## Geochemical methods in geothermal exploration and exploitation

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- The focus in the talk will be on the role of geochemistry in exploring and exploiting high-temperature geothermal systems (T > 180°C)
- I will emphasis the need of careful sampling of geothermal fluids
- And say a few words about data interpretation
  - Geothermometers
  - Fluid qualities, scaling

Geochemical methods are extensively used and play a major role in geothermal exploration and exploitation!



#### Geothermal exploration and development

- At the onset of a geothermal exploration project it is uncertain whether or not the results will be economically, technically and environmentally feasible.
- Geothermal exploration and development, therefore, invariably necessitate risk money.
- Because of the uncertainty involved it has become common practice to divide the preparatory work into several phases in order to minimize cost and maximize information for each phase.



#### Geothermal project strategy

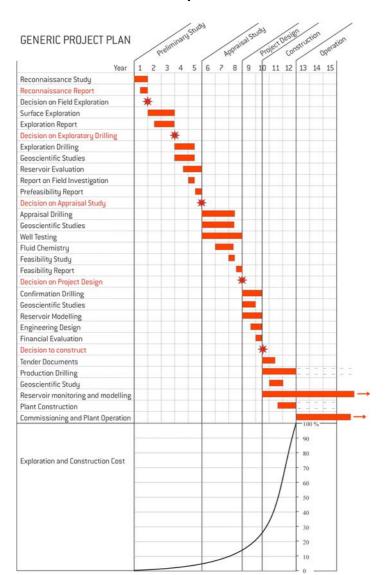
The main phases are (in a simplefied way):

- Surface exploration
- Exploration drilling
- Production drilling
- Preliminary power plant design
- Financing, additional production drilling, construction
- Operation, monitoring

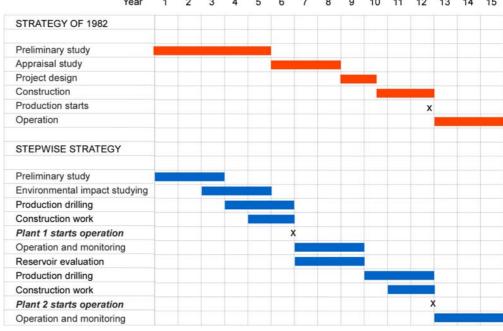




### In a more sophisticated way we can divide each phase into several phases and we can put a time scale on the project!









## Geochemistry and geochemical methods are extensively applied in all phases of geothermal exploration and development!







The basic philosophy behind using geochemical methods in geothermal exploration is that fluids on the surface (aqueous solutions or gas mixtures) reflect physicochemical and thermal conditions in the geothermal reservoir at depth!



Geochemical studies of geothermal fluids essentially involve three steps:

- Sampling
- Analysis
- Data interpretation

Obtaining representative samples of geothermal fluids require specific sampling techniques and containers



### In the exploratory phase the task of geochemistry is mainly to >

- Estimate subsurface temperatures by using chemical and isotope geothermometers as well as mixing models
- Identify the origin of the geothermal fluid, mainly with isotopic techniques
- Define chemical properties of the fluid with respect to environmental issues, scaling ....
- Provide data to a conceptional model of the geothermal system



### In the phase of exploration drilling the main task of geochemistry is to >

- Provide information on water to steam ration in the reservoir
- Assess the quality of the geothermal fluid with respect to the intended use
- Assess the quality of the geothermal fluid with respect to the environment
- Provide information on scaling tendencies of the fluid in production as well as injection wells and surface equipment
- Provide additional information to a conceptional model of the geothermal reservoir



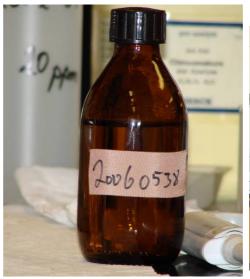
# In the phase of production drilling and operation of a power plant the main task of geochemistry is to >

- Identify recharge into the reservoir of shallow groundwater or deeper hot water
- Assess boiling processes in production aquifers
- Identify changes in the chemistry of the geothermal fluid
- Quantify changes in scaling and corrosion tendencies
- Monitor the quality of the geothermal fluid with respect to the environment



- Chemical and isotopic analyses are expensive and tedious and all is wasted if the sampling is incorrect
- Chemical data interpretation becomes meaningless or even worse, misguiding, if the sampling is incorrect







Important to emphasise the need of careful sampling



- ·Sampling in a high temperature field
- ·Safety first
- ·Selection of suitable sites
- ·Fumaroles
- ·Hot springs
- ·Sample thermal and non-thermal fluids









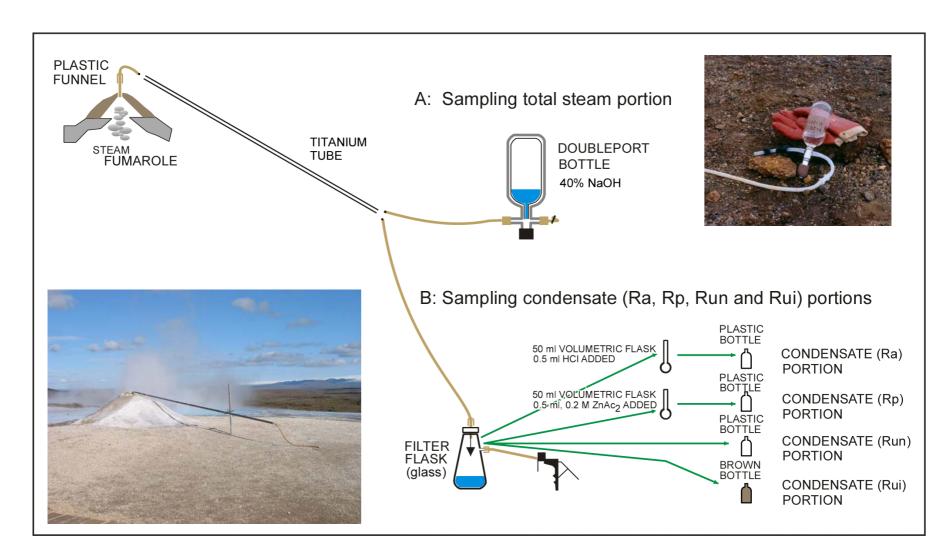












Collection of sample from a fumarole



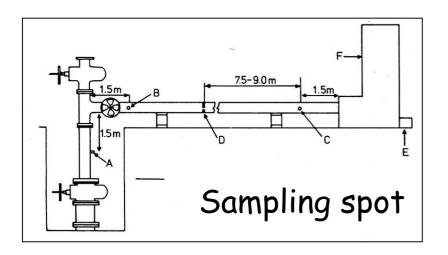




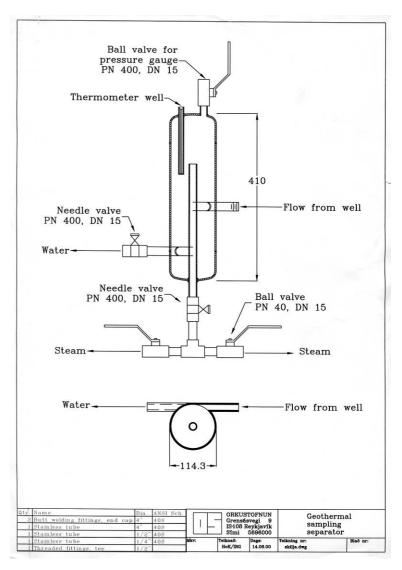


Sampling from: Exploration wells Production wells Power stations



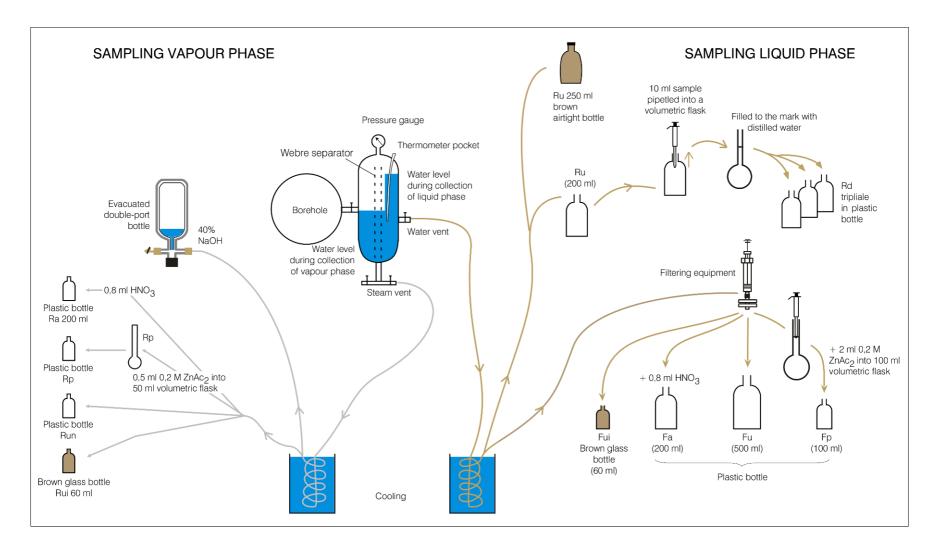






Webre separator





Collection of sample from a two-phase geothermal well



#### Data Interpretation - Geothermometers

- Chemical and isotope geothermometers probably constitute the most important geochemical tool for the exploration and development of geothermal resources.
- They are used to:
  - Estimate subsurface temperatures of a geothermal reservoir
  - Monitor temperature changes of the reservoir during production
- Geothermometers have been classified into three groups:
  - Water or solute geothermometers
  - Steam or gas geothermometers
  - Isotope geothermometers

Water and steam geothermometers are generally referred to as chemical geothermometers



#### Water or solute geothermometers

- Mostly developed from mid-1960's to mid 1980's
- The most important once are:
  - Silica
  - Na/K
  - Na-K-Ca
  - And less important are e.g.:
  - Na/Li, Li/Mg and Na-K-Mg



#### Silica geothermometer - a bit of history

- Suggested by Böðvarsson in 1960 and developed further by Böðvarsson & Pálmason 1961
- Fournier & Rowe, 1966, 120° 330°C
- · Arnórsson, 1975; Chalcedony
- Fournier, 1977. Silica-enthalpy mixing model
- Fournier & Potter 1982 new equation 20° 330°C and salinity accounted for

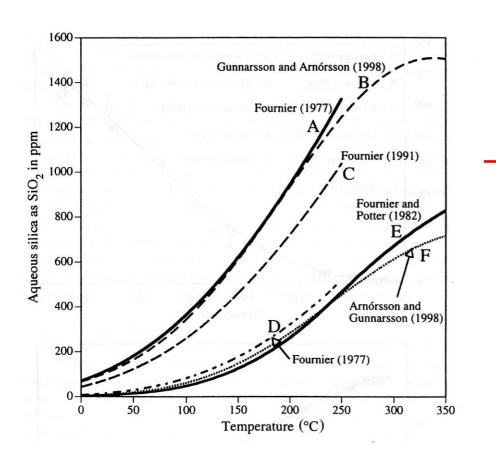


#### Silica geothermometer, cont'd

- Several known silica polymorphs in nature
- Quartz, amorphous silica, moganite, tridymite, cristobalite, coesite, stichovite.
- Chalcedony is a variety of quartz, composed of very fine quartz crystals, so fine that their surface energy contributes to their solubility and therefore explaining why chalcedony is more soluable than quartz.
- The Icelandic experience is that geothermal waters equilibrate with chalcedony below 180°C and with quartz at higher temperatures.



The solubility of quarts, chalcedony, opal and amorphous silica in water at 1 bar below 100°C and at the vapour pressure of the solution at higher temperatures.



#### Silica geothermometers, examples

S represents silica conc. as SiO2 in mg/kg

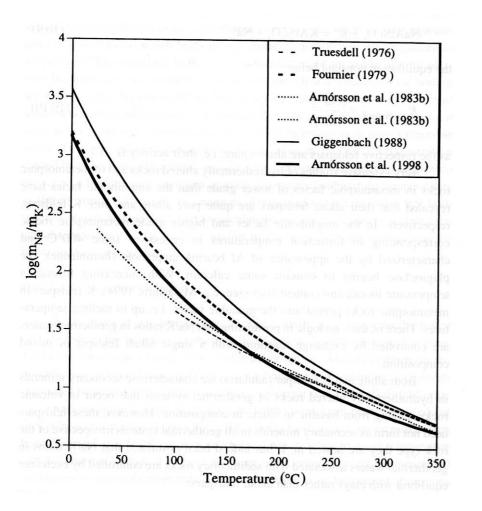
Geothermome	eter Equation (t in °C)	Range (°C)	Source
Quartz	$\frac{1309}{5.19 - \log S} - 273.15$	25–250	Fournier (1977)
Quartza	$\frac{1522}{5.75 - \log S} - 273.15$	25–250	Fournier (1977)
Quartz	$\begin{array}{l} -42.2 + 0.28831S - 3.6686 \times 10^{-4}S^2 \\ +3.1665 \times 10^{-7}S^3 + 77.034 log S \end{array}$	25–900	Fournier and Potter (1982)
Quartz <sup>a,b</sup>	$\begin{array}{l} -53.5 + 0.11236S - 0.5559 \times 10^{-4}S^2 \\ + 0.1772 \times 10^{-7}S^3 + 88.390 \mathrm{log} \ S \end{array}$		Fournier and Potter (1982)
Quartz	$-55.3 + 0.3659S - 5.3954 \times 10^{-4}S^{2} + 5.5132 \times 10^{-7}S^{3} + 74.360 \log S$	0–350	Arnórsson et al. (1988a)
Quartza	$\begin{array}{l} -66.9 + 0.1378S - 4.9727 \times 10^{-5}S^2 \\ + 1.0468 \times 10^{-8}S^3 + 87.841 \mathrm{log} \; S \end{array}$	0–350	Arnórsson et al. (1988a)
Chalcedony	$\frac{1032}{4.69 - \log S} - 273.15$	0–250	Fournier (1977)
Chalcedony	$\frac{1112}{4.91 - \log S} - 273.15$		Amoórsson et al (1983b)
Moganite <sup>c</sup>	$\begin{array}{l} -30.7 + 0.53113S + 1.2578 \times 10^{-4}S^2 \\ -5.9241 \times 10^{-7}S^3 + 19.576\log S \end{array}$	0–200	Gíslason et al. (1996)
α-Crisobalite	$\frac{1000}{4.78 - \log S} - 273.15$		Fournier (1977)

#### Cation geothermometers - a bit of history

- Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Ca<sup>+2</sup>, Mg<sup>+2</sup> are mostly used
- The Na/K ratio in geothermal water were initially used to locate upflow zones in Wairakei by Ellis and Wilson 1961
- At that time is was already proposed that the Na/K ratios were probably controlled by equilibrium between geothermal water and alkali feldspars and depended on temperature
- Many empirical calibrations have been proposed
- Recently Arnórsson et al. have retrieved a new calibration based on experimental thermodynamic data



#### Proposed temperature curves for the Na-K geothermometer



#### Na-K geothermometers, examples

	0.2. TEMPERATURE EQUATION GEOTHERMOMETER		
Conc	centrations are in ppm if not other	erwise spec	ified.
Geothermometer	Equation (t in °C)	Range (°C	C) Source
Na-K		100–275	Truesdell
	$0.857 + \log(\text{Na/K})$		(1976)
Na-K	1217	5	Fournier (1979)
Na-K	$\frac{1.438 + \log(\text{Na/K})}{1.438 + \log(\text{Na/K})}$		
and the second	833	5	Tonani (1980)
Na-K	$\frac{0.780 + \log(\text{Na/K})}{0.780 + \log(\text{Na/K})} - 273.15$		
	933	25–250	Arnórsson et al. (1983b)
Na-K	$\frac{300}{0.993 + \log(\text{Na/K})} - 273.15$		
Na-K	1319 - 273.15	250-350	Arnórsson et al. (1983b)
Nu-IX	$1.699 + \log(\text{Na/K})$	250-550	
Na-K			Nieva and Nieva (1987)
114-12	$1.470 + \log(\text{Na/K})$		
Na-K	1390		Giggenbach
Na-K	$\frac{1.750 + \log(\text{Na/K})}{1.750 + \log(\text{Na/K})} - 273.15$		et al. (1988)
N. Va	$733.6 - 770.551Y + 378.189Y^2$	0-350	
Na-K <sup>a</sup>	$-95.753Y^3 + 9.544Y^4$		Arnórsson et al. (1998)
w. v. b	2330		Fournier (1991)
K-Mg <sup>b</sup>	$\frac{2530}{7.35 + \log(K^2/Mg)} - 273.15$		
V M-s	1077		Faurrier (1001)
K-Mg <sup>c</sup>	$\frac{1077}{4.033 + \log(K^2/Mg)} - 273.15$		Fournier (1991)
V.M.	4410		Ci
K-Mg	$\frac{4410}{14.0 + \log(K^2/Mg)} - 273.15$		Giggenbach (1988)



#### Steam (gas) geothermometers

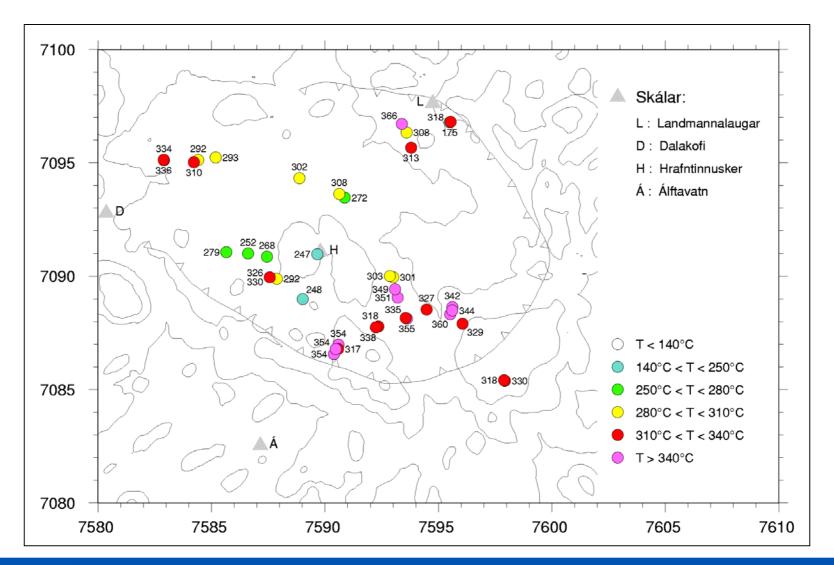
- The first gas geothermometer developed was that of D'Amore & Panichi (1980)
- Essentially three types of steam geothermometers
  - Gas gas equilibria
  - Mineral gas equilibria involving  $H_2S$ ,  $H_2$  and  $CH_4$  and assuming  $CO_2$  to be externally fixed
  - Mineral gas equilibria

The first two groups require only data on the relative abundance of gaseous components in the gas phase

The third group calls for information on gas concentration in steam



#### Torfajökull, Iceland CO2 / N2 - gas geothermometer





#### Isotope geothermometers

- Fractionation of isotopes of the light elements is quite significant and temperature dependent
- Possible to use the distribution of the stable isotopes of H, C and O between aqueous and gaseous compounds as geothermometers
- Several isotopic geothermometers have been developed and are quite extensively used



#### Examples of isotope geothermometers (SA, 2000)

$$1 {}^{12}\text{CO}_2 + {}^{13}\text{CH}_4 = {}^{13}\text{CO}_2 + {}^{12}\text{CH}_4$$

$$2 \quad CH_3D + H_2O = HDO + CH_4$$

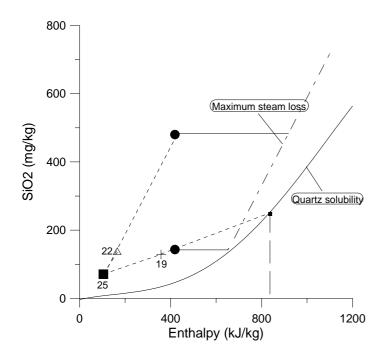
$$3 \quad HD + H_2O = H_2 + HDO$$

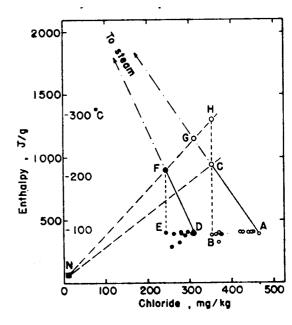
$$4 S^{16}O_4 + H_2^{18}O = S^{16}O_3^{18}O + H_2^{16}O$$

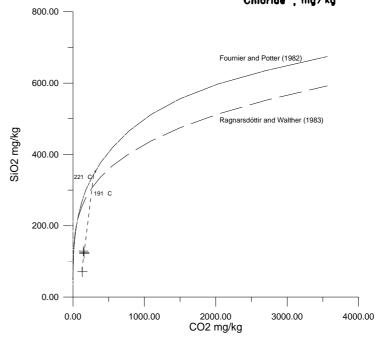
Thus, the first geothermometer is based on  $\delta^{13}$ C values in  $CO_2$  and  $CH_4$ , the second and third on  $\delta^2$ H in  $CH_4$  and steam and in  $H_2$  and steam, respectively. The fourth geothermometer uses  $\delta^{18}$ O in aqueous  $SO_4$  and liquid water.



# Mixing models are used to estimate temperatures in geothermal reservoirs



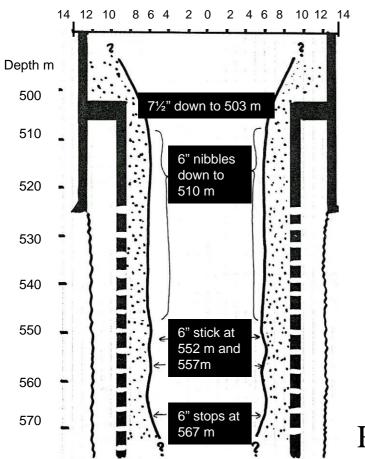






#### Scaling, corrosion

#### Wellhead diameter in inches







RN-9



# Some future geochemical tasks associated with e.g. UGR or IDDP (dealing with super critical fluids), EGS, CO<sub>2</sub> capture and storage, etc

- Many unsolved chemical problems may be associated with mining geothermal fluids from very deep and very hot reservoirs, IDDP-project, UGR, EGS etc.
- Hostile fluid super critical fluids!
- Precipitation, scaling, corrosion etc.
- Geochemical methods are heavily involved in a present project involved in capturing and geological storage of CO2 at Hellisheiði, SW-Iceland
- New methods and new technologies might be needed
- It is necessary to strengthen the thermodynamic database for computer programmes used for data evaluation and modelling
- Geochemical methods will be involved in many future geothermal projects





#### Thank you!



