parkhurst et al. 1980), show that the dolomitisationprocess is strongly temperature dependent. Increasing the temperature from 20°C up to 100°C will double the Ca/Mg-ratio in water. Increasing the NaCl-concentration in the fluid will only slightly enhance the Ca/Mg-ratio. The calculations support the observations shown in figure 3a.

The NaCl-concentrations in the Upper Muschelkalk aquifer are almost in all analyses significantly higher than in the Upper Jurassic. In contrast to the Upper Jurassic waters Magnesium in the fluids of the Upper Muschelkalk is rising with increasing calcium (Fig. 3b), so no recent dolomitisation should occur. While calcium is increasing, HCO<sub>3</sub> is decreasing (Fig 3b). To analyse the temperature and salinity effect on the calcium-carbon-ratio (Ca/C) we used the computer program PHREEQE (Parkhurst et al. 1980). The results showed that the Ca/C-ratio rises with both, increasing NaCl-content and/or increasing temperature. So, the observed increase in Ca and decrease in HCO<sub>3</sub> in the Upper Muschelkalk (Fig. 3b) is most probably an effect of increasing salinity and temperature.



Figure 3: Schoeller-Diagram of thermal waters in the Upper Jurassic (a) and the Upper Muschelkalk (b).

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TDS increases with depth and the thermal water in both aquifers develop to a Na-Cl-type water independent of the type of the aquifer rock (Fig. 3). In both aquifers the Chloride-concentration is increasing in SE-direction (Fig. 4a, 4b), resp. with increasing depth (Stober et al. 2013). While in the Upper Jurassic aquifer chloride in the area south of Ravenburg reaches values of up to 10 g/kg, the chloride-concentration in the Upper Muschelkalk is higher than 40 g/kg. However, the high salinity within the Upper Muschelkalk aquifer (and Upper Jurassic) is still far below saturation with respect to halite.



Figure 4: Chloride-distribution in the Upper Jurassic (a) and Upper Muschelkalk aquifer (b) of the SW-German Molasse basin, modified after Stober et al. (2013).

In the Upper Jurassic aquifer salinity is most probably caused by infiltration from the overlaying Molasse sediments. However, during Pleistocene these saline waters became exchanged with fresh water from NW-direction. In the Upper Muschelkalk aquifer the high salinity is probably caused by upwelling high saline waters, especially in the SE from the crystalline basement.

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### REFERENCES

- Bertleff B.: Das Strömungssystem der Grundwässer im Malm-Karst des West-Teils des süddeutschen Molassebeckens, *Abh. Geol. Landesamt Baden-Württemberg*, **12**, (1986), Freiburg i.Br.
- Bertleff B. Joachim H. Koziorowski G. Leiber J. Ohmert W. Prestel R. Stober I. Strayle G. Villinger E. Werner J.: Ergebnisse der Hydrogeothermiebohrungen in Baden-Württemberg. *Jh. Geol. Landesamt Baden-Württemb.*, **30**, (1988), 27–116, Freiburg.
- Geyer O.F. and Gwinner M.P.: Geologie von Baden-Württemberg. neu bearbeitete Auflage von Geyer M. Nitsch E. Simon T. (Hrsg.), 627 S., *Schweizerbart'sche Verlagsbuchhandlung* (Nägele u. Obermiller), (2011), Stuttgart.
- Jodocy M. and Stober I.: Geologisch-geothermische Tiefenprofile für den südwestlichen Teil des Süddeutschen Molassebeckens. Z. dt. Ges. Geowiss. 160(4), (2009), 359–366.
- Meyer R.K.F. and Schmidt-Kaler H.: Jura, in: Erläuterungen zur Geologischen Karte von Bayern 1:500.000, *Bayerisches Geologisches Landesamt*, (1996), 90–111, München.
- Parkhurst D.L. and Appelo C.A. J.: User's guide to PHREEQC (version 2) a computer program for speciation, batchreaction, one dimensional transport, and inverse geochemical calculations. In: Water-Resources Investigations Report 99-4259, pp. 312, U.S. Geological Survey, (1999), Denver/Colorado.
- Stober I.: Die thermalen Karbonat-Aquifere Oberjura und Oberer Muschelkalk im Südwestdeutschen Alpenvorland. *Grundwasser*, **18/4**, (2013), 259-269.
- Stober I. Jodocy M. Burisch M. Person R.: Tiefenwässer im Oberen Muschelkalk-Aquifer des Oberrheingrabens und des Südwestdeutschen Molassebeckens. *Grundwasser*, **18(2)**, (2013), 117-127.