Hydroisotop

Causes of abundant calcite scalings in the Bavarian molasse basin

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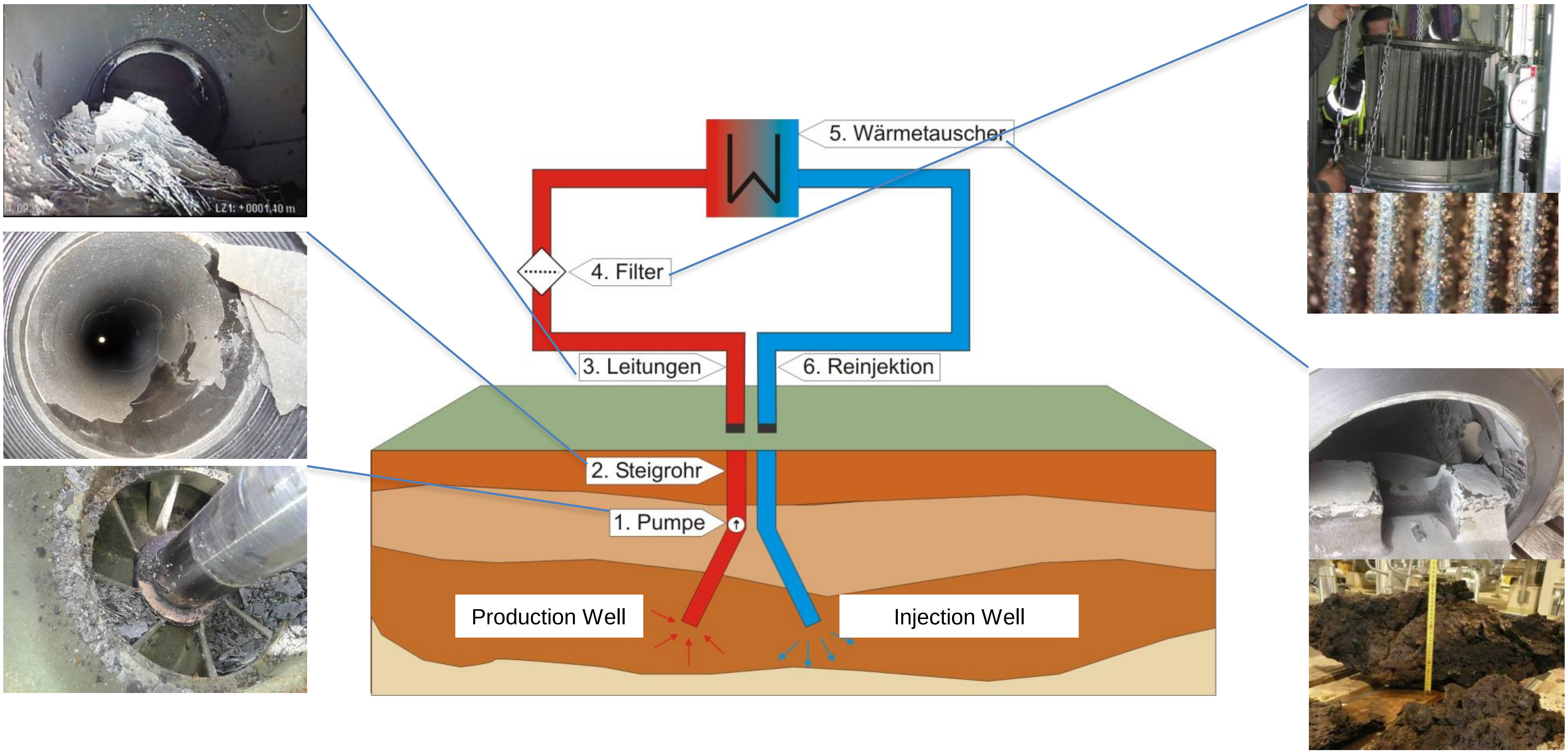
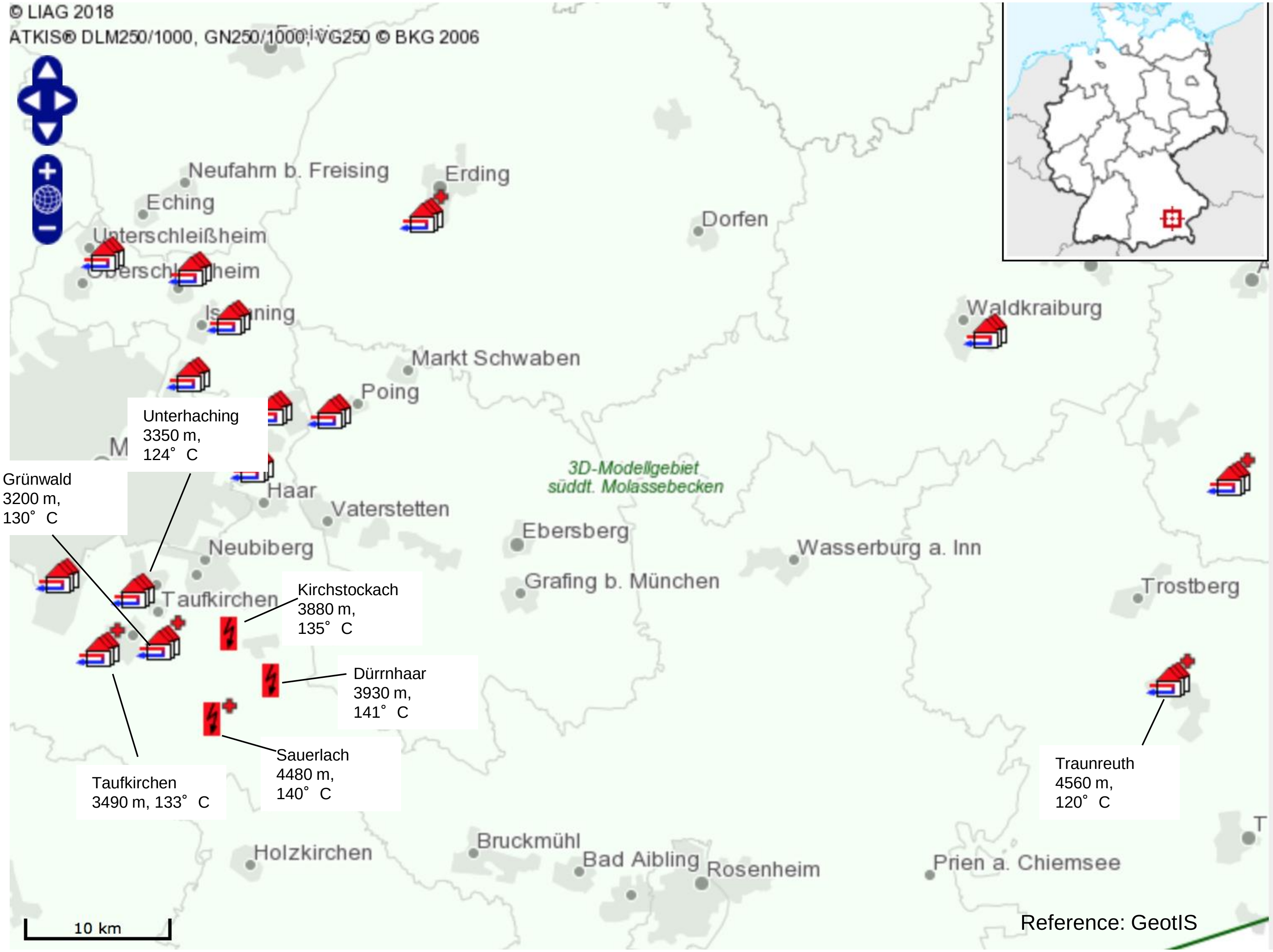
Occurence of carbonate scalings in deep hydrothermal plants in the Bavarian Molasse Basin



Regular operation not possible!

Occurence of carbonate scalings in deep hydrothermal plants in the Bavarian Molasse Basin



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Unterhaching
3350 m,
124° C

Grünwald
3200 m,
130° C

Kirchstockach
3880 m,
135° C

Dürrnhaar
3930 m,
141° C

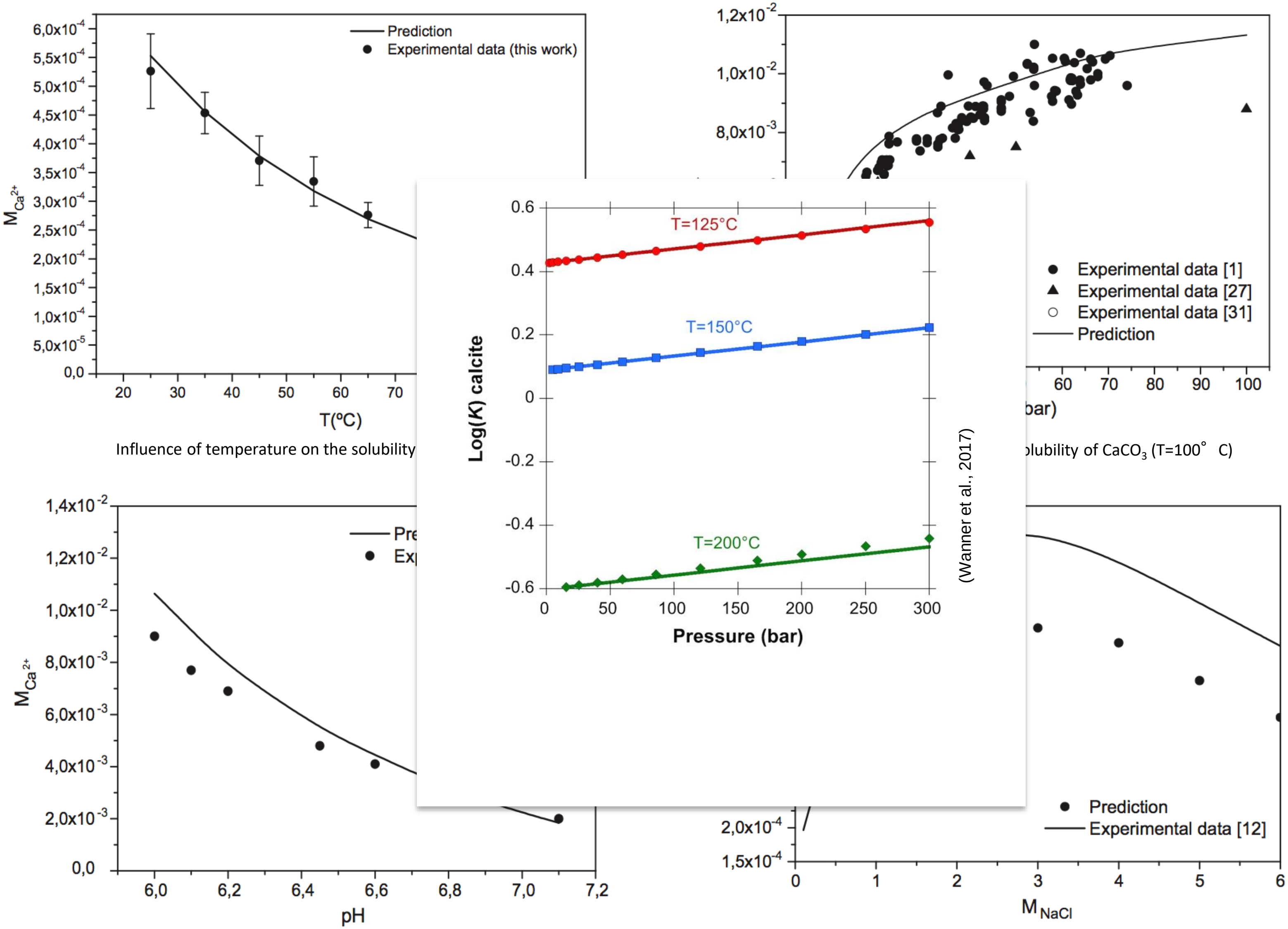
Sauerlach
4480 m,
140° C

Taufkirchen
3490 m, 133° C

Traunreuth
4560 m,
120° C

Reference: GeotIS

Potential mechanisms for the formation of carbonate precipitations



Influence of temperature on the solubility

lubility of $CaCO_3$ (T=100° C)

(Wanner et al., 2017)

(Quelle: Coto et al., 2012)

Influence of pH on the solubility of $CaCO_3$ (P=1bar, T=25° C)

Influence of ssalinity on the solubility of $CaCO_3$ (T=25° C, P_{CO2} = 0.97 atm)

Evaluation of carbonate formation processes in the geothermal plant Kirchstockach

- Mineralogical and geochemical investigations of scalings along the water path (from the pump to the heat exchanger)

- Analyses and evaluation of water chemistry and quantitative gas composition

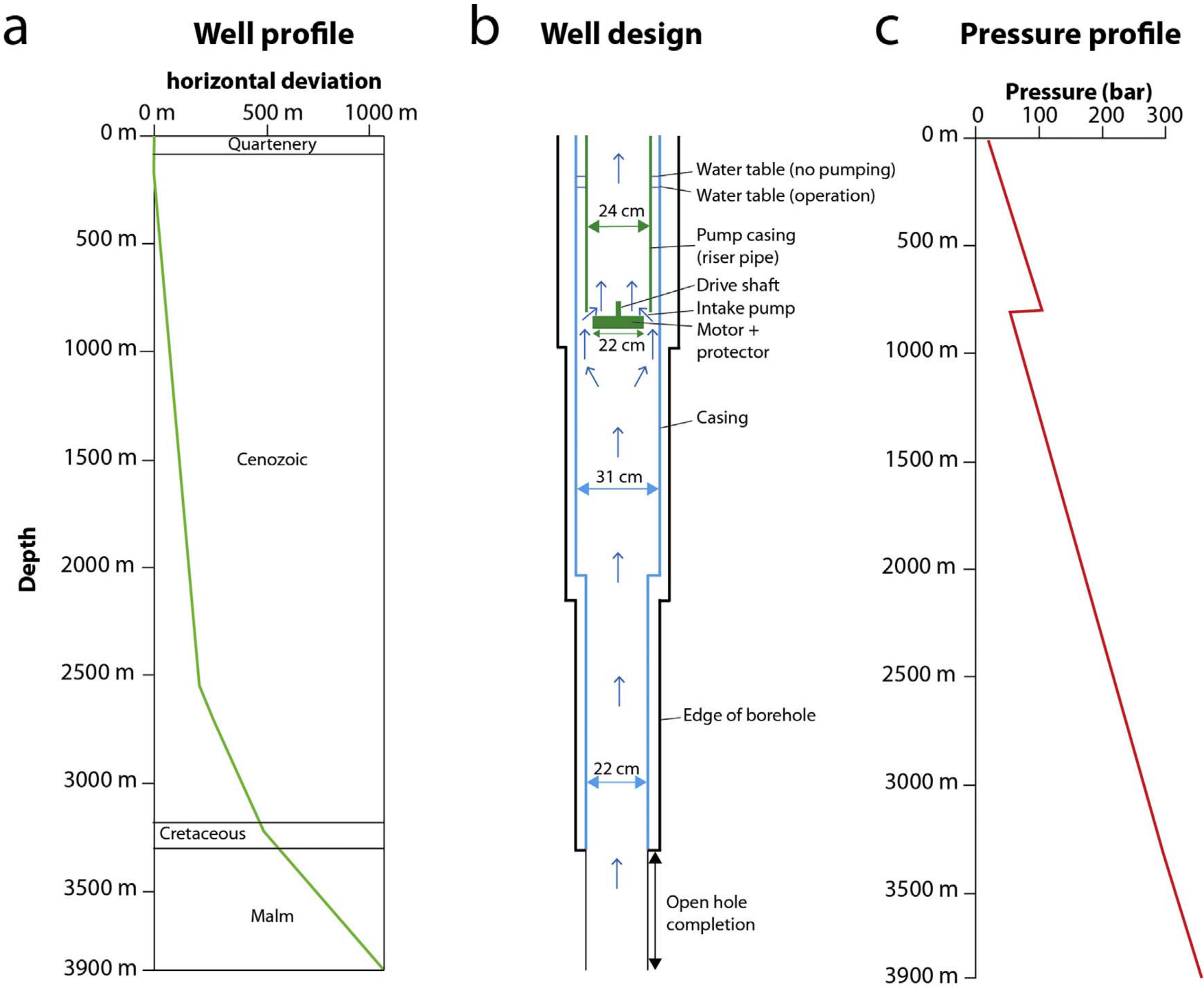
- Investigations of fluid inclusions in entrapped in carbonate scalings

- Modelling of saturation indecies along the water path

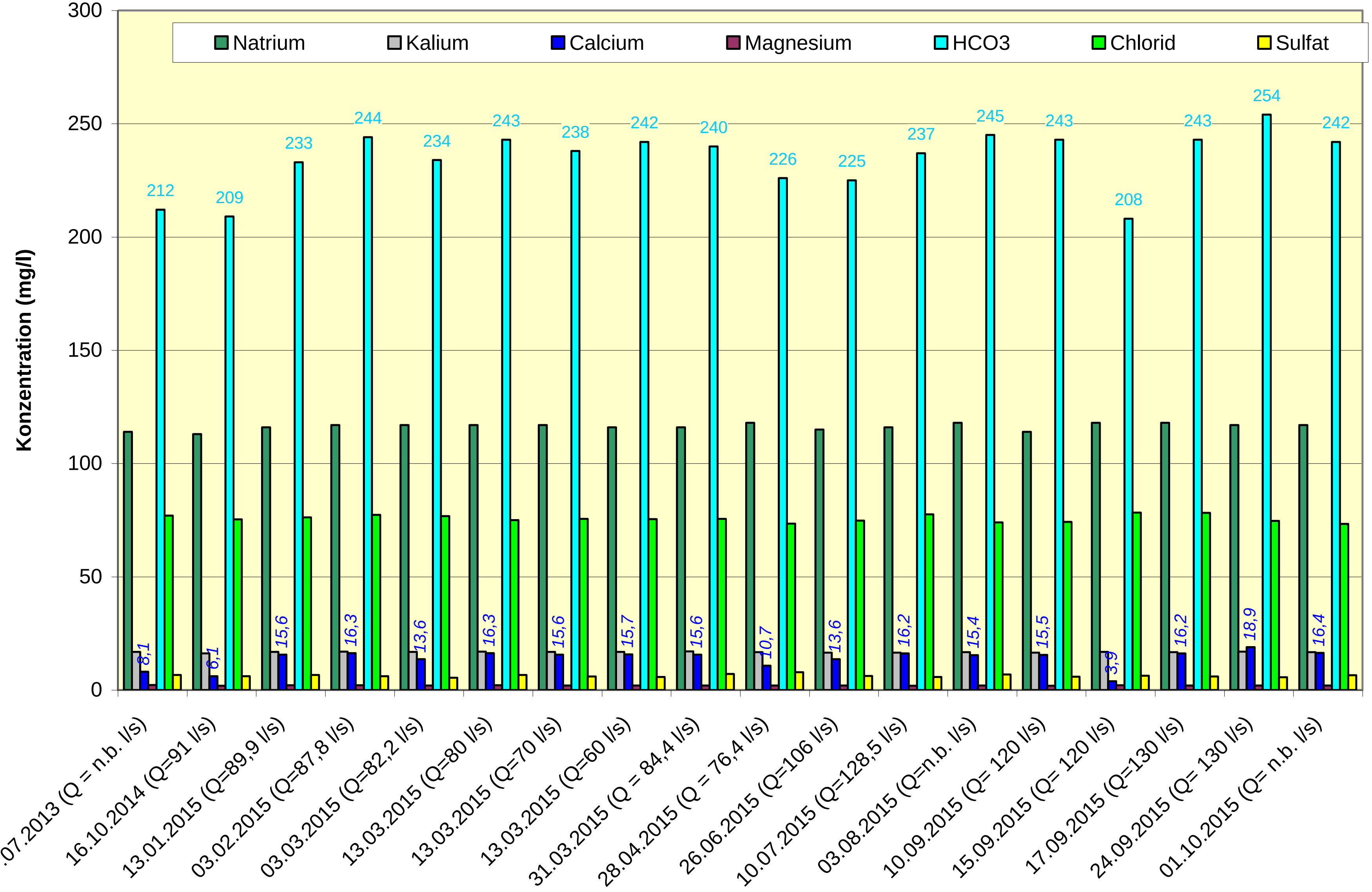
- Correlation to hydraulic properties in the borehole

- Modelling and integrative interpretation considering all data sets

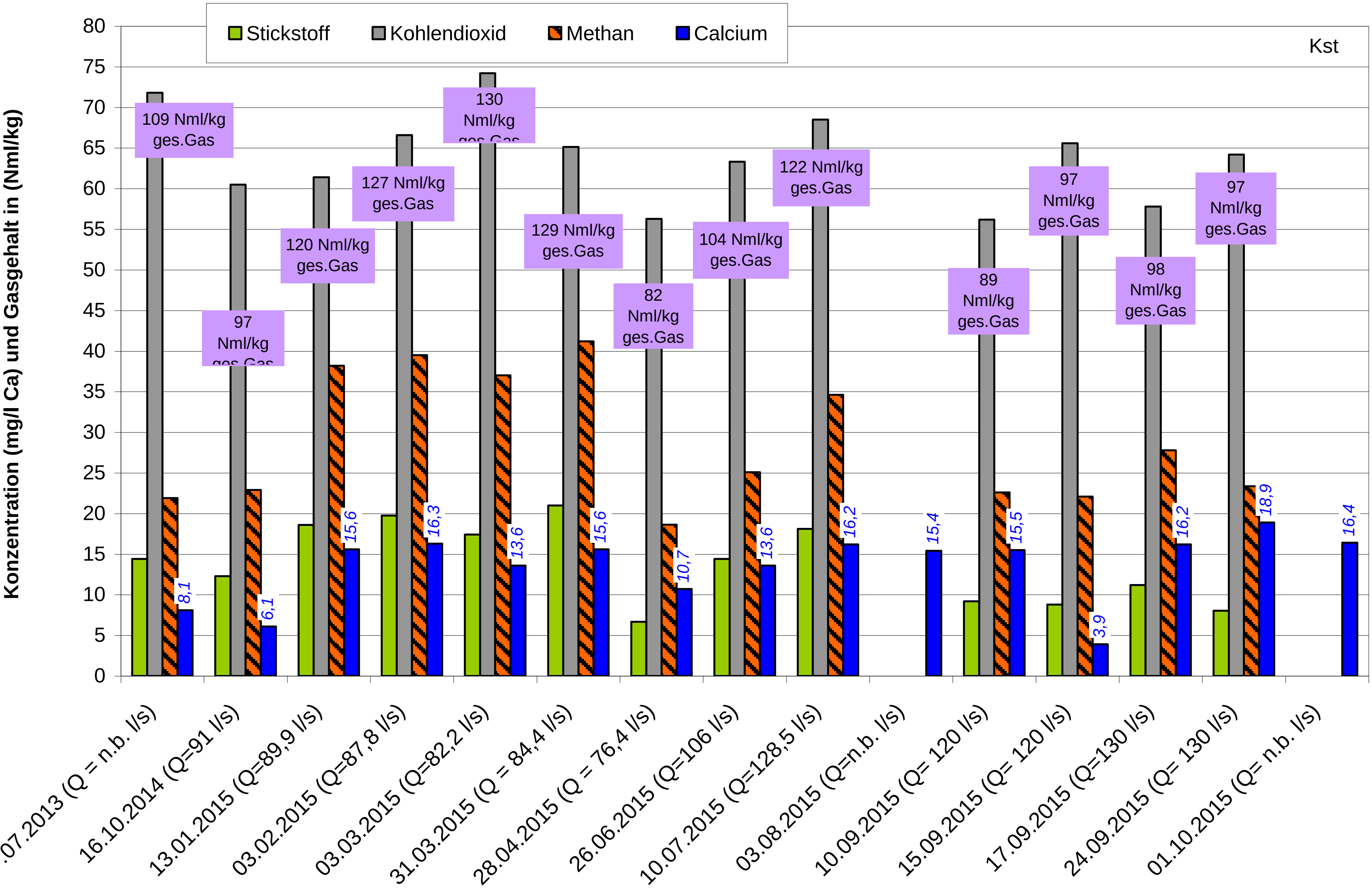
On site conditions, well properties and geometry



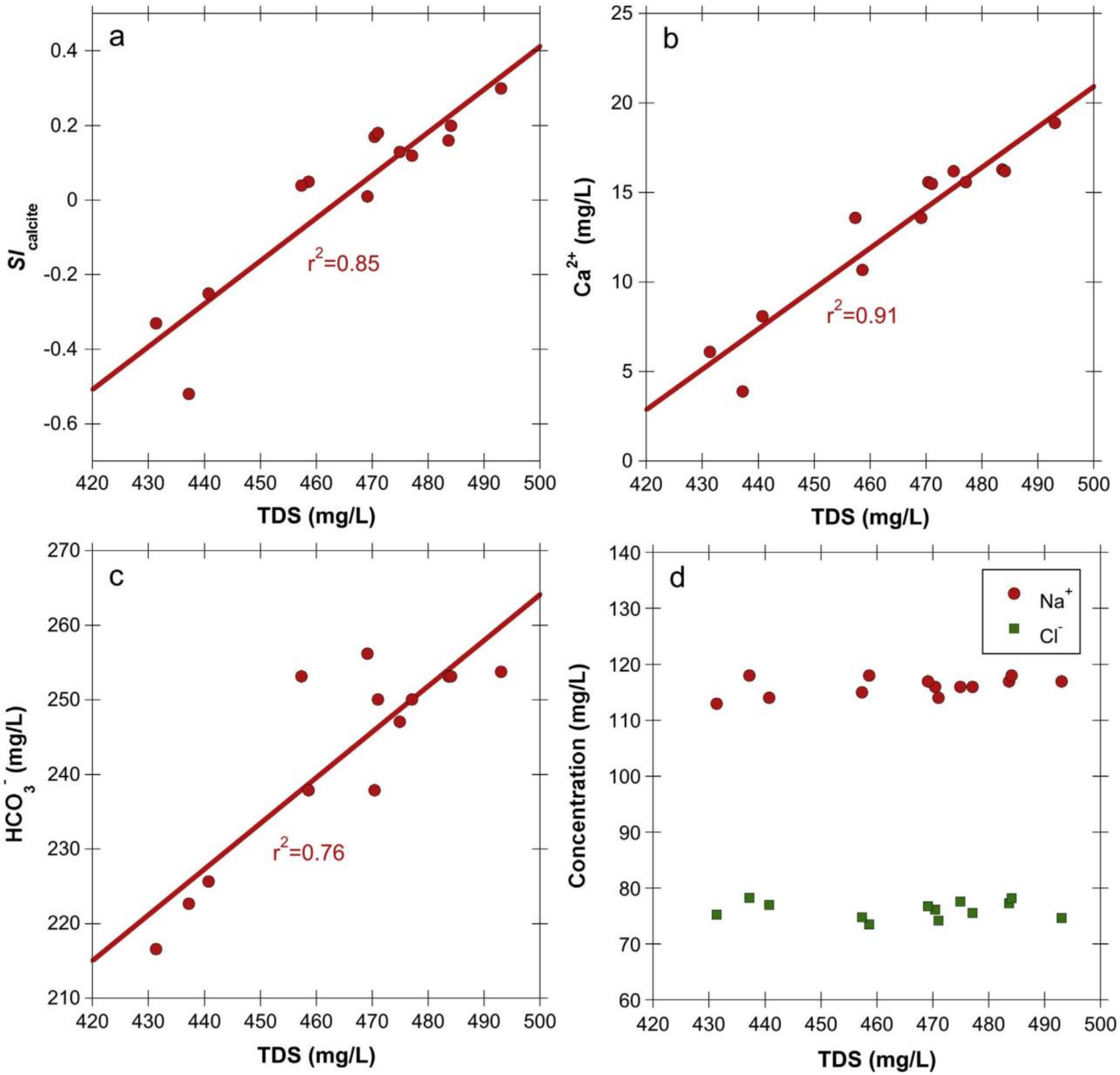
Water chemistry



Water chemistry



Water chemsitry and hydrochemical SI modelling



Hydrochemical modelling

		Well head sample	**Reservoir reconstruction (TOUGHREACT)**
Temperature	°C	135	135
Pressure	bar	18	340
pH	-	6.67	6.41
Ca^{2+}	mg/L	18.9	18.9
Mg^{2+}	mg/L	2.0	2.0
HCO_3^-	mg/L	254	245
$CO_{2(aq)}$	mg/L	126	238
SI calcite	-	0.32	0.06
SI dolomite	-	0.61	-0.04

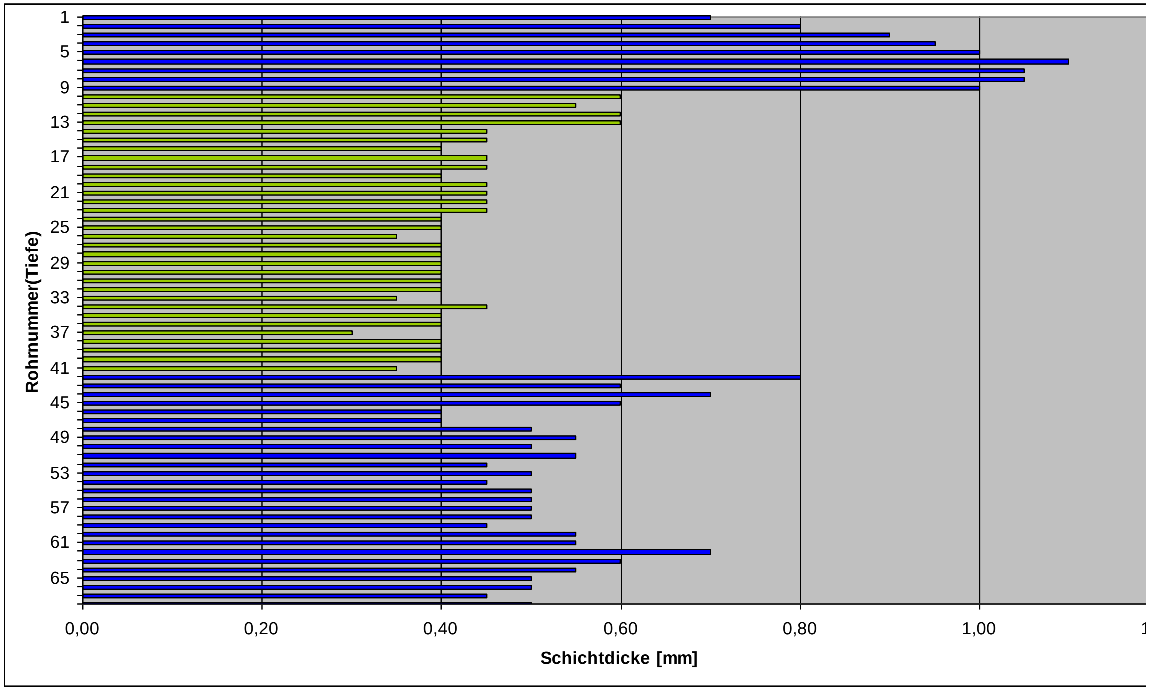
SI=saturation index
SI<0: undersaturation
SI>0: supersaturation

- Well head samples are supersaturated (SI>0) with respect to carbonates
- Calcite and dolomite dissolution rates are rather fast
  - ➢ Chemical equilibrium is likely to prevail under in-situ reservoir conditions
  - ➢ Well head composition does not reflect the composition at reservoir P,T
  - ➢ Effect of scaling formation
- Carbonate equilibrium (SI=0) is obtained by simply adding $CO_{2(aq)}$

Carbonate precipitations in rising pipe

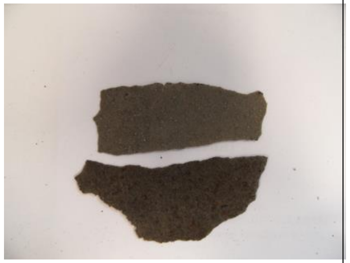
Evaluation of carbonate precipitations in rising pipes after an operation period of 3.5 months

- Thickness between 0.4 und 1.1 mm
- Thickness decreases with increasing depth
- Thickness is lower in coated than in uncoated pipes
- Grade of cristallisation decreases with increasing depth
- Thermal water looses 0.24 mg/l Ca und 0.27 mg/l CO_3 due to the formation of scalings

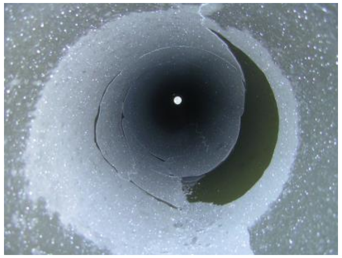


Rohr 4, 47 m u GOK, unbeschichtet, 0,95 mm

Rohr 15, 176 m u GOK, beschichtet, 0,45 mm



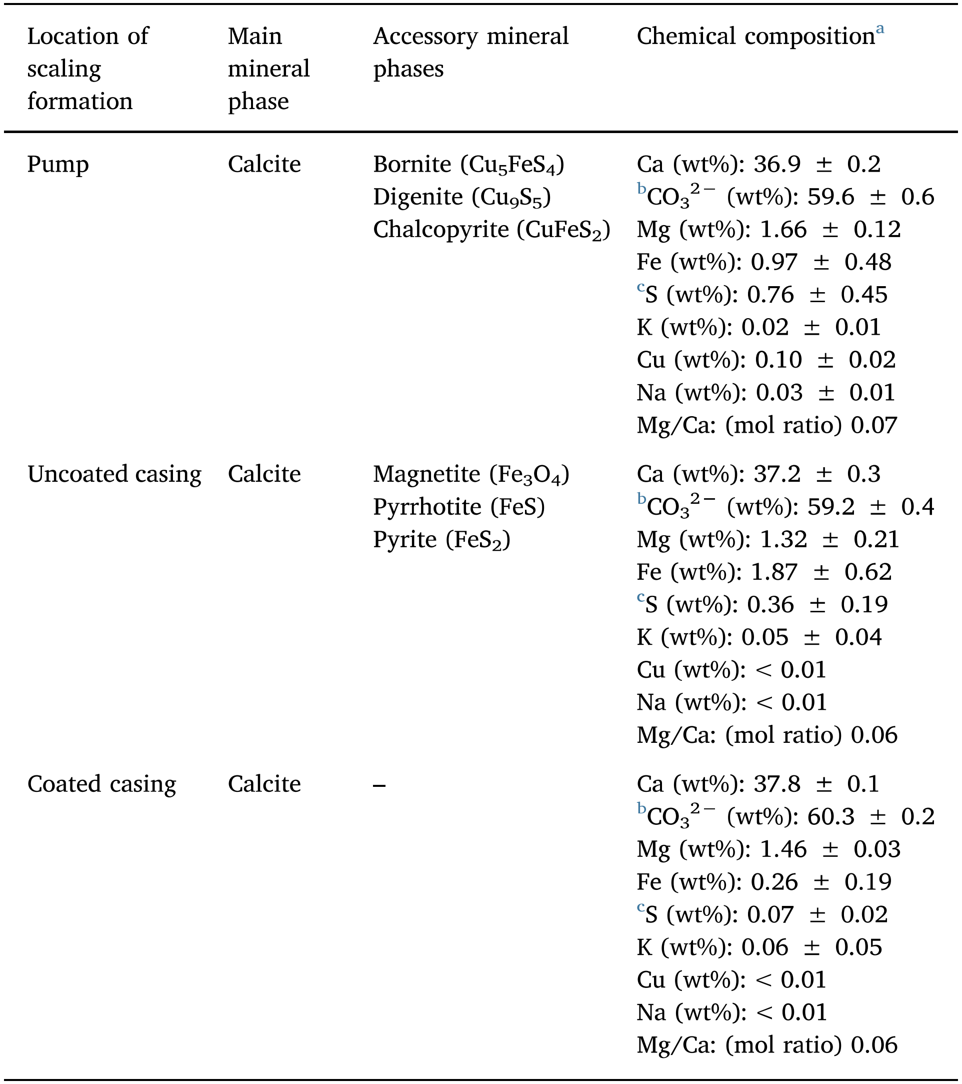
Rohr 65, 764 m u GOK, 0,50 mm



Ausfällungen am beschichteten Rohr

Carbonate precipitations in rising pipe and pump

Mineralogical and geochemical investigations of precipitations



Location of scaling formation	Main mineral phase	Accessory mineral phases	Chemical composition[a]
Pump	Calcite	Bornite (Cu_5FeS_4) Digenite (Cu_9S_5) Chalcopyrite ($CuFeS_2$)	Ca (wt%): 36.9 ± 0.2 [b]CO_3^{2-} (wt%): 59.6 ± 0.6 Mg (wt%): 1.66 ± 0.12 Fe (wt%): 0.97 ± 0.48 [c]S (wt%): 0.76 ± 0.45 K (wt%): 0.02 ± 0.01 Cu (wt%): 0.10 ± 0.02 Na (wt%): 0.03 ± 0.01 Mg/Ca: (mol ratio) 0.07
Uncoated casing	Calcite	Magnetite (Fe_3O_4) Pyrrhotite (FeS) Pyrite (FeS_2)	Ca (wt%): 37.2 ± 0.3 [b]CO_3^{2-} (wt%): 59.2 ± 0.4 Mg (wt%): 1.32 ± 0.21 Fe (wt%): 1.87 ± 0.62 [c]S (wt%): 0.36 ± 0.19 K (wt%): 0.05 ± 0.04 Cu (wt%): < 0.01 Na (wt%): < 0.01 Mg/Ca: (mol ratio) 0.06
Coated casing	Calcite	–	Ca (wt%): 37.8 ± 0.1 [b]CO_3^{2-} (wt%): 60.3 ± 0.2 Mg (wt%): 1.46 ± 0.03 Fe (wt%): 0.26 ± 0.19 [c]S (wt%): 0.07 ± 0.02 K (wt%): 0.06 ± 0.05 Cu (wt%): < 0.01 Na (wt%): < 0.01 Mg/Ca: (mol ratio) 0.06

Rohr 4, 47 m u GOK, unbeschichtet, 0,95 mm

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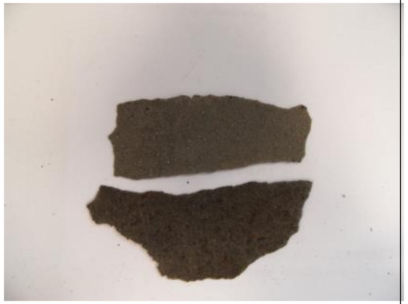
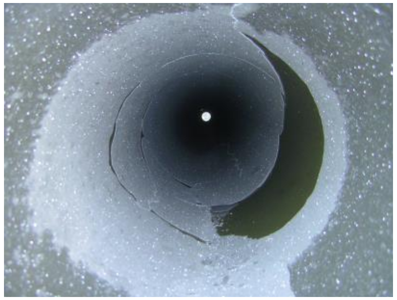


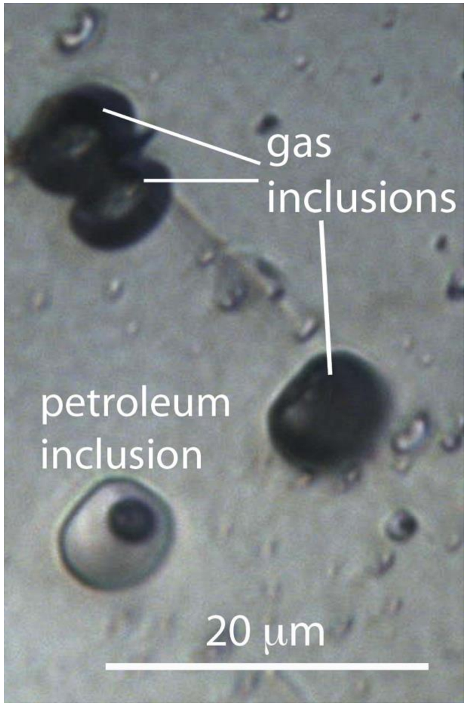
Rohr 65, 764 m u GOK, 0,50 mm



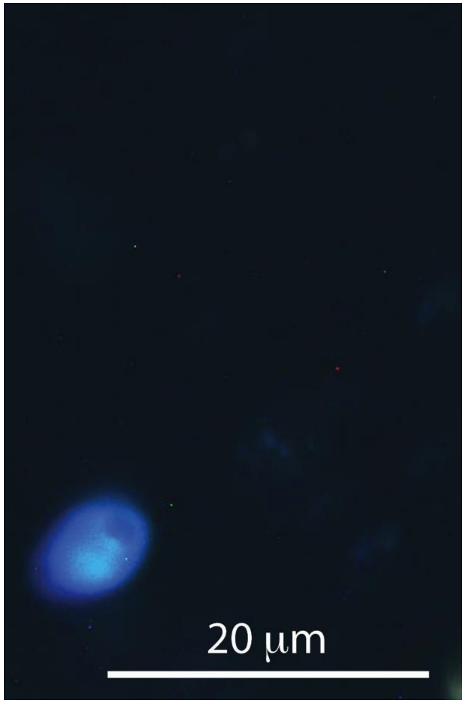
Ausfällungen am beschichteten Rohr

Fluid inclusions in carbonate precipitations

Transmitted light



UV light



Composition of gas inclusions

N_2	vol %	70-87
CO_2	vol %	13-30
CH_4	vol %	<1%

- Gas (N_2+CO_2) and petroleum inclusions are identified in calcite crystals
  - ➢ Demonstrates the presence of a free gas phase in the upflowing water + petroleum (3-phase system)
  - ➢ Dissolved gas concentrations of wellhead samples (N_2, CO_2, CH_4) are well below saturation (at $T=135^{\circ}$ C, 18 bar)

Scenarios leading to the formation of carbonate precipitations

Linear decompression scenario

The precipitation of calcite is controlled by the solubility decrease associated with the pressure drop of app. 280 bar occurring when the thermal water is pumped from the aquifer to the suface

Corrosion scenario

The precipitation of calcite is controlled by the corrosion of the casing and the associated increase in pH and decrease in calcite solubility

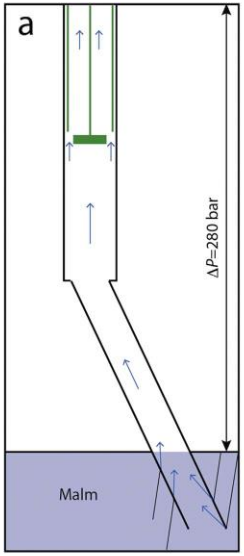
Gas influx scenario

The precipitation of calcite is controlled by an influx of a free gas phase into the production well, which based on gas analyses of crushed fluid inclusions which are dominated by N_2. As a consequence, dissolved CO_2 may be stripped into the gas phase, inducing a pH increase and hence a decrease in calcite solubility

Gas exsolution scenario

The precipitation of calcite is controlled by boiling of the produced thermal water within the pump at 800 m depth within the production well, due to a major, non-hydrostatically controlled pressure drop or to a major temperature increase.

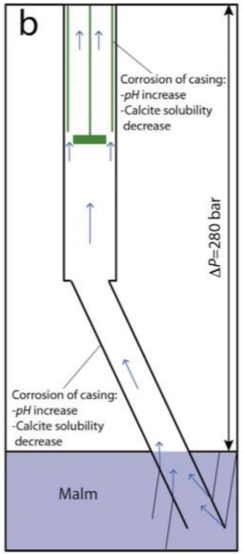
Scenarios leading to the formation of carbonate precipitations



Linear decompression scenario

Pressure drop during ascent of thermal water (app. 300 to 18 bar) yields to a slight oversaturation

→The decrease in DIC accounts for only 13 mol % of the amount that had to be numerically added to reconstruct the water composition at reservoir conditions.

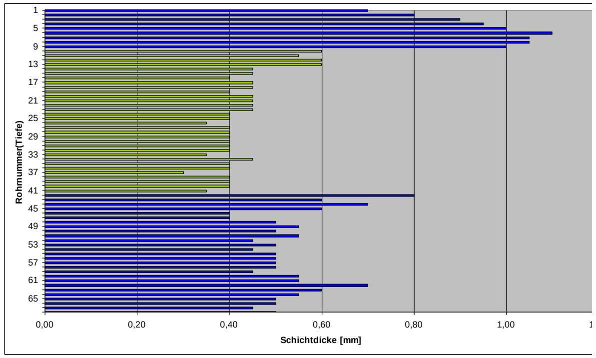


Corrosion scenario

Corrosion can have a minor influence on the formation of carbonate precipitation, but is not the main driving force.

$$\mathrm{Fe^0_{(s)}} + 2\mathrm{H^+} \rightarrow \mathrm{Fe^{2+}} + \mathrm{H_2}$$

$$\mathrm{HCO_3{}^-} + \mathrm{H^+} \rightarrow \mathrm{CO_{2(g)}} + \mathrm{H_2O}$$



→ **Both scenarios do not consider the presence of a free gas phase**

Scenarios leading to the formation of carbonate precipitations

Gas influx scenario

Gas influx from an distant source seems very unlikely in the occurring Geological setting.

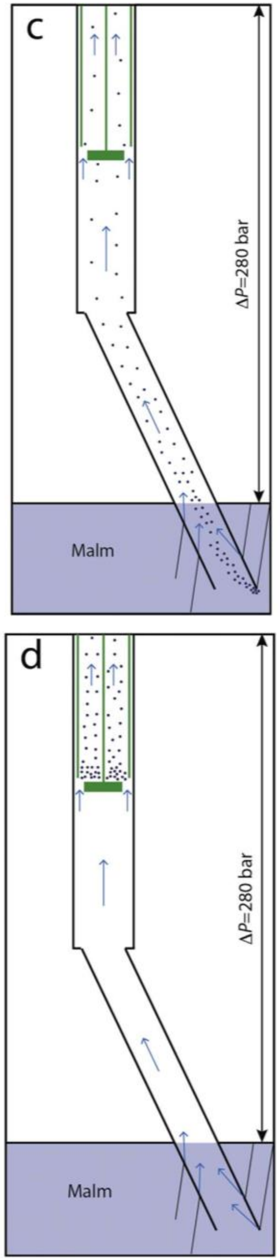
Thermal water is undersatureated with respect to occurring gas phases at given T and P conditions.

Gas exsolution scenario

Observations (e.g., gas inclusions, supersaturation) can be explained by boiling of the produced fluid within the production well

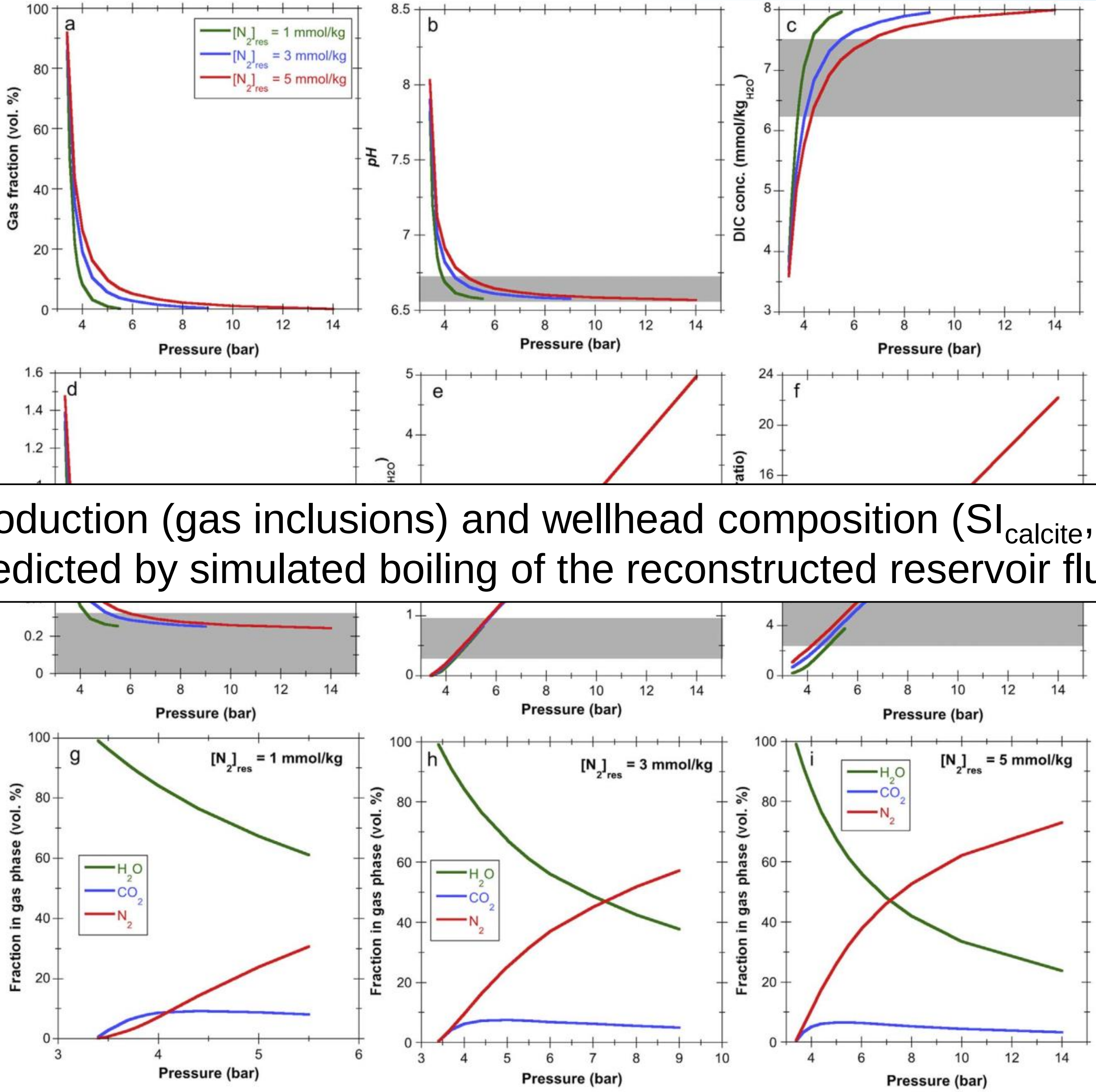
T_h of fluid inclusions correspond to the production temperature (T_h=128-138° C; T_{prod}=135° C)

- Boling is likely induced by a pressure-drop below the production pressure of 18 bar and not by a temperature increase
- The pump is the most likely location for observing such pressure-drop



Gas exsolution scenario

N_2	vol %	70-87
CO_2	vol %	13-30
CH_4	vol %	<1%



→ Gas production (gas inclusions) and wellhead composition ($SI_{calcite}$, pH, $[N_2]_{aq}$) can be predicted by simulated boiling of the reconstructed reservoir fluid at 4-6 bar

Summary and Conclusion

Conceptual scaling formation model:

- Carbonate equilibrium is prevailed at reservoir conditions (SI=0)
- Pressure drops to 4-6 bar at the pump
  - ➢ Effect of the rotating centrifugal pump (i.e., cavitation)
- Boiling of the produced fluid
- Calcite supersaturation
- Scaling formation during further upflow
- Trapping of gas (CO_2, N_2) in precipitating calcite crystals

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Causes of abundant calcite scaling in geothermal wells in the Bavarian Molasse Basin, Southern Germany

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ABSTRACT

The carbonate-dominated Malm aquifer in the Bavarian Molasse Basin in Southern Germany is being widely exploited and explored for geothermal energy. Despite favorable reservoir conditions, the use of geothermal wells for heat and power production is highly challenging. The main difficulty, especially in boreholes > 3000 m deep with temperatures > 120 °C, is that substantial amounts of calcite scales are hindering the proper operation of the pumps within the wells and of the heat exchangers at the surface. To elucidate the causes of scaling we present an extensive geochemical dataset from the geothermal plant in Kirchstockach. Based on chemical analyses of wellhead water samples, chemical and mineralogical analyses of scales collected along the uppermost 800 m of the production well, and chemical analyses of gas inclusions trapped in calcite-scale crystals, four processes are evaluated that could promote calcite scaling. These are (i) decompression of the produced fluid between the reservoir and the wellhead, (ii) corrosion of the casing that drives *pH* increase and subsequent calcite solubility decrease, (iii) gas influx from the geothermal reservoir and subsequent stripping of CO_2 from the aqueous fluid, and (iv) boiling within the geothermal well. The effectiveness of the four scenarios was assessed by performing geochemical speciation calculations using the codes TOUGHREACT and CHILLER, which explicitly simulate boiling of aqueous fluids (CHILLER) and take into account the pressure dependence of calcite solubility (TOUGHREACT). The results show that process i causes notable calcite supersaturation but cannot act as the sole driver for scaling, whereas ii and iii are negligible in the present case. In contrast, process iv is consistent with all the available observations. That is, scaling is controlled by the exsolution of CO_2 upon boiling at the markedly sub-hydrostatic pressure of 4–6 bar within the production well. This process is confirmed by the visible presence of gas inclusions in the calcite scales above the downhole pump, where the production fluid should nominally have been in the homogeneous liquid state. Whereas minor calcite scaling may have been triggered by fluid decompression within the production well, we conclude that the abundant scaling along the pump casing is due to cavitation induced by operating the pump at high production rates.

1. Introduction

The precipitation of mineral phases from geothermal fluids (i.e., scales) may pose a serious economic risk to the successful operation of geothermal plants (Thomas and Gudmundsson, 1989). Typical scaling phases include carbonates (Ámannsson, 1989; Arnórsson, 1989; Benoit, 1989; Lindal and Kristmannsdóttir, 1989), amorphous silica and silicates (Gunnarsson and Arnórsson, 2005 Kristmannsdóttir, 1989; Zarrouk et al., 2014), sulphates (Regenspurg et al., 2015) as well as mixed metal oxides and sulfides (Gallup, 1989; Regenspurg et al., 2015; Wilson et al., 2007), which are often associated with corrosion of parts of the geothermal plant (Honegger et al., 1989; Mundhenk et al., 2013). Scaling phases precipitate when they become supersaturated along the geothermal loop due to gas exsolution or due to a solubility decrease induced by changes in temperature and/or pressure as well as mixing between aqueous solutions with different chemical compositions (Bozau et al., 2015; García et al., 2006; Thomas and Gudmundsson, 1989). Typical problems associated with scaling include clogging of pipes and wells, reduced efficiency of pumps and heat exchangers, reduced reinjection capacity as well as accumulation of hazardous materials (e.g., Pb- and Ra-bearing scales) that require costly disposal (Bozau et al., 2015; García et al., 2006; Scheiber et al., 2013).

Over the past 15 years the Bavarian Molasse Basin in southern Germany has become a veritable hotspot for geothermal power

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Cavitation

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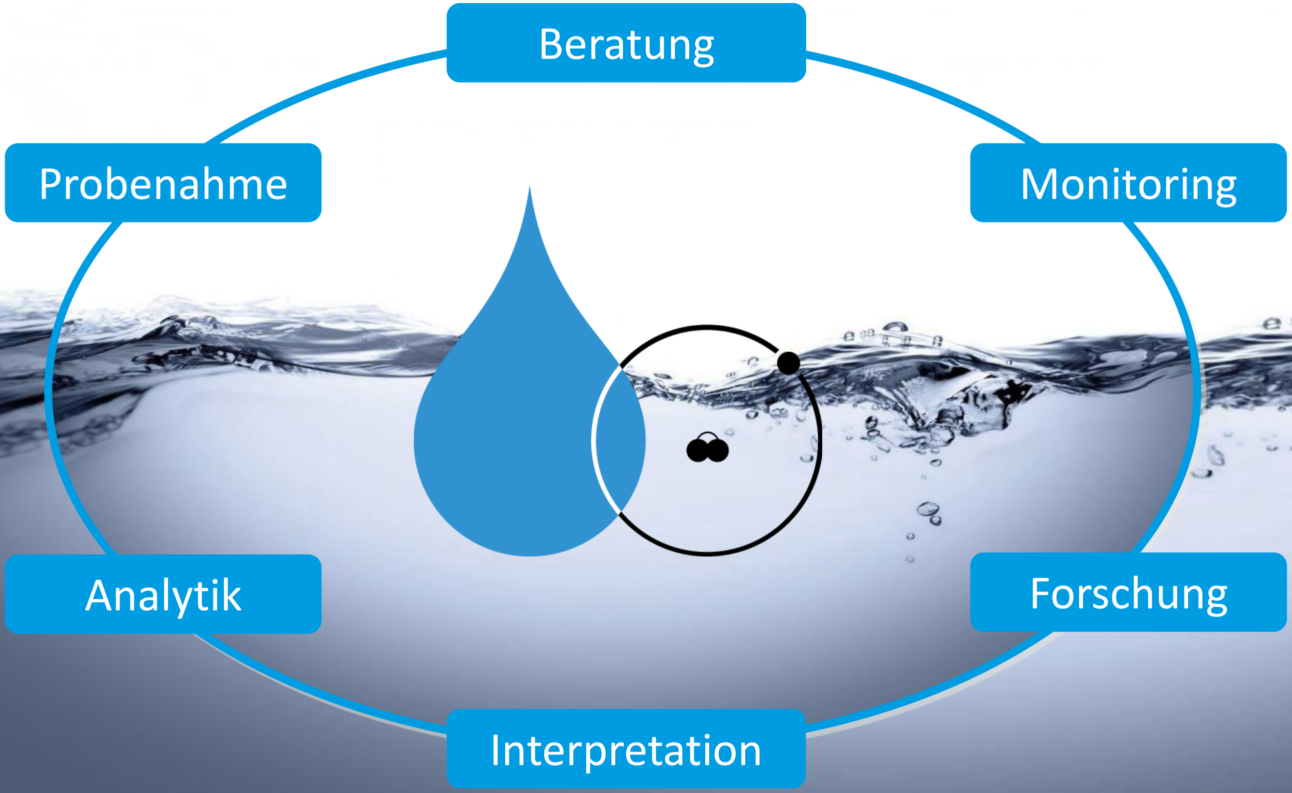
Thank you for your attention!

Questions?



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