# Fluid sampling and interpretation

Solutions in geothermal energy exploitation-Risks and benefits utilizing deep fluids

Simona Regenspurg

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# **Solutions**

Solution (chemistry): homogeneous mixture composed of two or more substances Example aqueous solution: Water as solvent



# Geothermal fluid



Hot spring: fluid reservoir is connected by faults and fractures to the surface

- Transported in the the pores and fractures of the geothermal reservoir
- Gas and liquid phase of high pressure and temperature
- Heat carrier for energy supply
- Often very saline with many chemical components



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## Geochemical risks and benefits utilizing deep fluids



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# Fluid ingredients may reveal:

- Origin (geology)
- Age
- History of migration and mixing processe
- Scaling and corrosion risks
- Environmental risks

- $\rightarrow$  Certain elements and isotopes (water and gas)
- → Radioactive deacy products (certain isotopes)
- $\rightarrow$  Certain elements and isotopes
- $\rightarrow$  Components that oversaturate; pH, redox, gasses

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- $\rightarrow$  Toxic and radioactive components
- Potential value (crm=critical raw materials) → CRM in sufficiently high concentration



## Low – and high enthalpy geothermal systems



## High enthalpy system

Low enthalpy system



## Water rock interactions determine fluid properties:



Surface near groundwater



Meteoric water, low salinity (< 1 g/L TDS)

Rock/ soil	water chemistry
carbonatic	Ca <sup>2+</sup> , Mg <sup>2+</sup> , HCO <sub>3</sub> <sup>-</sup> , high
aquifers	pH (>8)
Silici-	K⁺ (feldspar
clastic	weathering), pH 4-6

high enthalpy geothermal system



Fluid chemistry: meteoric water/ groundwater (volcanic rock) + gas + very high T → maturity → classification high enthalpy system

Different classification

low enthalpy geothermal system



Fluid chemistry: strong alteration due to old age, great depth →classification low enthalpy sytem



## A) High enthalpy geothermal systems

Giggenbach diagram (1988): CI-SO<sub>4</sub>-HCO<sub>3</sub> system:

SO







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## **Surface Manifestation:**

visible indication of geothermal activity e.g. hot springs, mudpools, fumaroles, hot steaming ground, rock alterations



Hot spring: geothermally heated groundwater

Mud pot: limited water

**Fumarole:** steam discharge from a hydrothermal or volcanic system  $\rightarrow$  solfatara: sulfur emissions







## Indonesia as example of high enthalpy geothermal system









## Hot springs sampled by GFZ in Indonesia (Nov 2010)



Sipoholon (North Sumatra)

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## Examples of hot springs sampled by GFZ in Indonesia



## After geochemical explorations: geophysical methods $\rightarrow$ e.g. Magnetotelluric



D Inversion of Magnetotelluric Data from the Sipoholon Geothermal Field , Sumatra , Indonesia (2014) <u>Sintia Windhi Niasari, Gerard Muñoz, Oliver Ritter</u>

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#### B) Low enthalpy geothermal systems

1. Fluid classification according to the geology of the fluid origin

#### rocks

sediment basin rock



sandstone

crystalline rock



granite



granite, gneiss, volcanic rock...



- 2. Fluid classification according to the salt content
  - = total dissolved solids (TDS)

TDS (g/L)	classification
< 1	freshwater
1-10	brackish water
10-100	saline water
>100	brine

#### Examples: Salt content in

- Seawater: 35 g/L
- Dead Sea: 200-300 g/L



Dead Sea



Salinity of geothermal fluids (TDS)

- TDS increases with increasing depth
- Most geothermal fluids are brines →
  high salt content (very corrosive)
- Highest known salt content of a geothermal fluid: Salina formation;
  Michigan Basin: TDS = 643 g/L

Case, 1945





Data from Hanor et al., 2004; Giehse et al., 2002; Wolfgramm et al., 2007; Frape et al., 2004; Pauwels et al., 1993

## Why increases the fluid salinity with increasing depth/age?

**Fluid History** 

- 1. Rock formation: porewater in equilibrium with minerals of the formation; Often the sedimentation area is already highly saline (e.g. aride salt pans) → Permische Rotliegendsandsteine
- Fluid mobilization: fluid moves along pores and fractures of the rock due to gravity and/ or given pathways.
- **3.** Reactions of the fluid with the surrounding material  $\rightarrow$  new equilibrium
  - dissolution/ precipitation (saturation)
  - redox reactions
  - diagenetic reactions/ mineral transformation

4. Mixing with other fluids or seawater  $\rightarrow$  new equilibrium



ROCK

**OPEN FRACTURE** 

HELMHO





final fluid  $\rightarrow$  increased salinity (increases with age and depth)

#### Fluid composition



#### Main components:

easily dissolvable cations and anions:

Ca, Na, Cl (78 - 98 wt.-% TDS)

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Daten aus Kharaka and Hanor, 2004; Hanor et al., 2004; Giese et al., 2002; Wolfgramm et al.; 2007, Frape et al., 2004

## Relevant properties of fluids to be measured

- pressure (p), temperature (T)
- physical parameters: density, viscosity, compressibility, heat conductivity
- chemo-physical parameters: pH-value, redox (E<sub>H</sub>-value), electric conductivity
- chemical parameters: cations, anions, undissociated compounds, gases, (isotopes)
- (Organics and microorganisms)





# Correct sampling



Avoid contamination Avoid reactions

 $\rightarrow$  clean, oxygen free, particle free, potentialy diluted





# Preparation in field

In –situ parameters: • site descirption

- pH
- redox
- electric conductivity
- dissolved oxygen
- bicarbonate
- Fe(II)
- monomeric silica

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**T7** 

Sample preparation:

- Cations
- Anions
- Silica
- Organics
- Microorganisms
- Certain isotopes



## Green Field sampling (hot springs; no wells)



### 1. Site desciption







## 2. Physicochemical parameters:

Probes for pH, electric conductivity, redox

 $\rightarrow$  Calibrate the pH probe every day!

Fluid properties indicating ongoing chemical processes

**Probes: electrochemical measurements /** Potentiometric on-line measurement of physico-chemical fluid characteristics

parameter	information/goal
electric conductivity	total salt content (cations and anions)
pH and redox value	Concentration of protons and electrones; redox reactions, speciation
dissolved oxygen	to predict oxidation





High p, T, and ionic strength represent a challenge for all electrodes

## 2. Reactive phases e.g. Fe(II) and monomeric silica

#### **Field photometer**

#### Lambert-Beer Law

$$A = \varepsilon \cdot c \cdot d$$

 $\boldsymbol{\epsilon} \cdot \boldsymbol{c} \cdot \boldsymbol{d} = -\mathbf{Ig} \, \mathbf{I} / \mathbf{I}_0$ 

- $I_0$ : light intensity before passing the sample
  - : measured intensity after
- A : absorption
- ε: absorption constant; addition of a complexing reagent requred



#### 3. Hydrogen carbonate and carbonate ions - titration

- I. Hydrogen carbonate  $(HCO_3^-)$  and carbonate  $(CO_3^{2-})$  ions are titrated with hydrochloric acid (HCI) against a mixed indicator.
- II. At the titration end-point (pH 4.3) the color changes to red.
- III. The carbonate hardness (acid capacity) is determined from the consumption of titration solution.







## 4. Sample preparation

- I. Filtration: 0.45 µm syringe filter
- II. One subsample: acidified: for cation analyis in the lab $\rightarrow$  pH< 2 $\rightarrow$  prevents formation of Fe(III)hydroxide $\rightarrow$  no precipitation
- III. One sample: only filtered for anion analyis → measure as quick as possible
- IV. Organics: store in dark glass (500 mL)
- V. Silica: often oversaturated already → dilute sample1:1 with destilled water
- VI. Microorganisms: sterile filtration (a lot)

VII. Certain isotopes: e.g. <sup>34</sup> S:precipitation as BaSO<sub>4</sub> by adding BaCl<sub>2</sub>







#### Fluid Monitoring (at a geothermal well)



FluMo I (field)

- -Fluid composition
- -density
- -pH-value
- -Redox-potential
- -oxygen
- -electric conductivity
- -P-, T-, volume flow



## **Chemical parameters: cations of importance**

- Na<sup>+</sup>, Ca<sup>2+</sup>: highest concentrated cations in geothermal fluids (highly mobile and due to halite (NaCl) dissolution)
- K<sup>+</sup>, Mg<sup>2+</sup>: less dominant, but important for geothermometer calculation (fluid-rock interaction)
- Fe<sup>2+</sup>, Mn<sup>2+</sup>: redox sensitive (Fe<sup>3+</sup> Mn<sup>4+</sup>), oxidized by O<sub>2</sub>, form hardly soluble minerals in presence of oxygen (O<sub>2</sub>), carbonates (CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>), or sulphide (S<sup>2-</sup>).
- Ba<sup>2+</sup> and Sr<sup>2+</sup>: form with sulphate hardly soluble barite (BaSO<sub>4</sub>) or coelestine (SrSO<sub>4</sub>)
- Heavy metals: Pb<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Hg<sup>+</sup> usually < 1 mg/l (bound as hardly soluble sulphides); high concentration due to formation of soluble complexes by binding to chlorine, bisulfide or organic matter
- Critial raw materials: Li, Sr, REY, Pt group elements





#### **Chemical parameters: Anions of importance**

- Chloride (CI<sup>-</sup>): highest concentrated anions in deep geothermal fluids (50-60 % of TDS in brines) due to low solubility of CI-minerals (very corrosive!)
- Sulphate (SO<sub>4</sub><sup>2-</sup>): usually <1000 mg/l; controlled mainly by anhydrite (CaSO<sub>4</sub>) solubility; input: oxidation of sulphides (esp. pyrite, FeS<sub>2</sub>), dissolution of sulphate minerals (e.g. CaSO<sub>4</sub>), seawater
- Carbonate (CO<sub>3</sub><sup>2-</sup>) and bicarbonate (HCO<sub>3</sub><sup>-</sup>): usually below a few hundred mg/L in solutions of salinities > 30 g/l

→ problem with sulfate and carbonate: facilitated oversaturation and precipitation as  $CaSO_4$ , (gypsum),  $BaSO_4$  (barite),  $FeCO_3$  (siderite),  $MnCO_3$  (rhodochrosite), or  $CaCO_3$  (calcite or aragonite).





## Chemical parameters: Silica

Dissloved SiO<sub>2</sub> / silicic acid =  $[SiO_x(OH)_{4-2x}]_n$ 

- concentration: mainly controlled by the solubility of quartz, chalcedon, amorphous silica (use of geothermometer)
- range: 10 to 1000 mg/L
- slow precipitation of amorphous silica → fluids are not in equilibrium → highly oversaturated (mainly in high enthalpy geothermal systems)
- silica precipitation is especially undesired in geothermal plants









Chemical parameters: Organics in geothermal fluids

- 1. Non dissolved organic matter: hydrophobic  $\rightarrow$  oil
- 2. Particulate organic matter: > 0.45  $\mu$ m  $\rightarrow$  clogg filters; transport heavy metals
- 3. Dissolved organic carbon (DOC): few to several thousand mg/L
- mainly mono-and di-carboxylic acids (e.g. acetate, propionate, butyrate, malonate and oxalate) and phenols
- generated by thermal alteration of kerogen (organic residues such as plants)
- acts as proton donor for pH dependent reactions (esp. for microbiol. induced reactions)
  →food for microorganisms

e.g. oxidation of acetate:  $CH_3COOH + O_2 \rightarrow 2 CO_2 + 2 H_2\uparrow$ 

- act as pH-, Eh- buffer
- complexing agent for (heavy) metals  $\rightarrow$  keep the complexed metal in solution

Organic content decrease with increasing temperature (low enthalpy geothermal)





## Chemical parameters: Gases

Geothermal gas (non condensable gas – NCG): N<sub>2</sub>, CO<sub>2</sub>, He, CH<sub>4</sub>, H<sub>2</sub>S, H<sub>2</sub>, (O<sub>2</sub>)

#### **Gas content**

Solubility ( $\lambda$ ) of gases in water:

depends on p, T, ionic strength, kind of gas





Importance during production of geothermal fluids: degassing due to pressure change → e.g. CO<sub>2</sub> degassing





Carbonate - carbonic acid - equilibrium

Dissolution of  $CO_2$  in water:

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 $H_2O + CO_2 \leftrightarrow 2H_2CO_3 \leftrightarrow HCO_3^- + H^+$  $\rightarrow$  acid release

In presence of limestone:  $H_2O + CO_2 + CaCO_3 \leftrightarrow 2HCO_3^- + Ca^{2+}$ 

 $\rightarrow$  limestone dissolution

Degassing:  $H_2O (+ CO_2) + CaCO_3 \leftrightarrow HCO_3^- + Ca^{2+} + OH^ \rightarrow$  pH increase and calcite precipitation GFZ Prevention of CO<sub>2</sub> degassing



Example: karst formation (stalactite cave)









## Geochemical Methods in exploration – geothermometer



**Definition:** A system that gives evidence on temperatures of the formation or transformation of a phase

Principle: Equilibria of solid and liquid systmes exists only in a certain T-, p- range

**Important:** Temperatures of melting point, transformation, demixing





#### **Example (mineralogy):** SiO<sub>2</sub> transformation







## Geothermometers in fluids

Information on the **reservoir temperature** of a fluid, **collected on the surface** of a high enthalpy geothermal system

 $\rightarrow$  Exploration: analysis of water/ gases (hot springs) at pre-drilling state

#### **Principle:**

Chemically reactive groups (geoindicators) react in a well understood manner at certain T with the rocks of the reservoir.





#### Types of geothermometer:

- Silica geothermometer
- Cation geothermometer
- Isotope geothermometer (<sup>18</sup>O)
- gas geothermometer

#### To be considered:

- Debit
- Steam
- pH, salinity

#### Assumptions for the use:

- Liquid is in equilibrium with relevant hydrothermal minerals in the reservoir
- No mixing of the geothermal liquid with shallow groundwater/ seawater
- No precipitation during the uplift

**Problem:** often inaccurate; best to apply several geothermometers





## Silica (SiO<sub>2</sub>) geothermometers

Reaction rates for different silica phases in a hydrothermal system are strongly dependent on T, p, acidity.

- based on T- dependent variations in SiO<sub>2</sub> solubility
- SiO<sub>2</sub> solubility decreases linearly with temperature at T < 340 °C (neutral pH)</li>
- dissolution and precipitation of quartz is fast at high T and slow at low T
- equilibrium/ saturation at high T → Si concentration
  is "frozen" (little change during fast uplift)

Estimating reservoir temperatures



Fournier, 1973, 1991

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Silica (SiO<sub>2</sub>) geothermometers (200 - 300 °C)

quartz no steam loss: T (°C) = (1309/5.19 – log Si) - 273.15

Erroneous results due to the:

 Effects of steam separation, which can concentrate the fluid causing early precipitation of silica.

> quartz, max. steam loss: T (°C) = (1522/5.75 – log Si) - 273.15

- Effects of precipitation after sampling, since the rate of quartz precipitation increases drastically as temperature drops.
- Effect of pH on quartz solubility.
- high salinity fluids, which alter quartz solubility.
- Effects of dilution due to cold water mixing.



Fournier, 1973, 1991



## Cation geothermometer

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- Example: Na-K, Na-K-Ca → source: feldspars → mixing ratio depends on T
- Principle: T- dependent ion exchange reactions

Feldspars: 3 types (endmembers):

- Orthoklas/Microcline KAISi
- Albite NaAlSi<sub>3</sub>O<sub>8</sub>
- Anorthite  $CaAl_2Si_2O_8$





## Cation geothermometer

- T- dependent ion exchange reactions
  - exchange of Na by K in alkali feldspars:

NaAlSi<sub>3</sub>O<sub>8</sub> + K → KAlSi<sub>3</sub>O<sub>8</sub> + Na K<sub>eq</sub> = Na/K → K<sub>eq</sub> varies little at T < 300°C (linear)

• decrease of the Na-K- ratio with increasing T

 $T (^{\circ}C) = 1390/(1.75 + \log (Na/K)) - 273.15$ 

(Giggenbach et al., 1988)

# Giggebach diagram: Water rock equilibrium temperature





#### **TABLE 4: Selected Geothermometers.**

	Geothermometer	Temperature Range (°C)	Sample	Sample	Sample
			BTHN	BTHS-1	BTHS-2
1	Na/K	Fournier (1979)	84	83	102
2	Na/K	Arnórsson et al2 (1983)	89	88	107
3	Na/K	Giggenbach et al. (1988)*	99	101	118
4	Na/K	Verma and Santoyo (1997)	85	87	104
5	Na/K	Arnórsson (2000)	84	85	88
6	Na/K	Can (2002)	103	103	112
7	Na-K-Ca (Mg-Corrected)	Fournier and Potter (1979)	213	211	238
8	Na-K-Ca	Fournier and Truesdell (1973)	136	264	223
9	Na-K-Ca	Kharaka and Mariner (1989)	240	236	281
10	Na-K-Mg	Nieva and Nieva (1987)	86	84	97
11	K <sup>2</sup> /Mg	Giggenbach et al. (1988)	64	59	70
12	Quartz	Truesdell (1976)	86	84	84
13	Quartz	No Steam Loss, Fournier (1977)	81	79	81
14	Quartz	Maximum Steam Loss, Fournier (1977)	84	83	83
15	Quartz	Fournier & Potter (1989)	81	81	81
16	Quartz	Fournier & Potter (1989)	80	79	79
17	Quartz	Arnórsson (2000)	66	65	65
18	Quartz	Verma (2000)	72	74	74
19	Chalcedony	Arnórsson et al. (1983)	65	67	67

Proceedings World Geothermal Congress 2015 Melbourne, Australia, 19-25 April 20151Comparison of Silica and Cation Geothermometersof Bath Hot Springs, Jamaica WIDeBonne N. Wishar



Example Indonesia

#### Sampling of hot spring water in Java, Mai 2009

	Measured T, surface	Quartz	Mg/Li	Na/Li	Na/K	NaKCa	Estimated reservoir T
	(°C)						(°C)
Reference *	-	(1)	(3)	(4)	(5)	(6)	
Padusan	49.7	162	220	138	318	225	225 ± 10
Cangar	50.4	138	198	16	352	232	140 ?
Songgoriti	46	172	269	194	200	174	<b>190 ± 10</b>
Tiris	38.6	160	249	168	286	219	<b>190 ± 30</b>
Kamojang	68	152	132	85	452	56	<b>100 ± 10</b>

\*References:

(1) Fournier, 1977 (3) Kharaka & Mariner, 1989;

(4) Kharaka et al., 1982;

(5) Fournier, 1979 ; (6) Fournier & Truesdell

\*Calculations by Francois Vuataz (CREGE/ UNINE)



Mud pool Kamojang

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## Summary: Geothermometers

- Can be a very useful (quick and cheap) tool to determine temperatures of reservoirs
- but since equilibria are often unknown, it is important to understand
  which geothermometer is applicable for a certain system
- and to compare always several geothermometer calculations



