

**Using the Geochemistry of Hydrothermal Fluids
to Understand and Manage
Geothermal Resources
Exploration, Assessment, Development and
Operations**

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**USC CGS
Distinguished Lecture Program**

GEOHERMAL FLUID GEOCHEMISTRY

- ◎ Provides tools for every stage of geothermal resource development
 - Exploration: discover hydrothermal system(s) of sufficient potential to support geothermal development
 - Resource Assessment: characterize the size and nature of geothermal resources for geothermal project development feasibility and design
 - Reservoir Monitoring: monitor changes in the reservoir during exploitation which affect the project resource

SUMMARY

USING GEOCHEMISTRY TO UNDERSTAND & EXPLORE GEOHERMAL SYSTEMS AND MANAGE GEOHERMAL RESERVOIRS

- What questions can we address at what stages of a project?
- Why does fluid geochemistry (sometimes) reveal characteristic of geothermal systems?
- What are typical geochemical fingerprints of different geothermal systems
- How do we investigate?
- Sampling, analysis and interpretation of surface manifestations
- Sampling analysis and interpretation of well fluids

first-basics

- ① Fluid geochemistry applications at various stages of development
- ① Basics of water/gas/rock interactions
- ① Various fluid chemistries found in different types of geothermal systems

STAGE 1: GEOTHERMAL EXPLORATION

What questions can a geochemist address before wells are available to sample?

Assuming there are surface manifestations to sample

- Reservoir temperature estimate (and if the temperature gradient is known depth)
- Water source
- Fluid phase (steam±gas, hot water-NaCl brine or other)
- Possible outflow and upflow zones
- Multiple reservoirs
- Degree of water/rock interaction/permeability
- Boundaries-sealed or open

STAGE 2: RESOURCE ASSESSMENT AND CHARACTERIZATION FOR UTILIZATION

Once there are wells to sample, what can we do?

In collaboration with good well testing and sampling and analysis:

- Characterize production zones
 - 1 or more feed zones, reservoirs, relative location, in communication
 - Fluid state (liquid, 2-phase, vapor)
 - Reservoir temperature vs measured
 - Noncondensable gas and gas pressure at separation*
 - Equilibration with observed mineralogy
- Processes: mixing/groundwater intrusion, conductive heating/cooling, boiling
- Scaling and corrosion
- Possible environmental issues
- Baseline for monitoring reservoir during operation

STAGE 3: RESERVOIR MONITORING DURING RESOURCE DEVELOPMENT AND OPERATIONS

- ◎ Test new wells for compatibility with project design
- ◎ Geochemical monitoring of fluid chemistry provides one of the few tools to measure changes in the reservoir which may affect the resource supply
- ◎ Monitor emissions for environmental compliance
- ◎ Manage fluid chemistry-related operations such as scale mitigation, corrosion and noncondensable gas handling

GEOCHEMICAL EQUATIONS: THE PUZZLE

The minerals that constitute various alteration assemblages depend on: temperature, pressure, primary rock composition, primary fluid composition and the ratio of fluid to rock in the reaction that produced the alteration. (Reed M. 1997).

temperature



water/rock (permeability)

time, closed/open

equilibrium

where i = initial and f=final

- The geochemist, if lucky, will get to see a piece of the final water (water_f)
- Then we try and assess the reservoir conditions that produced the changes from initial to final.
- Need to constrain some of the variables

CHEMISTRY OF A GEOTHERMAL SYSTEM

INPUT → REACTION → RESULTING FLUIDS

ADDRESSING THE GEOCHEMICAL PUZZLE

Initial-Derived

- ⊙ Reservoir rock (s)
 - quartz ± feldspar ± mica ± sulfides ± carbonates...
- ⊙ Water: meteoric ± sea ± metamorphic ±
 - O-18, D
 - TDS < 1000: HCO₃, Na, K, Ca, Mg, Cl...
- ⊙ Magmatic Volatiles
CO₂, SO₂, H₂, HCl, HF and H₂O

Changes

Reactions

Mixing

Temperature

Pressure

Final-Observed

- ⊙ Altered and Unaltered Minerals, Rock texture, fluid inclusions
- ⊙ Brine
 - Cl -conservative
 - Na, K, from mineral water reactions
 - pH
 - O-18, D-altered by the process
 - Dissolved gases: CO₂, H₂S, CH₄, H₂, NH₃,
- ⊙ ± Steam + gas

Heat Transfer / Permeability / Water / Rock / Time / Equilibrium

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SOME WATER/ROCK/GAS REACTIONS AT RESERVOIR TEMPERATURES

- Cl,B typically from rock/mineral dissolution or from deep magmatic fluid
- Quartz
$$\text{SiO}_{2,\text{qtz}} + 2 \text{H}_2\text{O} = \text{H}_4\text{SiO}_4$$
- K-spar/Na-spar
$$\text{NaAlSi}_3\text{O}_8 + \text{K}^+ = \text{KAlSi}_3\text{O}_8 + \text{Na}^+$$
- Carbonate
- $\text{CaCO}_3 + \text{H}^+ = \text{Ca}^{++} + \text{HCO}_3^-$
- Clinozoisite+calcite +quartz=garnet+ $\text{H}_2\text{O} + \text{CO}_2$
or + $\text{H}_2\text{O} = \text{prehnite} + \text{CO}_2$
- pyrite + pyrrhotite +prehnite + water =epidote + H_2S
or pyrite + $\text{H}_2\text{O} = \text{Fe-Al-silicate} + \text{H}_2\text{S}$
- + dissolution
- + magmatic volatiles

NONCONDENSIBLE GAS-SOURCES AND REACTIONS

- ⊙ Magmatic Influx
 - $\text{CO}_2, \text{SO}_2, \text{H}_2, \text{HCl}, \text{HF}$ and H_2O
- ⊙ Mineral/Gas reactions
 - Epidote, prehnite, garnet, clinozoisite Pyrite, pyrohtite, magnetite, etc. controlling $\text{CO}_2/\text{H}_2\text{S}/\text{H}_2$
- ⊙ Gas-gas reactions
 - ⊙ $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$
- ⊙ Vapor-Liquid Distribution, Temperature Dependent Distribution Coefficients, $B = C_v/C_l$
 - ⊙ $C_{\text{tot}} = C_v(y) + C_l(1-y)$

RESERVOIR PROCESSES TRANSFORM ORIGINAL GEOTHERMAL FLUIDS

Even after $\text{water}(s)_f \pm \text{gas}_f + \text{rock}_f$ are established, their chemistry can change

- ⦿ Boiling and partitioning of constituents into steam+volatiles and brine+solubles
- ⦿ Precipitation/dissolution
- ⦿ Steam condensation, gas absorption,
- ⦿ Mixing with shallow cooler fluids (ground water)
- ⦿ Phase segregation
- ⦿ Mixing
- ⦿ Influx of hot fluid and/or gas

CONCEPTUAL MODELS OF VARIOUS GEOHERMAL SYSTEMS

WHAT ARE THE IMPLICATIONS FOR OBSERVED FLUID
CHEMISTRY IN WELLS AND SURFACE MANIFESTATIONS?

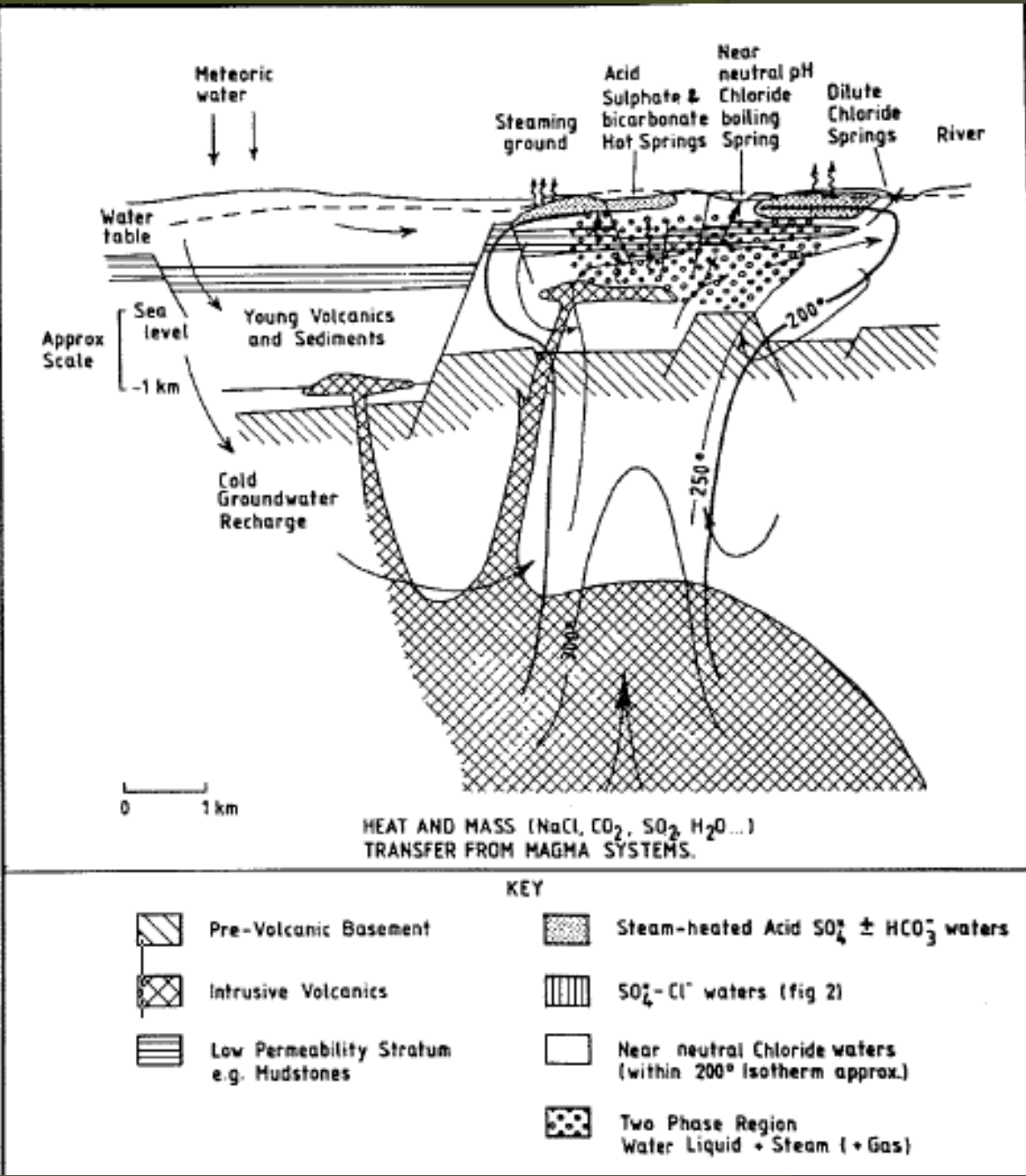
CONVERSELY

HOW CAN FLUID CHEMISTRY CONSTRAIN GEOHERMAL
RESERVOIR MODELS OR MODEL COMPONENTS

SILICIC MAGMATIC/INTRUSIVE

- Water source: meteoric ± gas
- Surface manifestations: steaming ground, acid sulfate-bicarbonate hot springs overlying the system
- Neutral sodium-chloride (boiling to dilute) springs on the edges

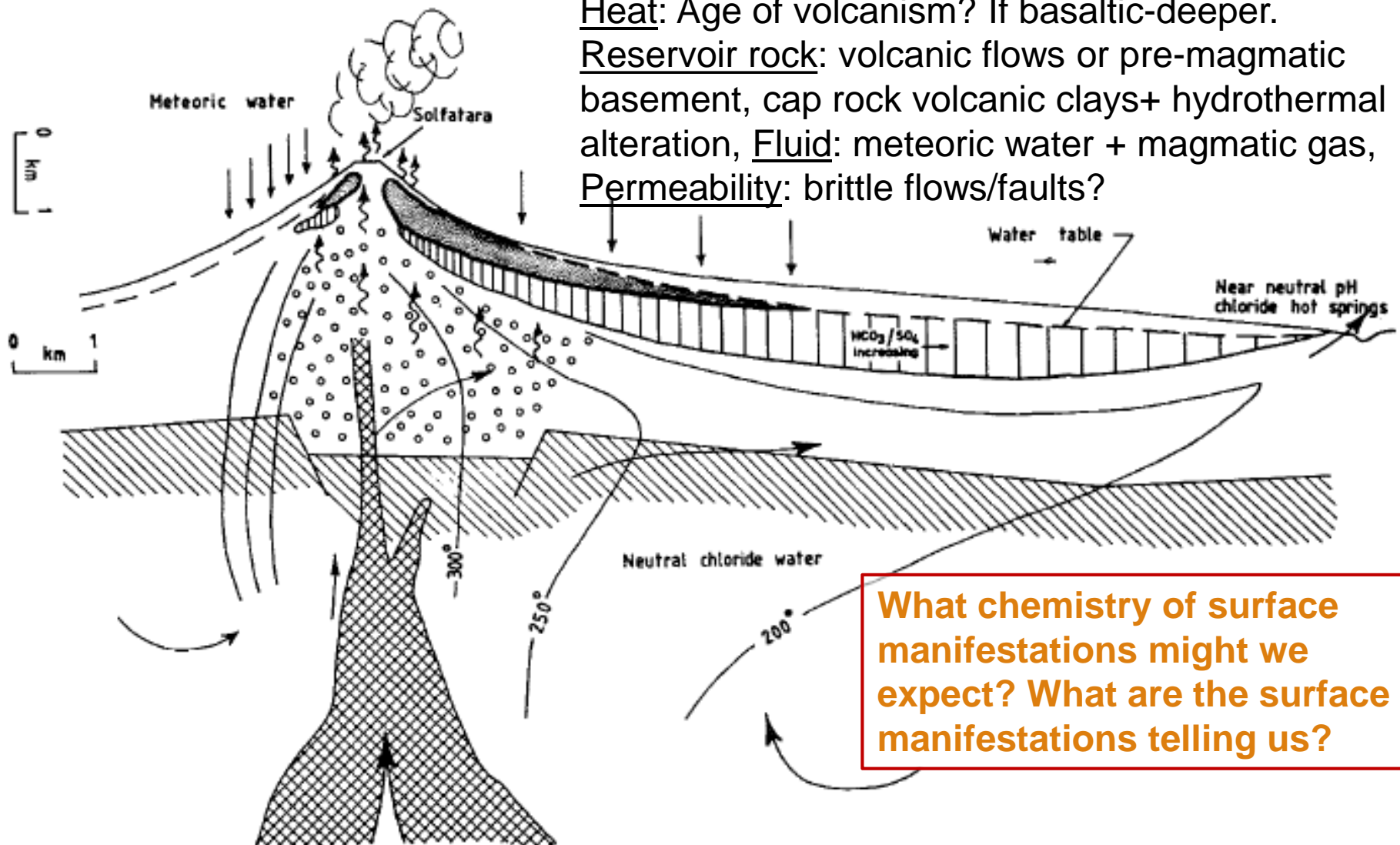
From Henley et al., 1984
reproduced from Henley
and Ellis, 1983



What are the surface manifestations telling us?

- ① What do acid-sulfate springs suggest?
- ① What do sodium-chloride springs suggest?
- ① What do neutral pH boiling springs vs acid boiling springs?
- ① What do concentrated warm springs vs dilute warm springs suggest?

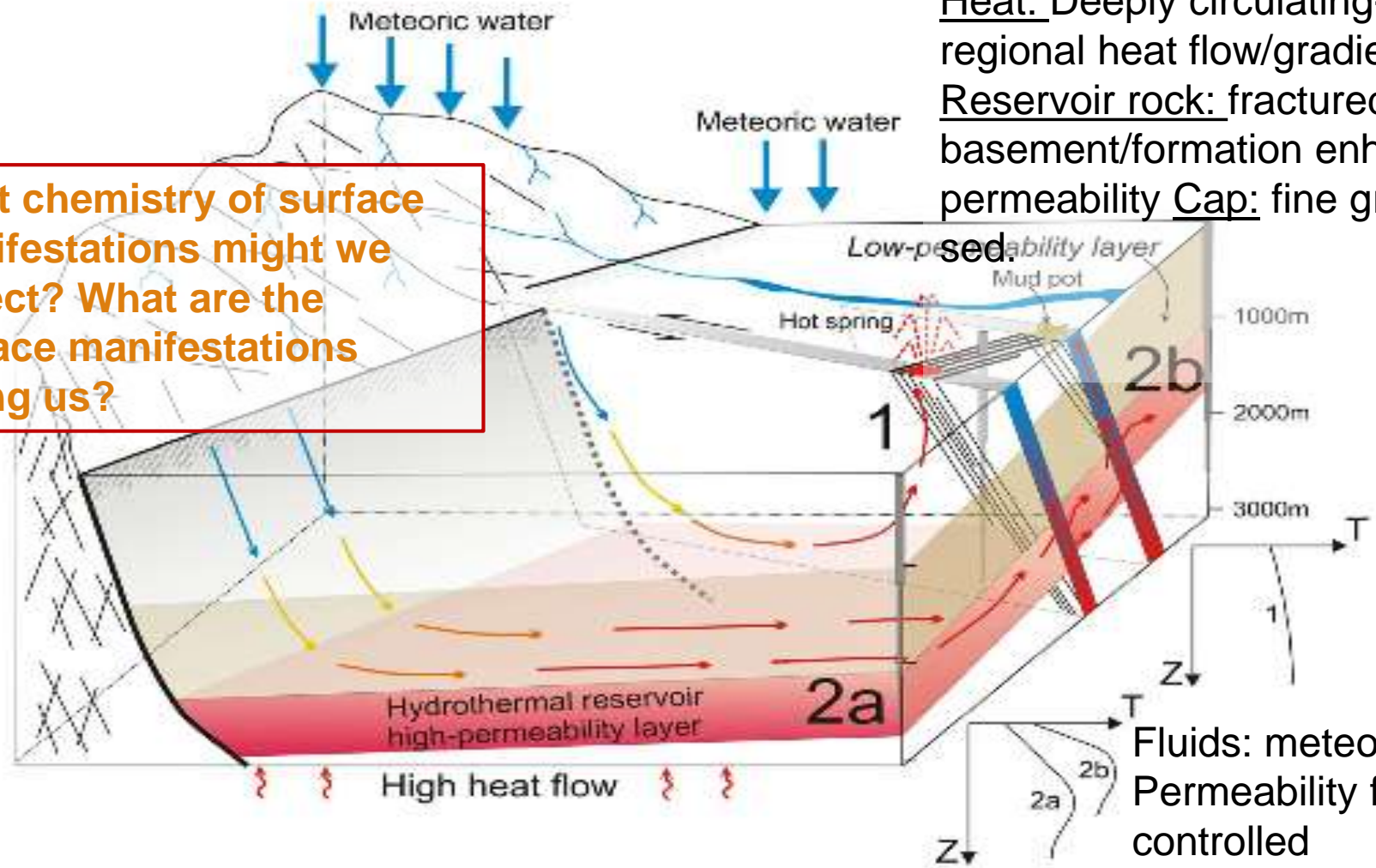
Heat: Age of volcanism? If basaltic-deeper.
Reservoir rock: volcanic flows or pre-magmatic basement, cap rock volcanic clays+ hydrothermal alteration, Fluid: meteoric water + magmatic gas, Permeability: brittle flows/faults?



From Henley et al., 1984 reproduced from Henley and Ellis, 1983
Scheme of Andesitic Volcanic Hydrothermal System

Heat: Deeply circulating-regional heat flow/gradient
Reservoir rock: fractured basement/formation enhanced permeability
Cap: fine grained sed.

What chemistry of surface manifestations might we expect? What are the surface manifestations telling us?



Fluids: meteoric,
 Permeability fault controlled

Fig. 5. Non-magmatic active geothermal play system in active extensional terrains with different types of reservoirs (1, 2a and 2b) (compiled from [9,16,22,49]). Type 1 is a convection cell from infiltration to discharge along one fault. Temperature gradient is gradually increasing at well site 1. Type 2a and 2B are fault leakage controlled plays. The temperature gradient of a well drilled into such an area rises up to the permeable layer and drops below the layer (well 2a and 2b).

Hot Spring Chemistry? Hydrothermal Reservoir Chemistry? From Moeck, 2013

Next: methodology

- ◎ Various types of sampling & analytical plans
- ◎ Sampling & Analysis (not laboratory work)
- ◎ Interpretation for Exploration
- ◎ Interpretation for resource assessment and project design
- ◎ Interpretation for reservoir management

EXPLORATION SAMPLING OF SURFACE MANIFESTATIONS

- Plan to sample as many surface manifestations as possible including all different types
- Fumaroles require gas sampling, warm springs water sampling and boiling springs both
- Sample the inlet (hottest part)
- Sample shallow cold water (recharge) to unmix groundwater+ brine→mixing
- Collect duplicates and field measurements
- Quality laboratory analysis, QA/QC results
- Characterize surface features such as boiling and steam heated features vs brine discharges

EXPLORATION SAMPLING AND ANALYSIS PLAN

Sample to provide analyses to address exploration questions

- ◎ Warm and Hot Springs/Cold Waters
 - Cl, SO₄, HCO₃, pH, TDS, NH₃, Na, K, Ca, Mg, Li, B, As, Hg, F, B, Al, SiO₂,
 - Oxygen-18 and deuterium
- ◎ Field measurements
 - Temperature, pH, conductivity
 - Alkalinity, et
- ◎ Fumaroles/Steam from boiling springs
 - Ar, O₂, N₂, CH₄, H₂, CO₂, NH₃, H₂S, Total NCG, B
 - Oxygen-18 and deuterium
- ◎ Other isotopes: He³/He⁴, carbon on HCO₃ (water), CH₄ and CO₂ or sulfur on SO₄ (water), and H₂S

Sample Everything!



WELL TEST SAMPLE PLAN

-Driven by Laboratory Analysis

-Steam and Brine sampled separately ASTM E 1675-95

-Multiple Samples under different conditions/time/flow rates

-Calculate combined chemistry based on sampling conditions

○ Brine

- Cl, SO₄, HCO₃, pH, TDS, NH₃, Na, K, Ca, Mg, Li, B, As, Hg, F, Sr, B, Al, SiO₂,
- Oxygen-18 and deuterium
- Etc.

○ Field Measurements-pH, conductivity, etc.

○ Steam

- Ar, O₂, N₂, CH₄, H₂, CO₂, NH₃, H₂S, Total NCG, B
- Oxygen-18 and deuterium
- Etc.

○ Field Measurements-pH, conductivity

RESERVOIR MONITORING DURING OPERATIONS FOR RESOURCE and WELLFIELD MANAGEMENT

- ◎ Production Well Fluid Sampling
- ◎ Injection Well Sampling
- ◎ Power Plant Sampling
- ◎ Scale Inhibitor Monitoring
- ◎ Power plant inlet chemistry

Sampling during Well Testing



Sampling at the Plant Inlet



Olkaria I, Kenya Plant Inlet
Steam



Kizildere I, Turkey,
Production Well
Monitoring



Kizildere II, Turkey,
Plant Inlet

INTERPRETATION 1: ORGANIZE THE GEOCHEMICAL AND RELATED DATA

- ◎ QA/QC lab results
- ◎ Surface Manifestations: Use field observations and input from geologists and geophysicists to establish geologic and hydrogeologic setting, likely reservoir rocks and minerals
- ◎ For well testing and production data, collect physical conditions of sampling
- ◎ Prepare a data base that can be used for well test data as well as surface manifestations

Databases

- ⦿ Powell & Cumming
- ⦿ Integrated Databases
- ⦿ Develop your own on a project/regional basis
- ⦿ Exploration data supplemented with locations, descriptions
- ⦿ Well data also requires sampling conditions in order to correct for two-phase sampling

WELL TEST/PRODUCTION DATA PREPARATION BEFORE INTERPRETATION

Combining 2-phase chemistry into Single phase total flow (reservoir) by calculation y, steam fraction

- $H_{tot} = H_l (1-y) + H_v (y)$
- $C_{tot} = C_l (1-y) + C_v (y)$
- $y = (H_{tot} - H_l) / (H_v - H_l)$
- H_{tot} = enthalpy of liquid at reservoir temperature
- H_l = enthalpy of liquid at sampling P,T
- H_v = enthalpy of steam at sampling PT
- C_{tot} = concentration in the total fluid or reservoir
- C_v is concentration in steam sample
- C_l = concentration in brine sample

For volatile, steam, components (gases):

$$C_{tot} = C_v * y$$

For brine

$$C_{tot} = C_l (1-y)$$

For semi-volatile components where $B = C_v / C_l$

$$C_l = C_{tot} / ((1-y) + By) \text{ or } C_{tot} = (C_v / B)(1-y) + C_v(y)$$

Excess steam

- ◎ More steam at the wellhead than would occur by boiling liquid at the reservoir temperature to the surface pressure
- ◎ Correcting brine and steam data for steam loss requires a different calculation of y

Excess steam

$$Y_{\text{meas}} = (H_{\text{tot}} - H_{\text{Lsep}}) / (H_{\text{vsep}} - H_{\text{Lsep}})$$

$$Y_{\text{exs}} = (H_{\text{TD}} - H_{\text{Lqa}}) / (H_{\text{vqa}} - H_{\text{Lqa}})$$

Where TD is total discharge, sep= means separator or surface measured, v=vapor (steam), L=liquid, qa means quartz adiabatic temperature.

The correction for measured brine concentrations, C_L to reservoir liquid concentration C_{Lres} is:

$$C_L * \{(1 - Y_{\text{TD}}) / (1 - Y_{\text{exs}})\} = C_{\text{Lres}}$$

For non-excess steam or just brine wells,

$$Y_{\text{TD}} = (H_{\text{TD}} - H_{\text{Lsep}}) / (H_{\text{vsep}} - H_{\text{Lsep}})$$

And the correction is:

$$C_L * (1 - Y_{\text{TD}}) = C_{\text{Lres}}$$

- ⊙ (equations become the same as Y_{exs} goes to 0.

INTERPRETATION 2: START WITH BASICS

EXPLORATION

- ⦿ Temperature dependent water/rock reactions
→ Chemical geothermometers
- ⦿ Variations in chemistry: fluid flows, inflows and out flows → isochemical concentration maps
- ⦿ Use shallow cold water (recharge) to unmix groundwater+ brine → mixing
- ⦿ Use analogies/geochemical data integration and modeling to back into reservoir rocks/minerals and processes from fluid chemistry

INTERPRETATION 2: BASICS

WELL TEST DATA INTERPRETATION

- ⦿ One or more reservoir fluids? Potential for coldwater influx? Lateral variations?
- ⦿ Boiling in the reservoir? Excess steam
- ⦿ Geothermometer temperatures relative to downhole measured temperatures?
- ⦿ Gas loading, scaling, corrosion for project design
- ⦿ Baseline for reservoir monitoring

Chemical Geothermometers

- ◉ Which ones?

Depends on the temperature, geologic setting, mixing...

- ◉ Silica

- Fast reacting, but can re-equilibrate
- Because it's a single parameter, affected by mixing (dilutions) and boiling (concentration), and
- assumes equilibrium with a specific form of SiO_2 mineral
- pH

- ◉ Cations

- Assumes equilibrium with unknown minerals, slow reacting, affected by precipitation, empirical have temperature range limits

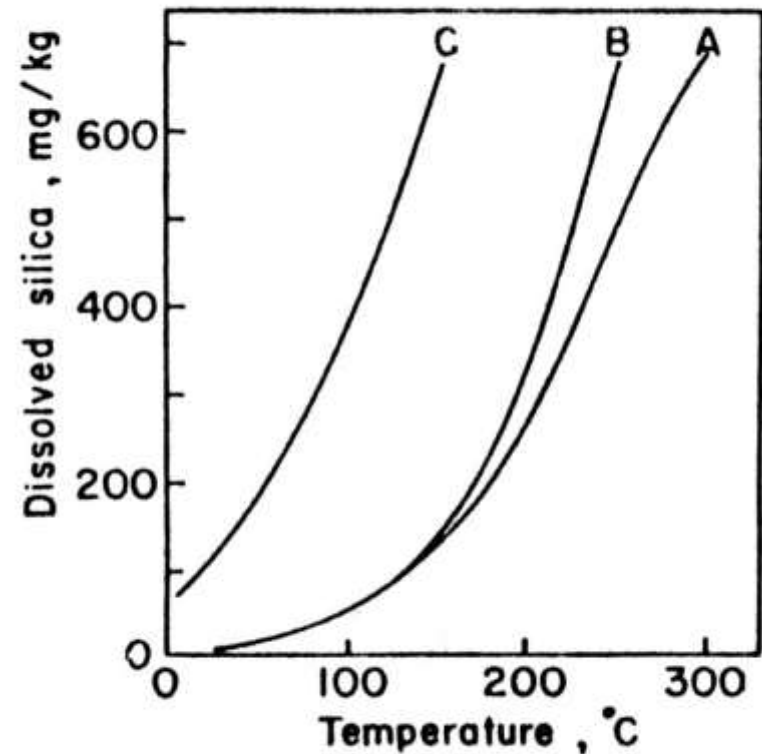
- ◉ Gas

- Assumes equilibrium with gas/gas and mineral gas reactions

- ◉ Multiple

Silica Geothermometers

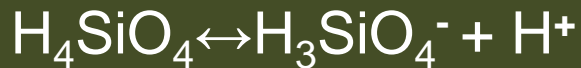
- Based on lab experiments on solubility of various silica minerals.
- This one is from Fournier and Truesdell, 1976 where A=Quartz (conductive) B= Quartz (boiling) and C=amorphous silica



Geothermometer	Equation	Reference
Quartz-no steam loss	$T = 1309 / (5.19 - \log C) - 273.15$	Fournier (1977)
Quartz-maximum steam loss at 100 °C	$T = 1522 / (5.75 - \log C) - 273.15$	Fournier (1977)
Quartz	$T = 42.198 + 0.28831C - 3.6686 \times 10^{-4} C^2 + 3.1665 \times 10^{-7} C^3 + 77.034 \log C$	Fournier and Potter (1982)
Quartz	$T = 53.500 + 0.11236C - 0.5559 \times 10^{-4} C^2 + 0.1772 \times 10^{-7} C^3 + 88.390 \log C$	Arnorsson (1985) based on Fournier and Potter (1982)
Chalcedony	$T = 1032 / (4.69 - \log C) - 273.15$	Fournier (1977)
Chalcedony	$T = 1112 / (4.91 - \log C) - 273.15$	Arnorsson et al. (1983)
Alpha-Cristobalite	$T = 1000 / (4.78 - \log C) - 273.15$	Fournier (1977)
Opal-CT (Beta-Cristobalite)	$T = 781 / (4.51 - \log C) - 273.15$	Fournier (1977)
Amorphous silica	$T = 731 / (4.52 - \log C) - 273.15$	Fournier (1977)

From Guler, 2012

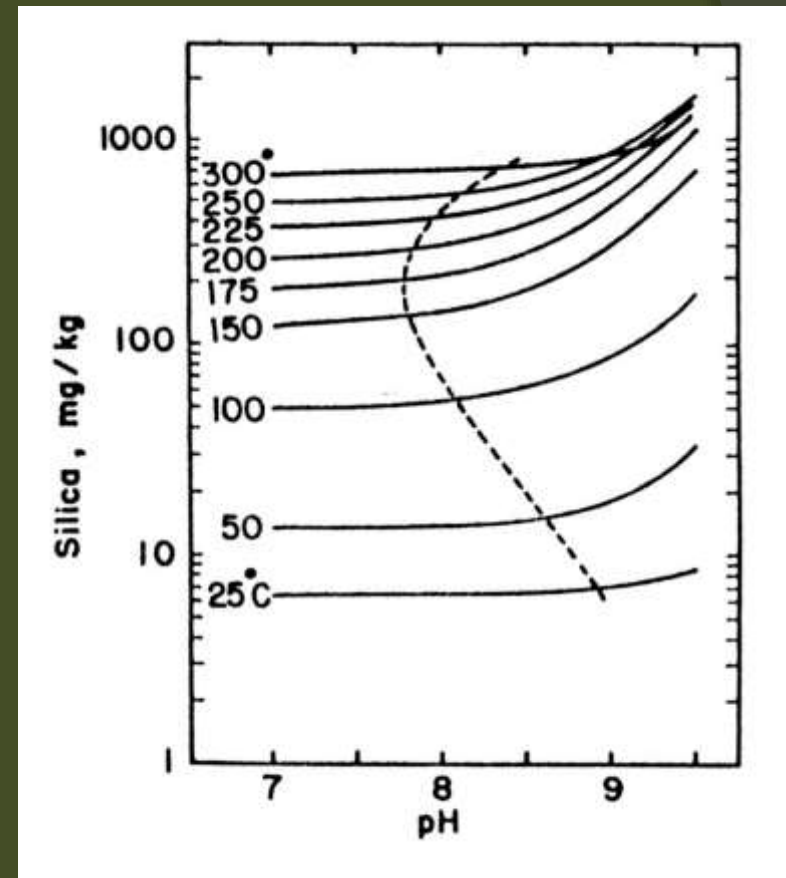
Silica and pH



If silicic acid dissociates, more silica can enter solution, giving a concentration above equilibrium. Rarely an issue in high temperature reservoir but maybe in some hot springs.

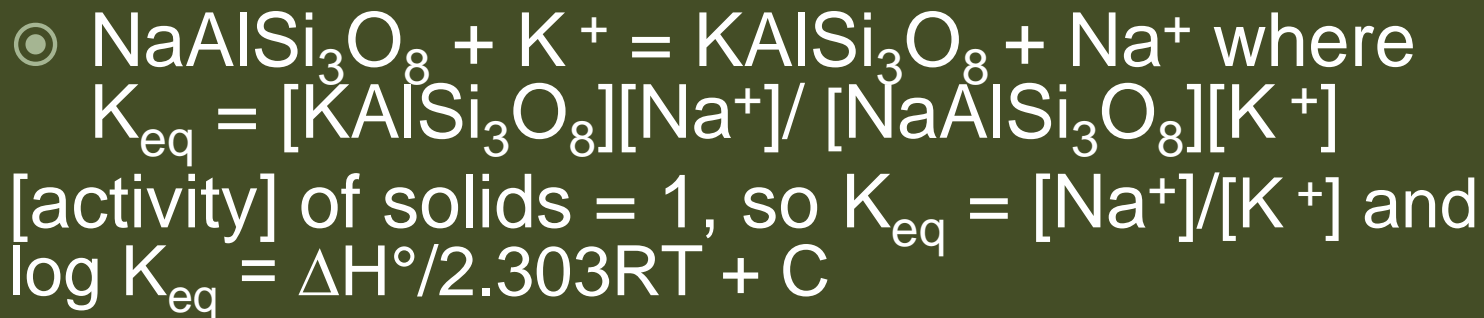
Dashed line shows pH of +10% silica at different temperatures

Fournier (1981)



Cation Geothermometers

- Mostly based on ratios-eliminating boiling and mixing issue.
- Based on equilibrium between feldspars of relatively pure end members:

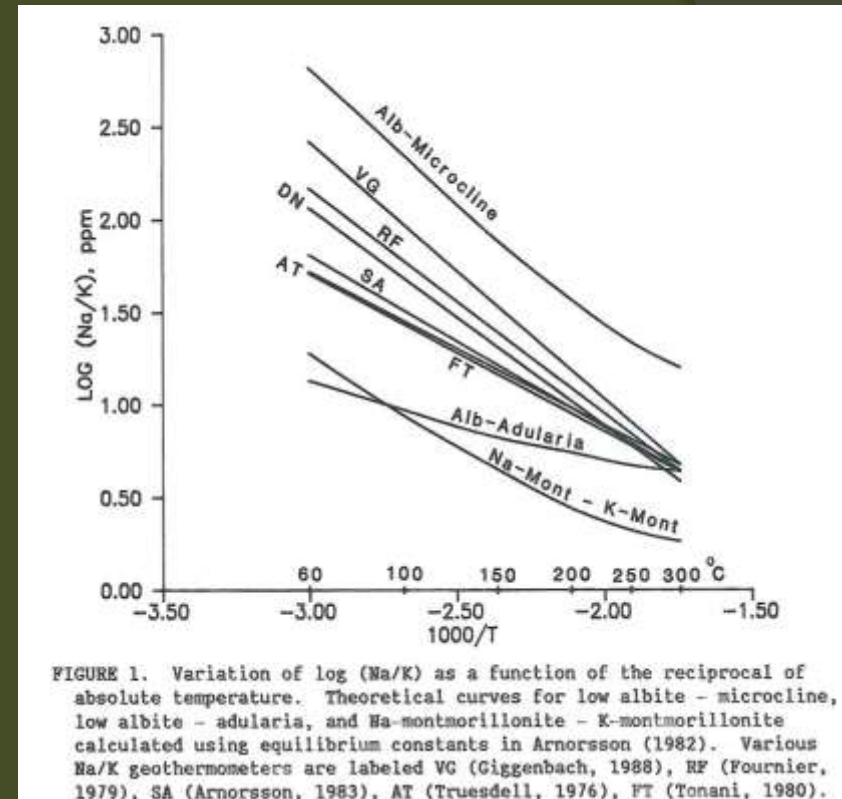


change in heat of solution, ΔH° , doesn't change much 0-300°C, $[\text{Na}^+]/[\text{K}^+]$ and $\log K_{\text{eq}} \sim$ linear with temperature

Using Cation Geothermometers

But:

- Takes long to equilibrate
- Minerals involved not always pure solutions
- Sometimes clays not feldspars-correct equation depends on local mineralogy-hard to know without drilling



Cation Geothermometer Equations as of 1981 (Fournier, 1981)

Subsequently many “new and Improved” including one from Santoyo and Diaz-Gonzales, 2010 calibrated with measured temperatures:
 $t^{\circ}\text{C} = \{876.3 / (\log(\text{Na}/\text{K}) + 0.087750)\} - 273.15$

TABLE 1. Equations for cation geothermometers (concentrations in mg/kg).

Geothermometer	Equation	Source
Na-K	$t^{\circ}\text{C} = \frac{856}{0.857 + \log(\text{Na}/\text{K})} - 273.15$	Truesdell (1976)
Na-K	$t^{\circ}\text{C} = \frac{883}{0.780 + \log(\text{Na}/\text{K})} - 273.15$	Tonani (1980)
Na-K	$t^{\circ}\text{C} = \frac{933}{0.993 + \log(\text{Na}/\text{K})} - 273.15$	(25-250°C) Arnorsson (1983)
Na-K	$t^{\circ}\text{C} = \frac{1319}{1.699 + \log(\text{Na}/\text{K})} - 273.15$	(250-350°C) Arnorsson (1983)
Na-K	$t^{\circ}\text{C} = \frac{1217}{1.483 + \log(\text{Na}/\text{K})} - 273.15$	Fournier (1983)
Na-K	$t^{\circ}\text{C} = \frac{1178}{1.470 + \log(\text{Na}/\text{K})} - 273.15$	Nieva (1987)
Na-K	$t^{\circ}\text{C} = \frac{1390}{1.750 + \log(\text{Na}/\text{K})} - 273.15$	Giggenbach (1988)
K-Mg	$t^{\circ}\text{C} = \frac{4410}{14.00 + \log(\text{K}/\sqrt{\text{Mg}})} - 273.15$	Giggenbach (1988)
K-Li	$t^{\circ}\text{C} = \frac{2200}{5.470 - \log(\text{Li}/\sqrt{\text{Mg}})} - 273.15$	Kharaka & Mariner (1988)
Na-Li	$t^{\circ}\text{C} = \frac{1590}{0.779 + \log(\text{Na}/\text{Li})} - 273.15$	Kharaka et al. (1982)
Na-Li (Cl<0.3M)	$t^{\circ}\text{C} = \frac{1000}{0.389 + \log(\text{Na}/\text{Li})} - 273.15$	Fouillac & Michard (1982)
Na-Li (Cl>0.3M)	$t^{\circ}\text{C} = \frac{1195}{0.130 + \log(\text{Na}/\text{Li})} - 273.15$	Fouillac & Michard (1982)
Na-Ca	$t^{\circ}\text{C} = \frac{1096.7}{2.370 - \log(\text{Na}/\sqrt{\text{Ca}})} - 273.15$	Tonani (1980)
K-Ca	$t^{\circ}\text{C} = \frac{1930}{2.920 - \log(\text{K}/\sqrt{\text{Ca}})} - 273.15$	Tonani (1980)
Na-K-Ca	$t^{\circ}\text{C} = \frac{1647}{\log(\text{Na}/\text{K}) + \beta[\log(\sqrt{\text{Ca}}/\text{Na}) + 2.06] + 2.47} - 273.15$	Fournier & Truesdell (1973)

$$\beta = 4/3 \text{ for } t < 100^{\circ}\text{C}; = 1/3 \text{ for } > 100^{\circ}\text{C}$$

Other cations:

- Na-K-Ca

$\text{Log } K_{\text{eq}} = \{1647/[\log (\text{Na}/\text{K}) + \beta\{\log (\text{Ca}^{1/2}/\text{Na})+2.06\}+2.47]\} -273.15;$

If $\{\log (\text{Ca}^{1/2}/\text{Na})+2.06\} >0$, $\beta=4/3$, if $\{\log (\text{Ca}^{1/2}/\text{Na})+2.06\} <0$ $\beta=1/3$, calculate $t^{\circ}\text{C}$.

If $t^{\circ}\text{C} > 100^{\circ}\text{C}$, when $\beta=4/3$, use $\beta=1/3$

Empirical geothermometer which adds calcite

PCO₂ dependent, affected by carbonate precipitation and requires a Mg correction if Mg high (implying low temperature)

- $\text{K}/\text{Mg}^{1/2}$ – fast acting, seeps most appropriate in volcanic systems (Giggenbach, 1988)
- Li/Na , $\text{Li}/\text{Mg}^{1/2}$ -fast acting, empirical, sedimentary systems (Sanjuan, et al., 2010)

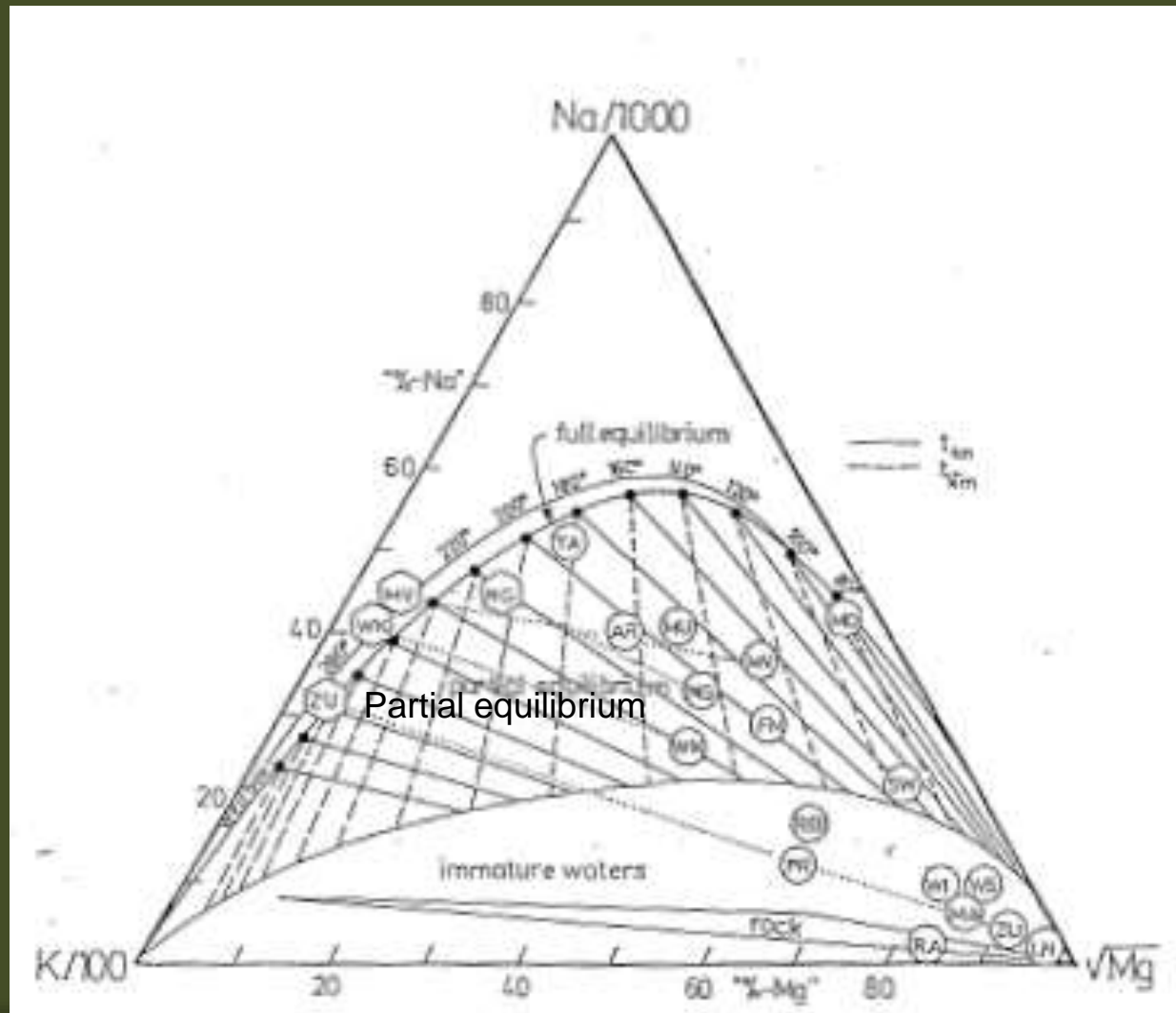
How to choose?

- ⦿ Compare geothermometers against each other and measured temperatures
- ⦿ Apply appropriate to expected mineralogy
- ⦿ Be especially careful of high temperature geothermometer estimates in hot springs which lack indications of high temperatures: moderate in temperature and high in Mg or low in Cl
- ⦿ Check for “maturity” as defined by Giggenbach

Evaluating degree of water-rock equilibrium Giggenbach, 1988

Cation geothermometers applicable in the partial equilibrium range

Simultaneously evaluating fast reacting K-Mg and slow reacting Na-K. Spring waters and waters derived from rock dissolution tend to be shifted towards the Mg corner.



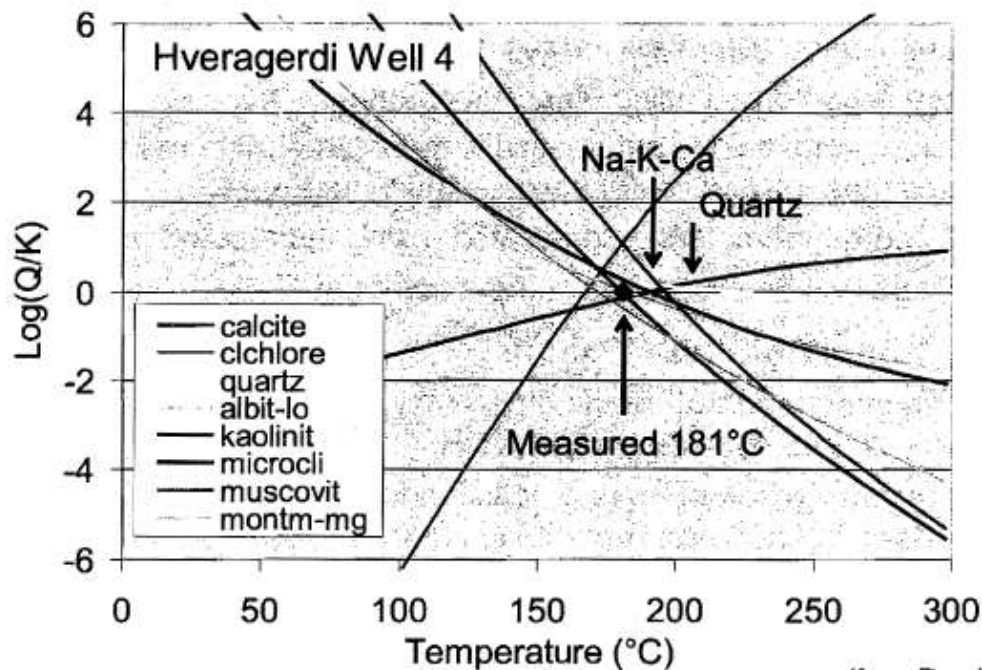
From Dr. Spycher at the 2013 year's GRC course on Exploration



ESD

Example

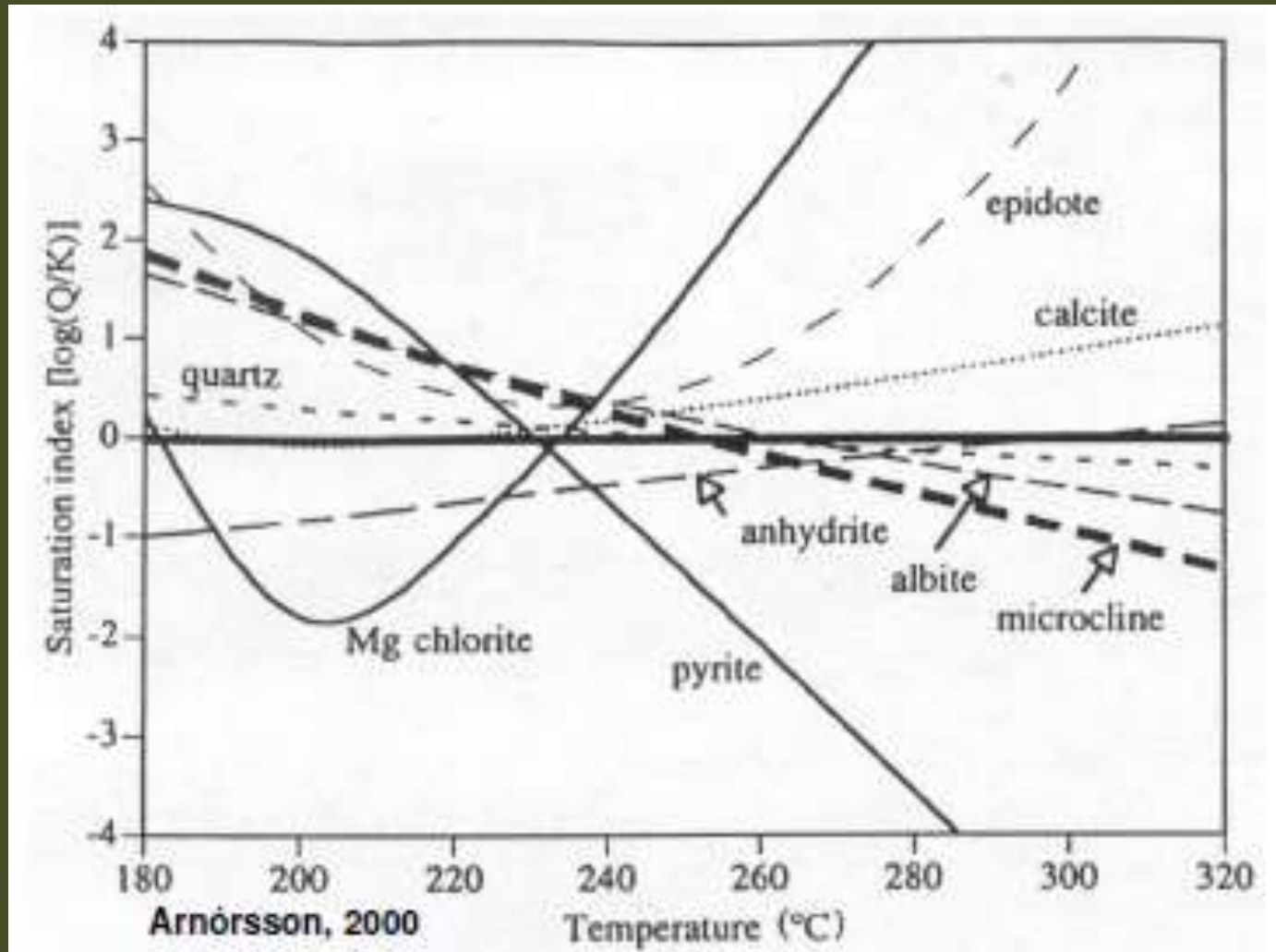
- Saturation indices of multiple minerals cluster near zero at the reservoir temperature



(from Reed & Spycher, 1984)

6

A similar approach by Arnórsson (2000)



Noncondensable gases

⊙ Gas-gas reactions

- $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O}$
- $2\text{NH}_3 = 3\text{H}_2 + \text{N}_2$
- $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$
- Etc.

⊙ Gas-mineral reactions

- $3\text{FeS}_2 + 2\text{H}_2 = \text{Fe}_3\text{S}_4 + \text{H}_2\text{O}$
- $\text{FeS}_2 + \text{H}_2 = \text{FeS} + \text{H}_2\text{S}$
- $\text{CaCO}_3 + \text{K-mica} = \text{CaAl-silicate} + \text{Kspar} + \text{CO}_2$
- Etc.

Gas solubility

Concentration in vapor, C_v ; concentration in liquid, C_l , $C_v/C_l =$ distribution coefficient B , different for each gas and temp dependent
 $C_{\text{tot}} = C_l (1-y) + C_o (y)$ or $C_{\text{tot}}/C_l = (1-y) + By$

Gas Geothermometers Powell, 2000 SGP-TR-165

Table 1: Gas geothermometer equations

$$FT^1: \log P_{CO_2} + 4 \log P_{H_2} - \log P_{CH_4} - 2 \log P_{H_2O} = 10.76 - 9323/T$$

$$NAH^1: \log P_{N_2} + 3 \log P_{H_2} - 2 \log P_{NH_3} = 11.80 - 5400/T$$

$$HSH^1: 3 \log P_{H_2S} - \log P_{H_2} = 15.71 - 10141/T \text{ (py-mag)}$$

$$\log P_{H_2S} - \log P_{H_2} = 4.94 - 2874/T \text{ (py-pyh)}$$

$$DAP^2: T = 24775 / (2 \log (CH_4/CO_2) - 6 \log (H_2/CO_2) - 3 \log (H_2S/CO_2) - 7 \log P_{CO_2} + 36.05)$$

$$H_2S^3: \log P_{H_2S} = 6.05 - 3990/T$$

$$CO_2^4: \log P_{CO_2} = -8.366 + 0.0168 T$$

$$CO_2-H_2^5: \log P_{CO_2} + 2 \log P_{H_2} = 16.298 - 8982/T$$

$$CO^6: \log (P_{CO} / P_{CO_2}) - \log (P_{H_2} / P_{H_2O}) = 2.485 - 2248/T$$

$$H_2O^1: \log P_{H_2O} = 5.51 - 2048/T$$

$$z \text{ factor}^7: \log z = \log P_{H_2O} - 3.041 + 2118/T - \log T$$

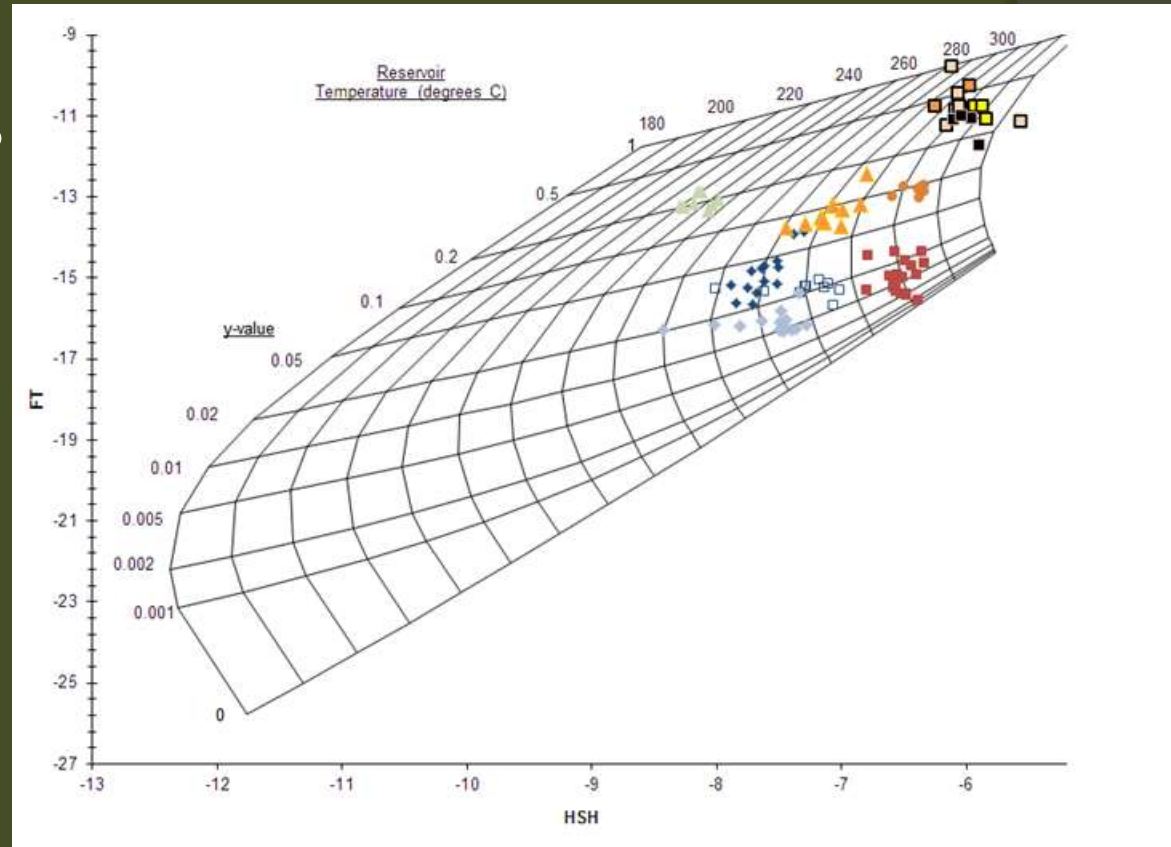
All temperatures in degrees Kelvin

References:

1. Giggenbach (1980)
2. D'Amore & Panichi (1980)
3. Giggenbach (1997)
4. Adapted from Giggenbach & Goguel (1989)
5. Henley, Truesdell & Barton (1984)
6. Giggenbach (1987)
7. This study (150°C - 350°C)

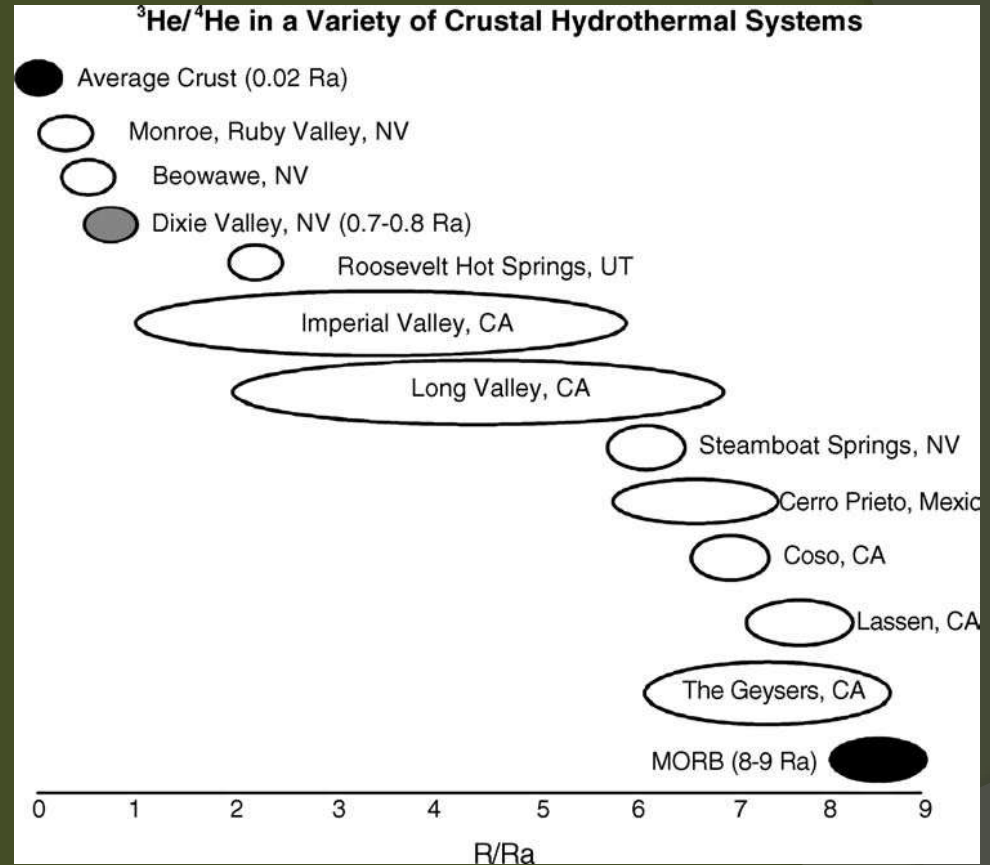
Reservoir Liquid Saturation and Gas Geothermometers

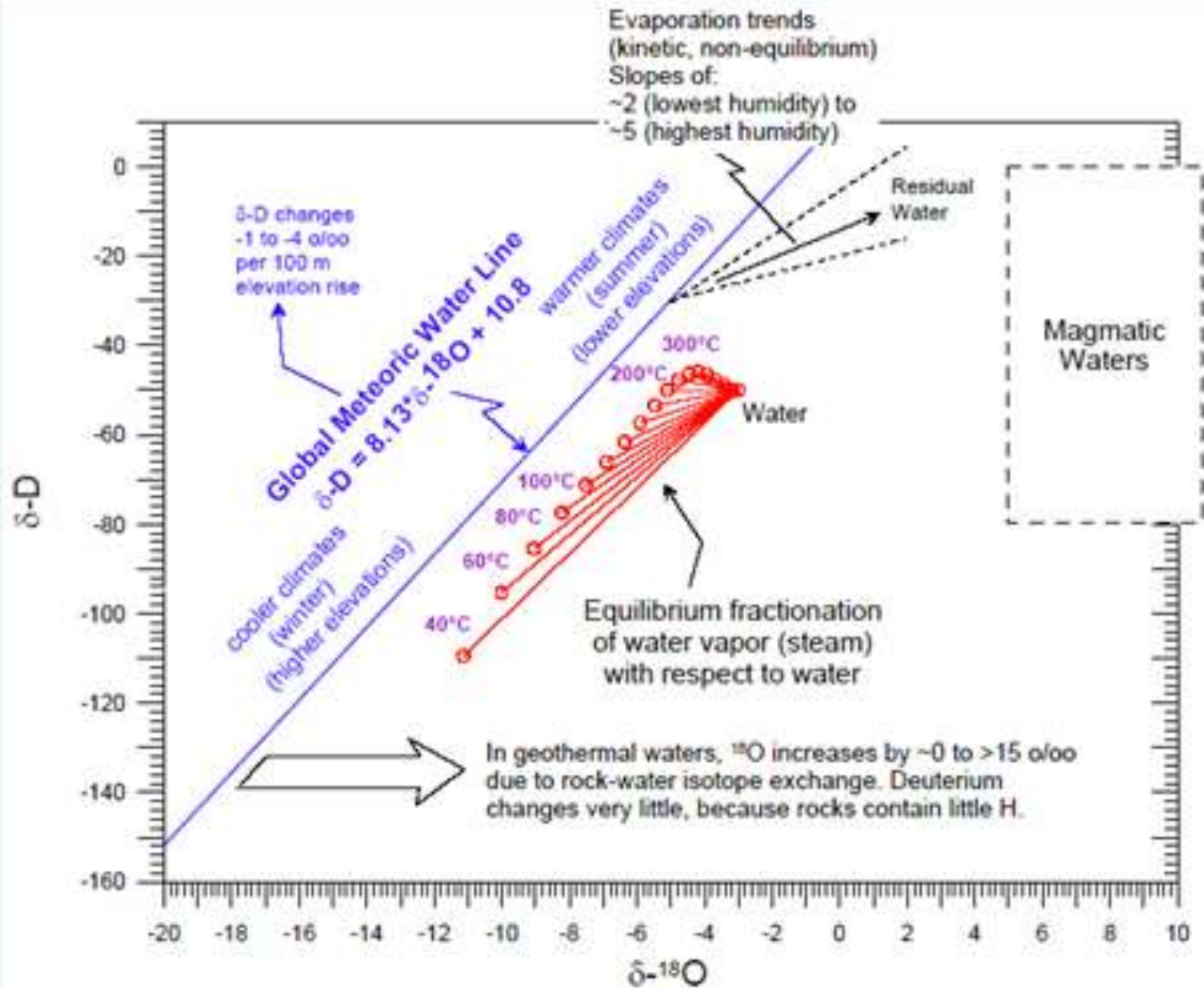
- Simultaneous solution of two gas geothermometers providing temperature and reservoir vapor
- Applicable to high temperature vapor or two phase steam samples



Helium Isotopes for Magmatic Source

- ③ $^3\text{He}/^4\text{He}$ can be used to detect mantle-derived volcanic gases
- ③ Difficult to sample (Kennedy 2006)





Basic Processes Affecting Oxygen and Hydrogen Isotopes in Geothermal Water

Sept.8-9, 2006

GRC Exploration Workshop - GeothermEx, Inc.

12

Origin of geothermal fluids: mostly meteoric + 0-18 shift from water/rock interaction

- Source water- meteoric, sea water, metamorphic
- Water/rock interaction
- Boiling-fractionation between liq and vapor
 - Single step
 - Multi-step
 - continuous
- Evaporation

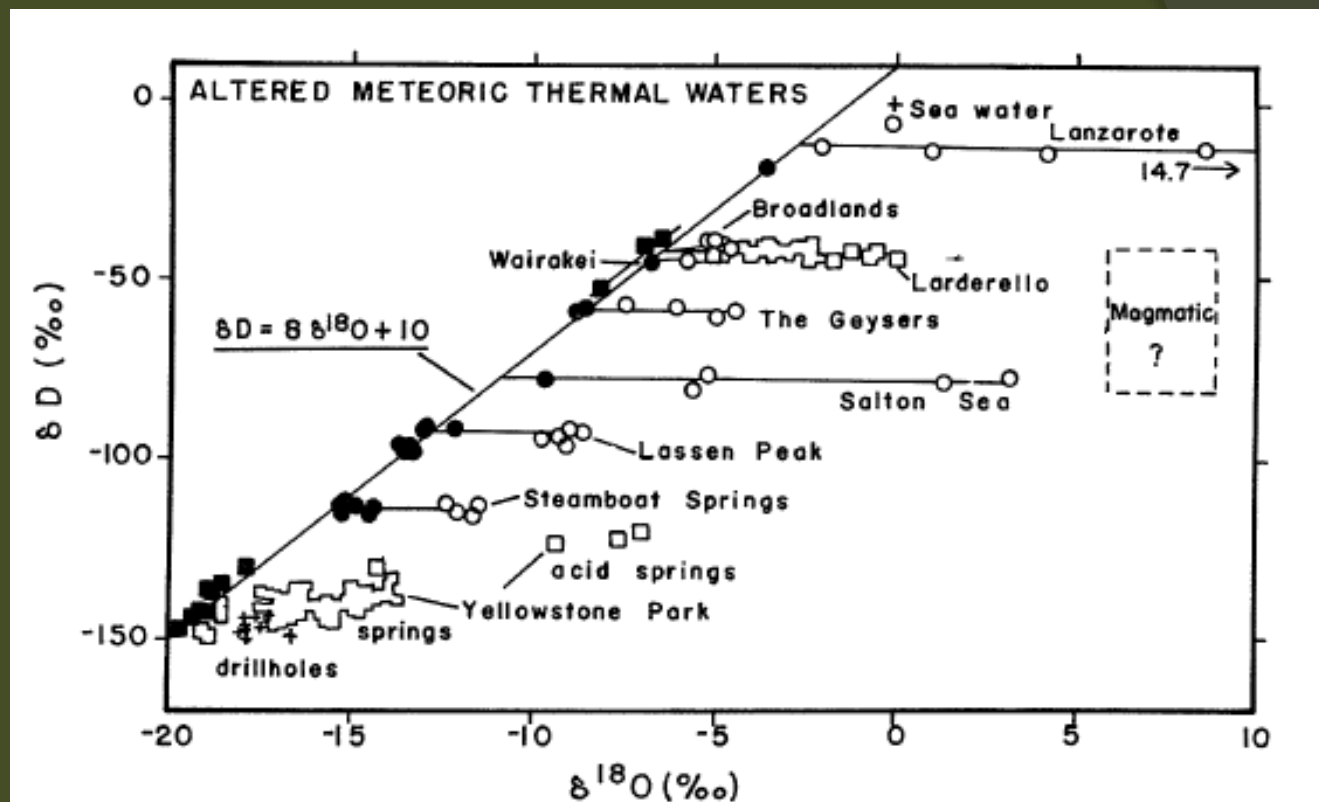
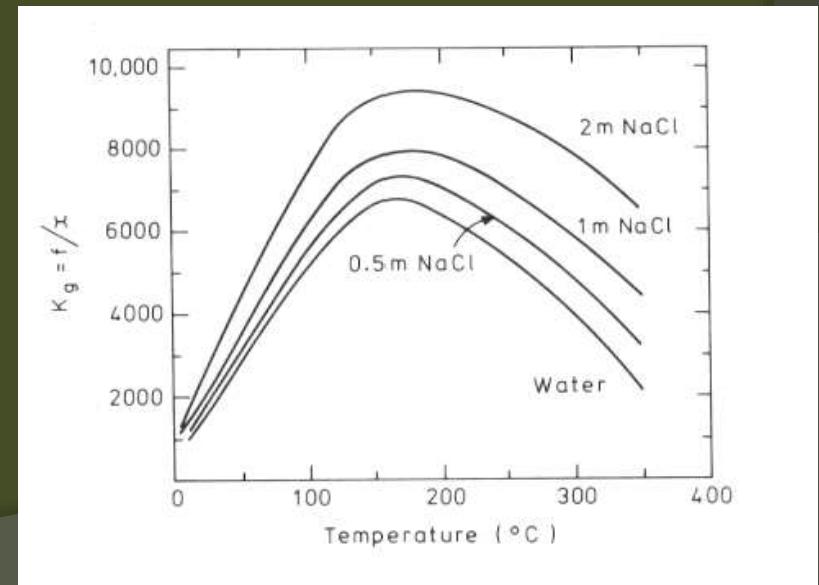
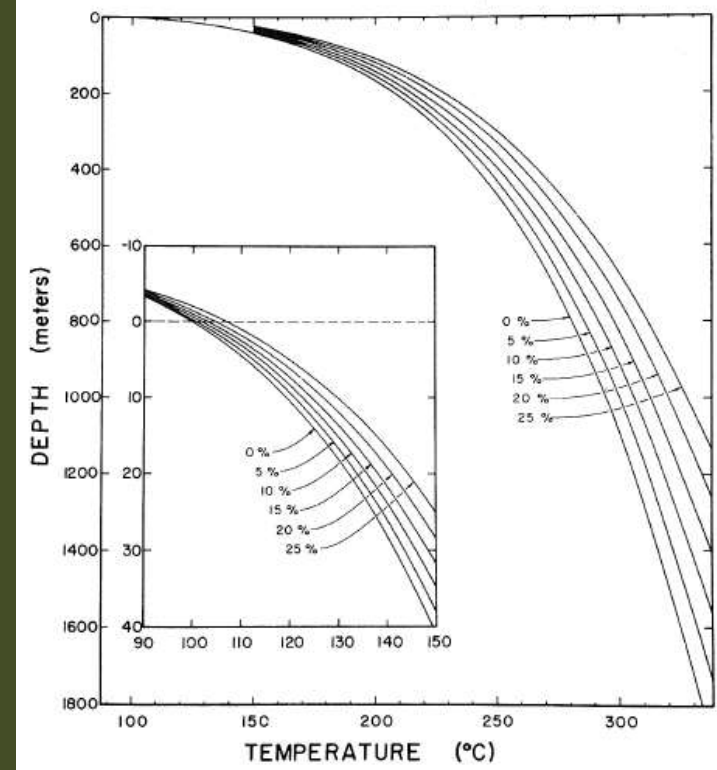


FIG. 10.1

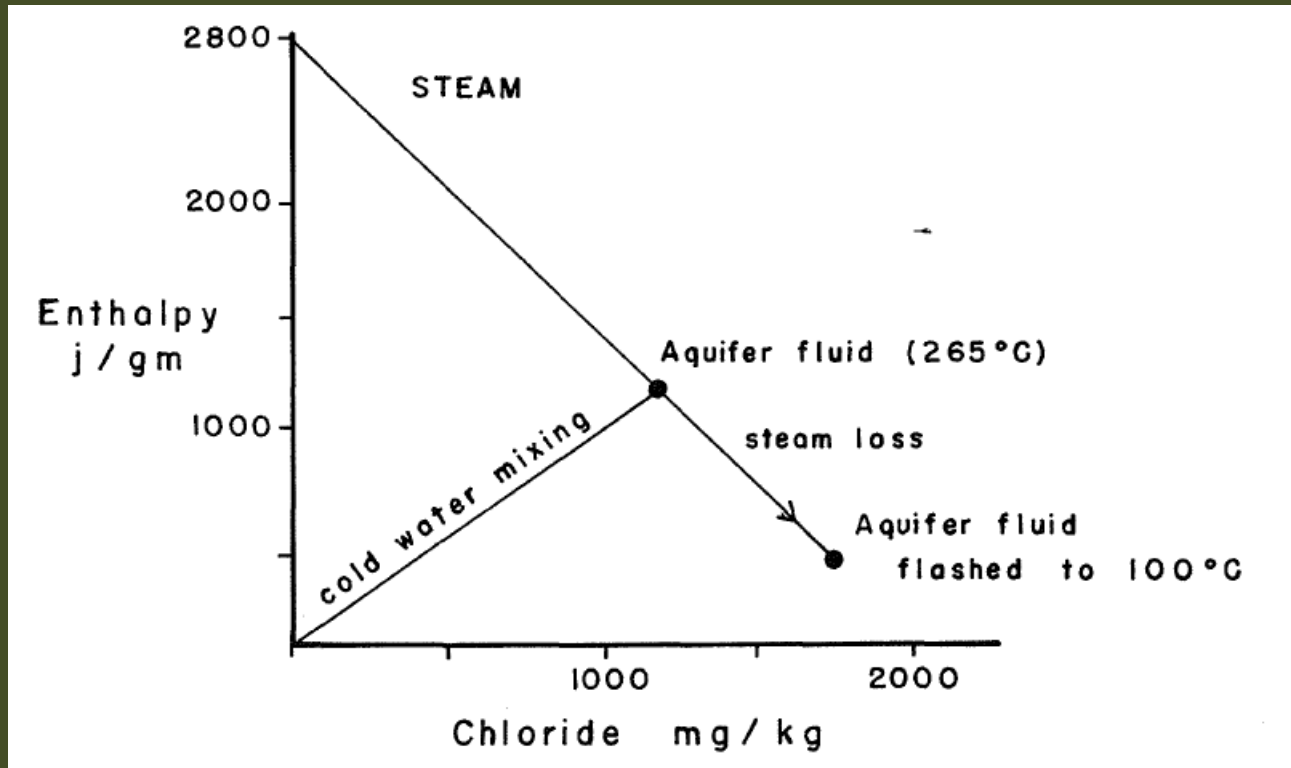
Figure 10.1. Oxygen-18 and Deuterium compositions of hot spring, fumarole, and drill hole thermal fluids derived from meteoric waters (open symbols) and of meteoric waters local to each system (closed symbols). From Truesdell and Hulston (1980).

Boiling

- Evidence of boiling springs, fumaroles,
- gas fractionation,
- acid gas/liquid/mineral interaction,
- Solute concentration in liquid,
- isotope fractionation
- Depth of boiling depends on temperature/enthalpy of liquid phase
- Gas pressure affects and boiling depth



Mixing waters



Data Integration/Modeling

- ◎ “mature” vs “immature”
- ◎ Minerals in equilibrium with geothermal fluids
- ◎ Partitioning based on boiling
- ◎ Speciation and activity coefficients
- ◎ WATCH, ToughReact, etc.

Requires extensive and thorough database of fluid analysis

Depends on thermodynamic data/equilibrium

INTERPRETATION OF WELL TEST/PRODUCTION DATA RESERVOIR CHARACTERIZATION

- From 2-phase samples, calculate chemistry of the reservoir fluid using y , or y -excess steam, providing a common baseline
- Combine with physical well test data-mass flow, enthalpy, measured temperatures
- Apply methods described above to characterize the feed zones-boiling, mixing, temperatures using geothermometers
- Reservoir variation- compare with other wells-one big reservoir or reservoir zones
- constraints on production/injection

SO NOW THAT WE HAVE RESERVOIR CHEMISTRY-PROJECT DESIGN CRITERIA

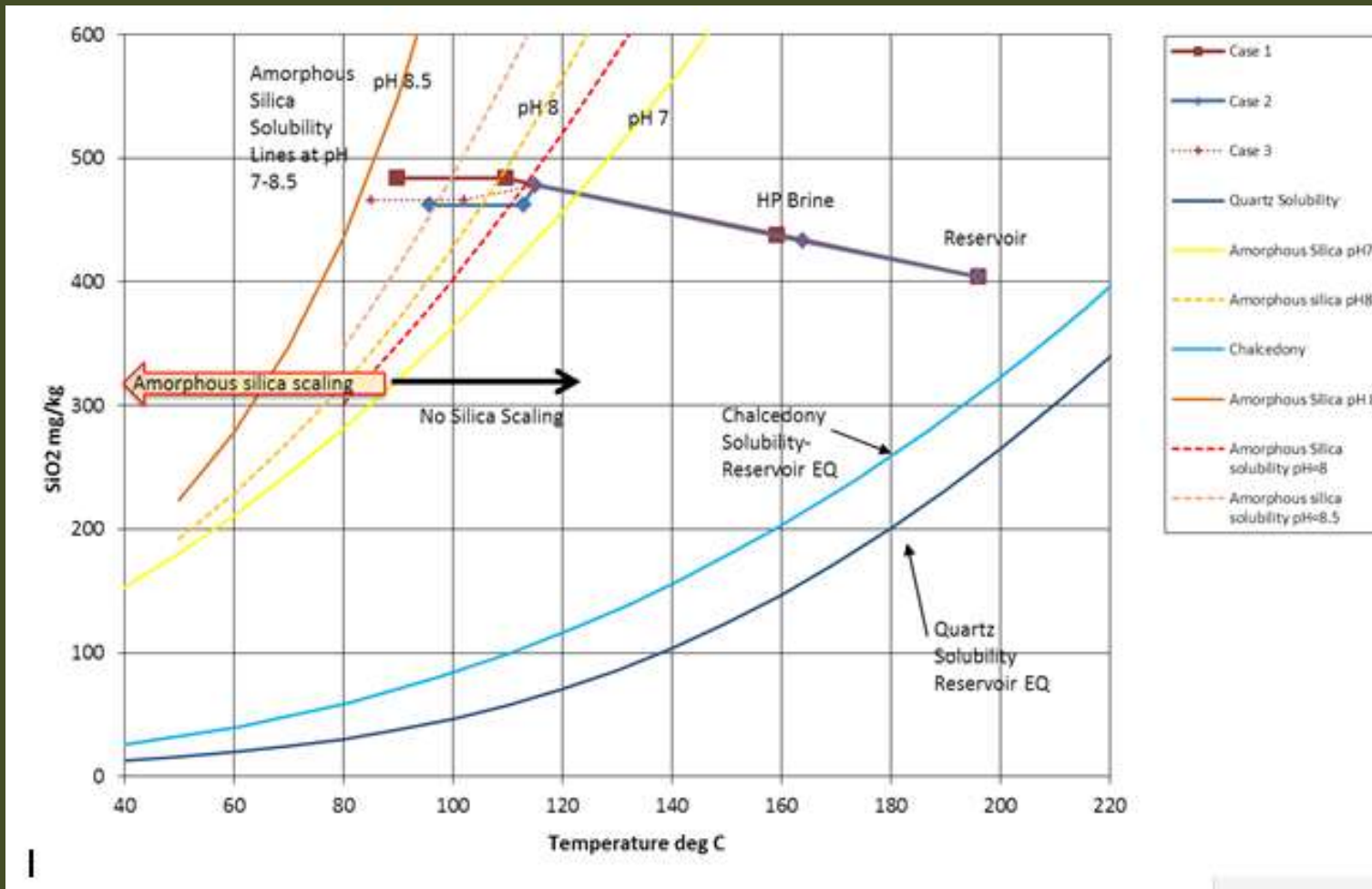
- ⦿ Chemistry of fluid delivered to the plant
- ⦿ Gas breakout pressure-when and where does the fluid boil
- ⦿ Gas Pressures in Separators
- ⦿ Gas extraction
- ⦿ Scaling potential/scale mitigation
- ⦿ Corrosion potential
- ⦿ Chemistry of Potential Discharges-either steam or brine

WEIGHTED AVERAGE TOTAL FLUID: AS DELIVERED TO THE PLANT. TO CALCULATE STEAM AND BRINE, USE REVERSE OF CALCULATION OF 2-PHASE SAMPLES, CALCULATE C_v , CONCENTRATION IN STEAM AND C_L , CONCENTRATION IN BRINE, AT PLANT INLET FROM C_{TOT} BY FLASHING AT PLANT INLET PRESSURE /TEMPERATURE

Weighted average of chemistry, corrected to reservoir (mg/kg)*

Na	555.9	As	0.18	CO2	351897
K	78.7	HCO3	1351.98	H2S	117
Ca	2.53	NH4	21.53	N2	386
Mg	0.05	Cl	154.38	CH4	630
Fe	0.02	F	3.92	Ar	4.71
Al	0.34	Ba	0.66	O2	9.84
SiO2	398.7	Br	0.66	H2	8.94
B	103.9	B	103.93	NH3	40.93
Li	6.73	SO4	11.40	He	0.01
				C2H6	0.77
				C3H8	0.09

Scaling Potential-Silica



Total Noncondensable gas corrected to reservoir conditions

WHP (bara)	T _{sep} (°C)	P _{sep} (bara)	Reservoir Temp/Total Flow (°C)	H td (kJ/kg)	HI-sep (kJ/kg)	Hs-sep (kJ/kg)	Ytd	g/s (mole fraction)	g/s (kg/kg)	g/H ₂ O (kg/kg)	Well Average g/H ₂ O (kg/kg)
								Sampling		Reservoir	
9.6	167.8	8.5	193	820.8	709.5	2765.7	0.05	0.2710	0.662	0.0359	0.036
10.9	168.1	8.7	193	820.8	710.8	2766	0.05	0.2730	0.667	0.0357	
45.9	138.8	2.8	193	820.8	584	2731.9	0.11	0.1390	0.340	0.0375	
6	149.0	4.5	188.5	800.8	627.9	2744.7	0.08	0.1630	0.398	0.0325	0.034
6.2	150.0	4.5	188.5	800.8	632.2	2745.9	0.08	0.1590	0.389	0.031	
19	139.2	3.1	188.8	800.8	585.7	2732.4	0.10	0.1470	0.359	0.036	
37	126.0	1.7	188.5	800.8	529.3	2714.5	0.12	0.1170	0.286	0.0355	0.034
37.0	146.6	5.2	198	843	617.5	2741.8	0.12	0.084	0.21	0.026	0.026
28.1	159.6	7.9	198	843	671	2756	0.08	0.066	0.16	0.013	
40.0	149.0	4.30	202.5	863.6	627.9	2744.7	0.11	0.103	0.25	0.028	0.028
3.9	138.2	2.88	187.2	795.0	581.40	2731.1	0.10	0.112	0.27	0.027	0.027
12	133.1	2.25	187.2	795.0	559.6	2724.3	0.11	0.097	0.24	0.026	
35.9	146.6	4.1	197.5	841	617.5	2741.8	0.11	0.144	0.35	0.038	0.038

CALCITE SCALE MITIGATION

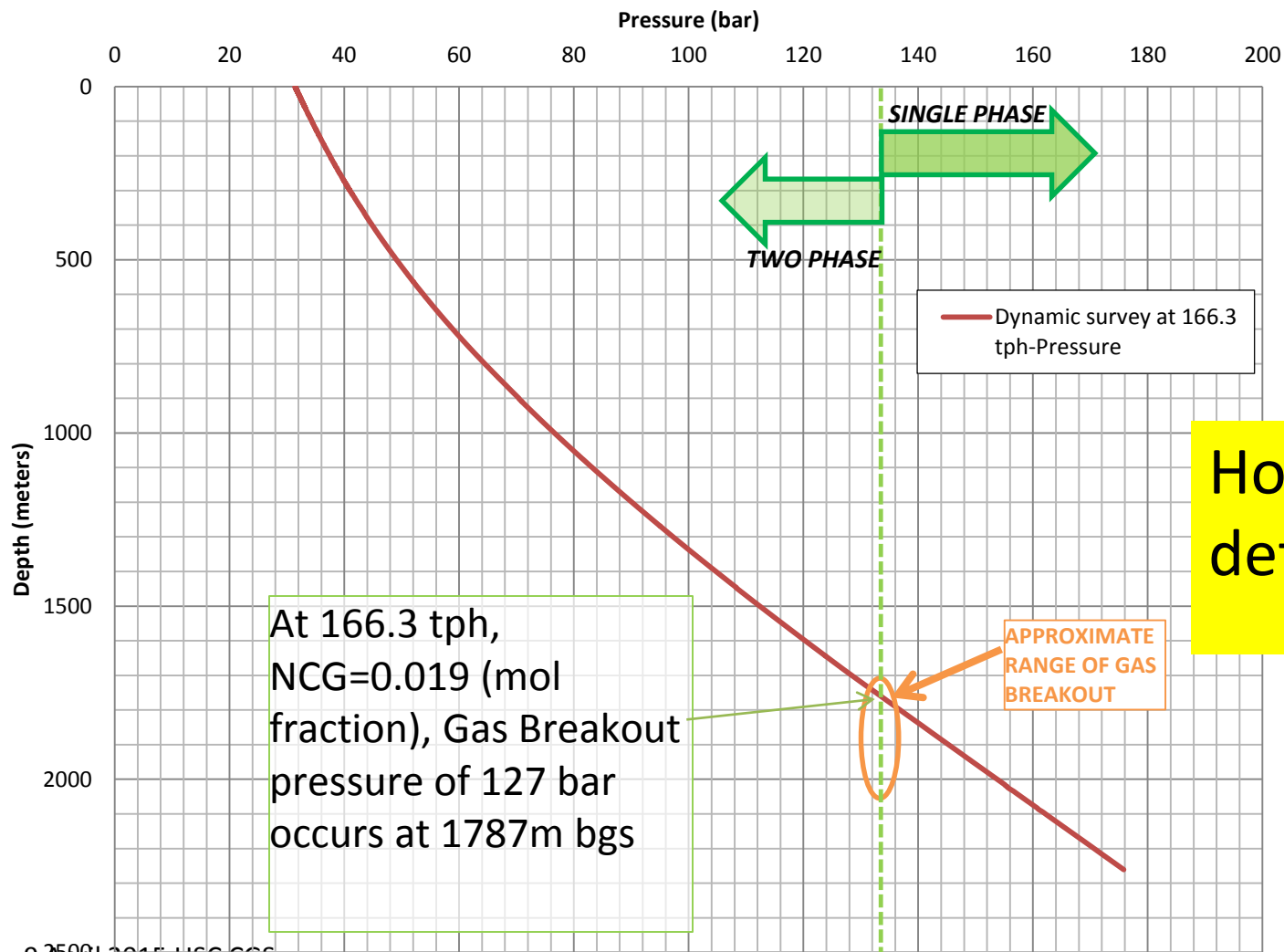
GAS BREAKOUT OR BUBBLE POINT

- Gas breakout pressure or bubble point or point at which two-phase condition occurs = the pressure at which the sum of the gas pressure and the water pressure, $P_{\text{tot,BP}}$ exceeds the total pressure, $P_{\text{tot, meas or sim}}$
- P_{gas} can be estimated using Henry's Law and the minimum single-phase water pressure, P_{liq} , can be estimated using steam tables:

- $P_{\text{gas}} = X_{\text{gas}} * K_H$
- $P_{\text{liq}} = P_{\text{water@sat T}}$
- $P_{\text{totBP}} = P_{\text{gas}} + P_{\text{liq}}$
- $P_{\text{totBP}} = P_{\text{tot, meas or sim}}$

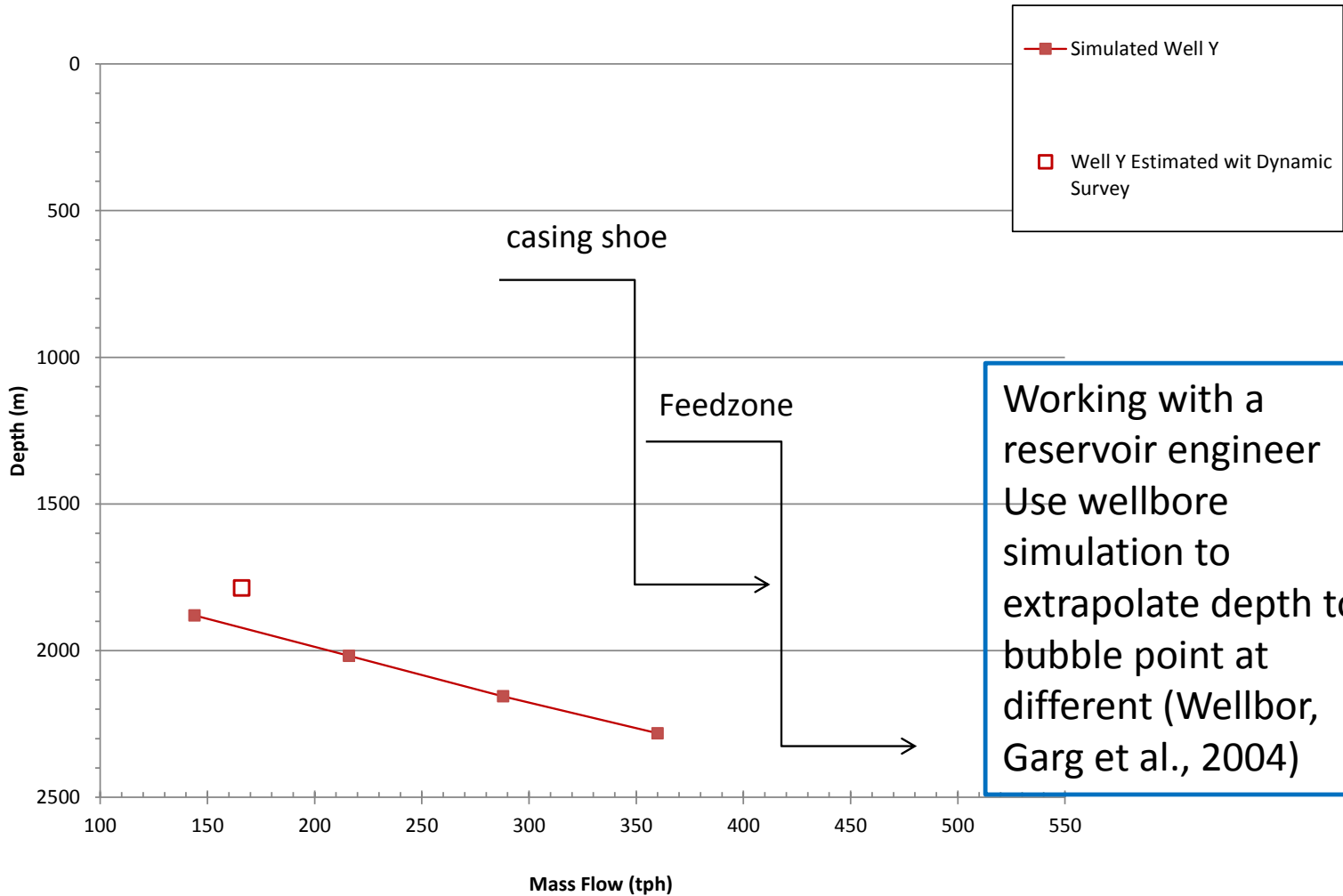
- Where K_H = Henry's law constant at the reservoir temperature and X_{gas} is the mole fraction of gas in reservoir.
- The depth at which this pressure occurs during flowing conditions can be observed in dynamic survey measurements or simulated and depends on the flow rate

Well Y Calculated Gas Breakout Pressure Compared to Measured Dynamic Total Pressure VS Depth



How determined?

Depth to Casing Shoe and Feedzone Bubble Point vs Mass Flow Well Y



GEOCHEMICAL TOOLS FOR GEOTHERMAL RESERVOIR OPERATION AND MAINTENANCE

- **Monitoring Objectives**

- Monitor changes in reservoir conditions affecting production and injection to enable reservoir management
- Managing operational issues such as scale, corrosion control, NCG loading and air emissions

- **Methodology**

- Periodic, consistent sampling and analysis of production and injection well fluids
- Database

- **Changes affecting geothermal fluid supply and injection that can be monitored by geochemistry**

- Mixing and Cooling by injection or groundwater breakthrough
- Pressure decline and boiling or cooling
- Lateral variation indicating developing zone differentiation
- Scaling-related flow restrictions or permeability decline
- Etc.

FOCUSING ON RESERVOIR MONITORING BOILING & COOLER WATER BREAKTHROUGH

- ⦿ Enthalpy, H , changes; remediation depends on cause
- ⦿ Compare measured enthalpy, H_{meas} with fast reacting enthalpy from silica geothermometer temperature, H_{silica} and slow reacting cation geothermometer temperature, H_{NKCC}
- ⦿ Boiling – steam increases H_{meas} , decreases H_{silica} , Cooling by mixing depends on the fluid (injectate or cold water)
- ⦿ Cerro Prieto and Ahuacapan from Truesdell et al., 1995



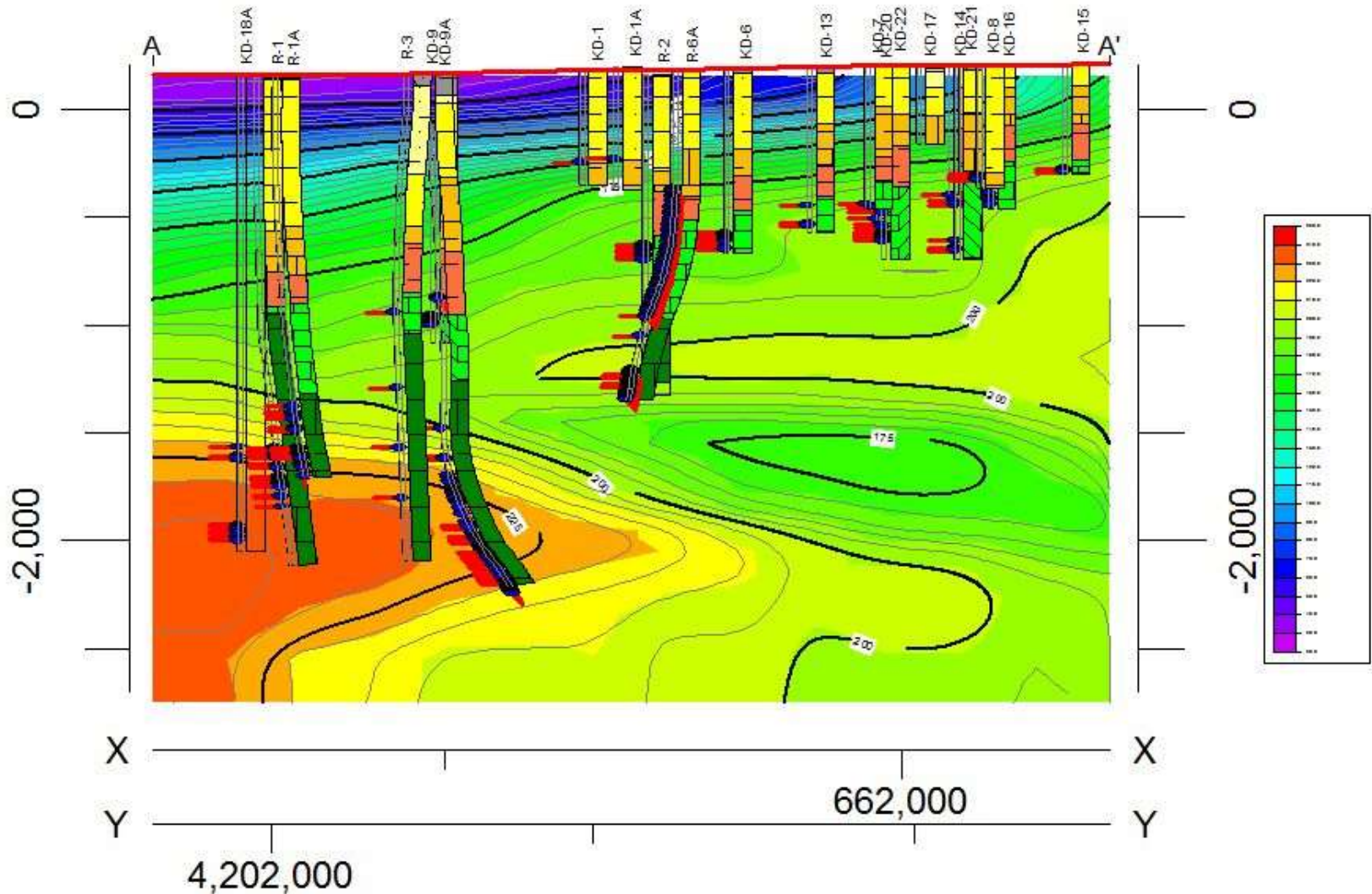
Thank you

Please e-mail me at jhaizlip@geologica.net

Presentation will posted on the USC CGS website

EXAMPLES

Kizildere (Haizlip and Tut, 2011) Temperature Profile from NNE to SSW

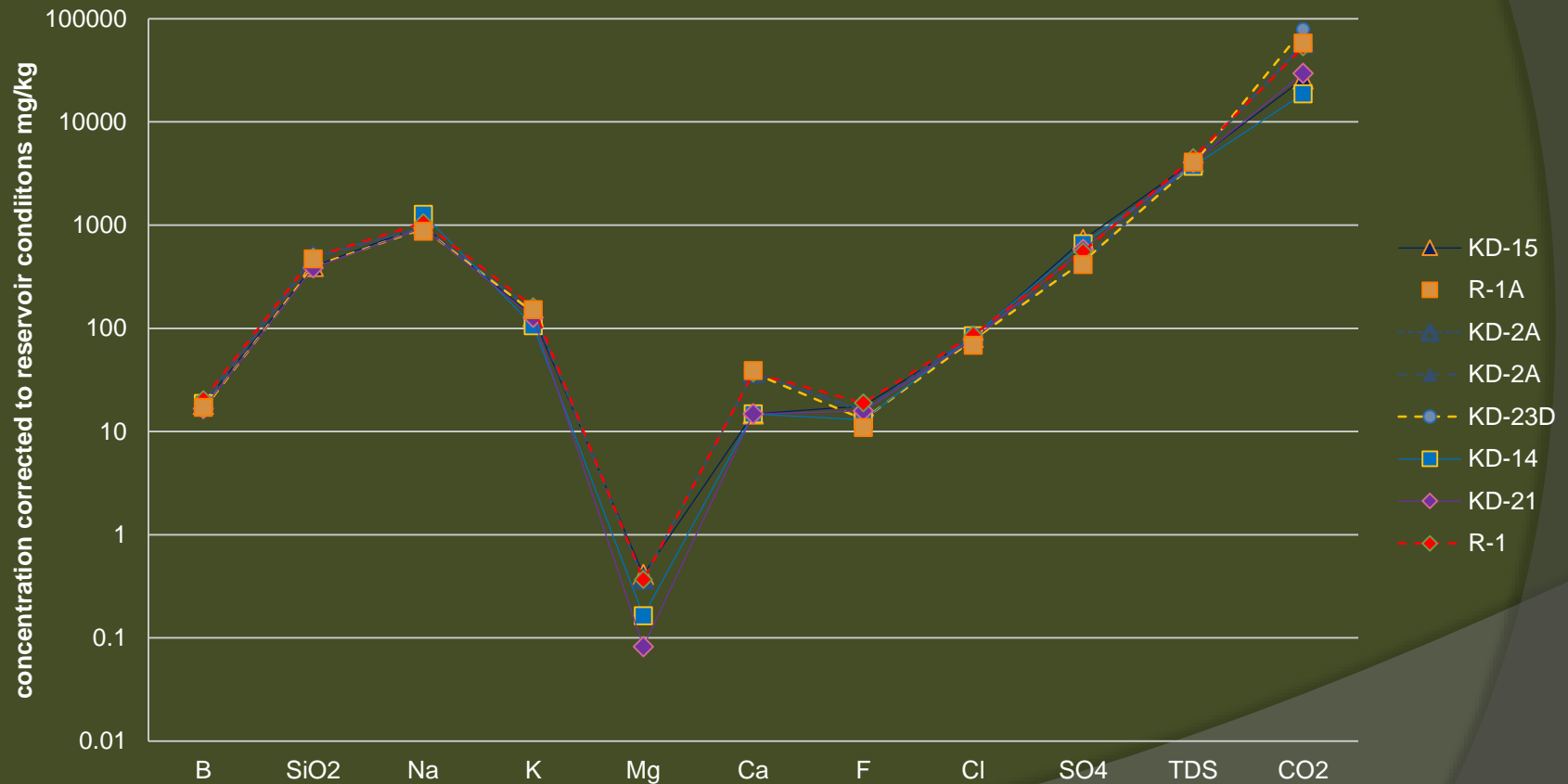


Differences Between Layers

	TDS in reservoir	Depth to Gas Breakout	Depth to top of reservoir	Total Pressure P _{tot}	Gas Pressure P _{CO2}	Temperature
Kizildere Reservoir Layer	mg/kg	m	m	bara	bara	°C
Deep	4180	1200-1800	>1600	100-160	67-85	220-242
Intermediate	3970	300-600	400-1000	40-60	17-36	190-210

Brine Characteristics

Kizildere Deep and Intermediate Reservoir Fluid Chemistry



Brine and Geothermometers

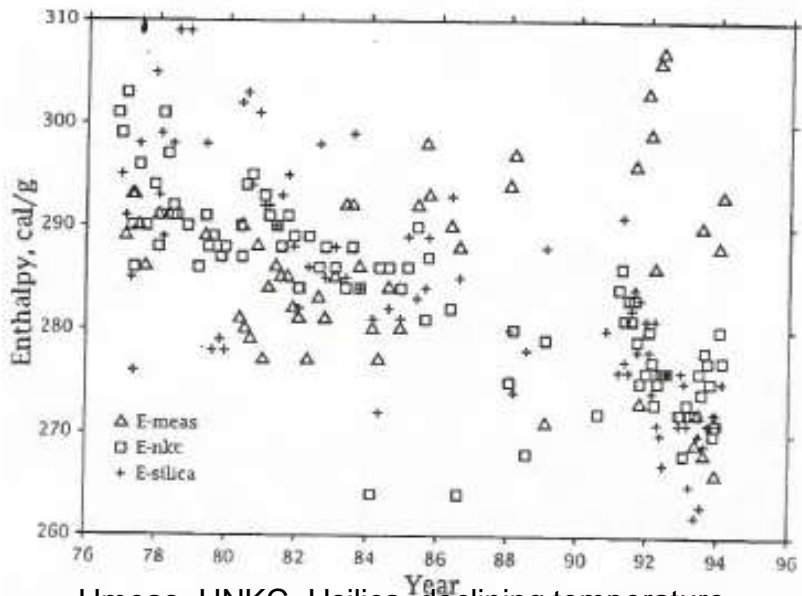
Total Reservoir (mg/kg)	Calcium	Magnesium	Sodium	Potassium	Lithium	Sulfate SO4	Tot Carb	Flouride	SiO2	Boron	Chloride
Intermediate Reservoir	-	1	1060	113	3	564	1167	17	391	19	92
Deep Reservoir	-	3	1132	178		576	2309	19	485	22	98

Kizildere Reservoir Layer	Quartz (Arnorsson et al., 1983)	Chalcedony	Na/K (Fournier, 1979)	Na/K Truesdell
	°C	°C	°C	°C
Deep	242	259	263	247
Intermediate	195	206	224	196

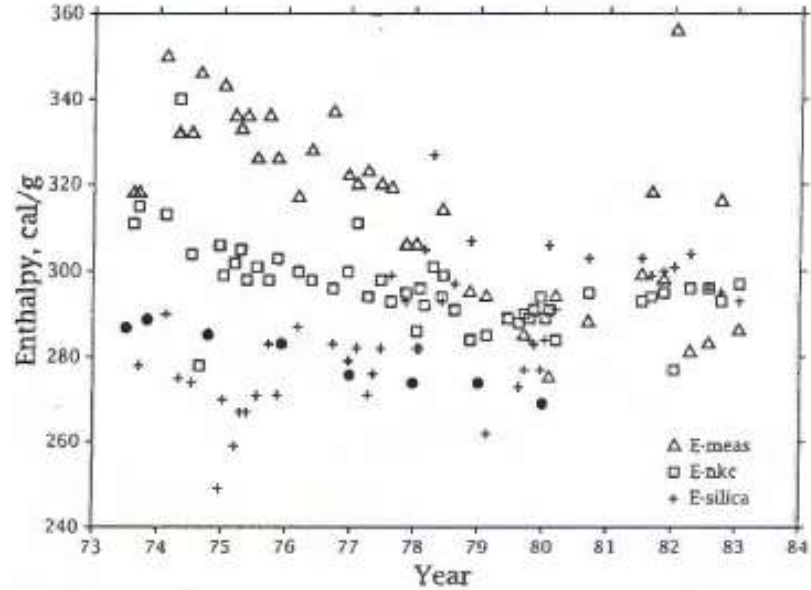
Reservoir fluids are the same except for temperature-related constituents suggesting similar origin but some separation. Upflow into the deep reservoir, cooling by equilibration not mixing.

Reservoir Monitoring

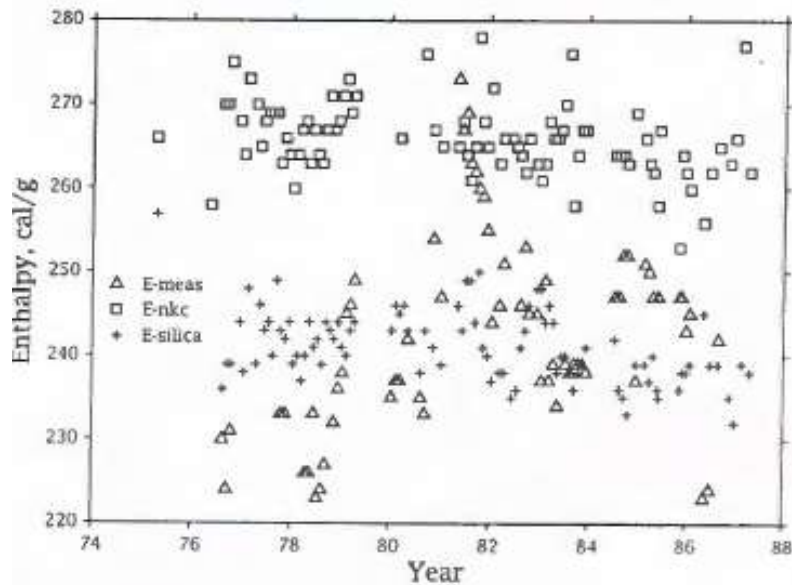
Cerro Prieto and Ahuacapan



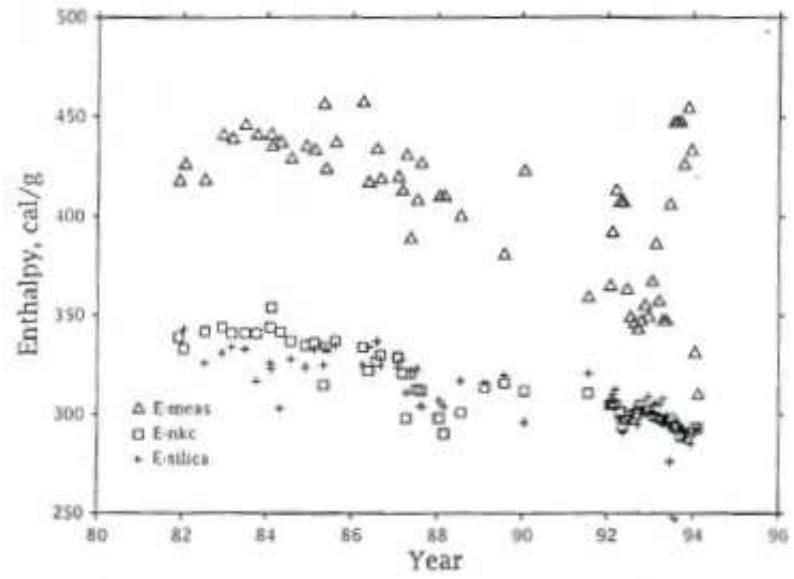
Hmeas=HNKC=Hsilica, declining temperature equilibrated liquid



Hmeas>HNKC>Hsilica, boiling, near wellbore cooling from boiling, equilibrated after 1980



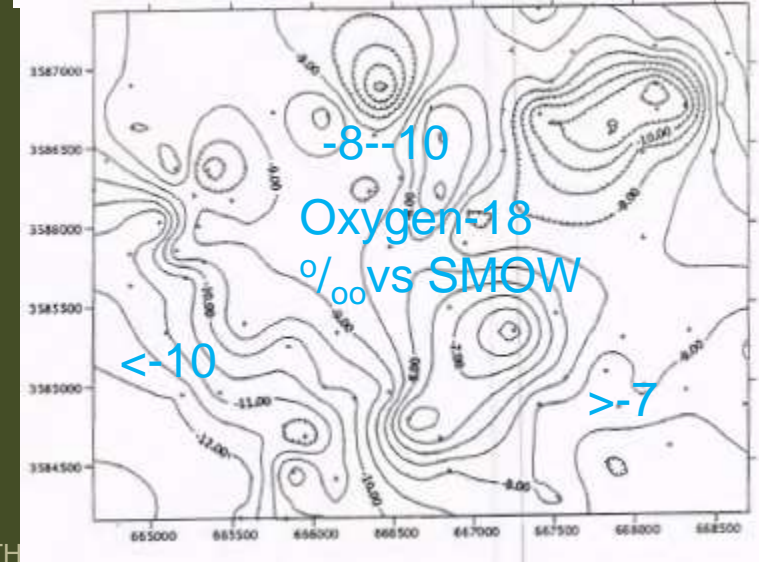
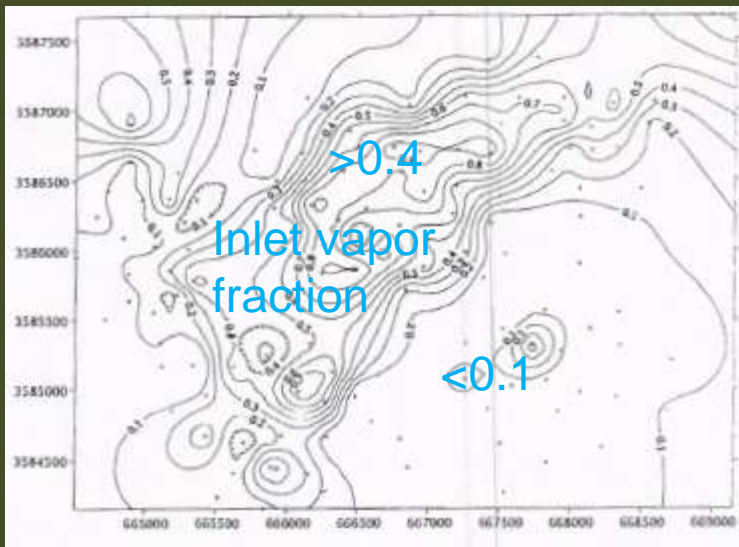
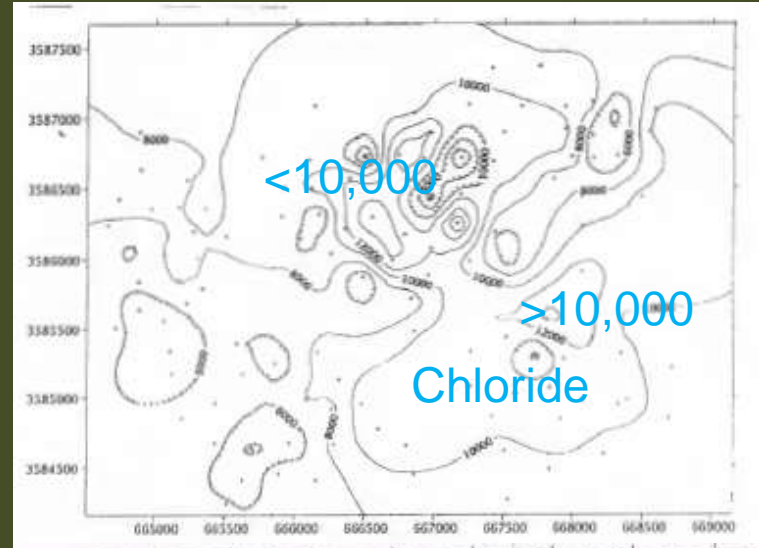
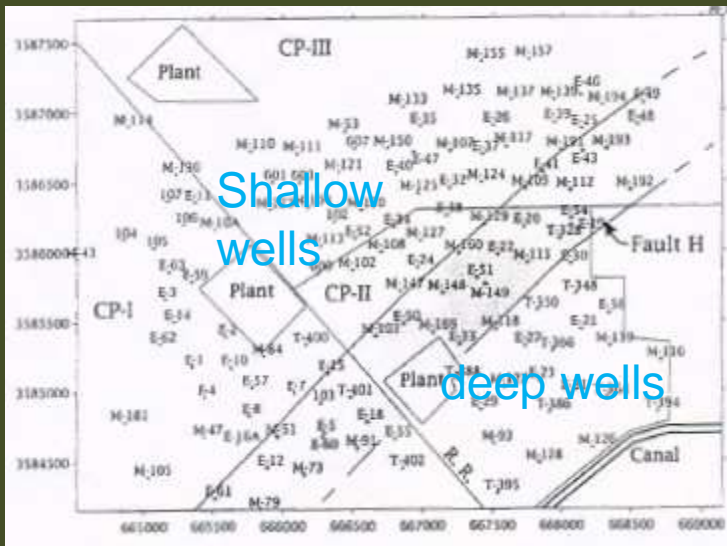
HNKC>Hmeas=Hsilica, or Hmeas>silica cooler water influx, injectate



Hmeas>HNKC=Hsilica, declining enthalpy influx of steam

FIELDWIDE RESERVOIR CHANGES

High chloride marks the deepest and hottest part of the field, SE of fault H



Inlet vapor fraction calculated from the difference between Hmeas and HNKC, lowest in the SE. Highest oxygen-18 also in the SE

Example: Coso Hot Springs

Early Exploration

◎ Geologic Setting

- Located on the eastern side of a young (<39,000y) bimodal volcanic center,
- Basement of mesozoic/metamorphics of the Sierra Nevada to the west
- Partially molten silicic magma at >5 km (seismic low v),
- High seismic activity

What can geochemistry contribute?

Coso Surface Manifestations

- Fumaroles-steaming ground and mud pots at boiling temps
- Sulfur and acid alteration
- Scinter ~238,000 y
- Travertine on EF >300,000 y
- Chemistry: Acid sulfate, isotopes lighter than local meteoric water
- Located near faults



What could we have said about Coso from pre-drilling chemistry?

- Multiple hydrothermal systems, historical liquid dominated but oldest not that hot
- Fumaroles: system is hot enough to boil shallow, steam + gas upflow along faults
- Gases include sulfide are in high enough concentrations so then when the steam condenses, absorbed gas generates $\text{pH} < 2$, dissolves rock, oxidizes sulfide to sulfate
- Boiling extends from Devils Kitchen to South Pool
- Travertine- $< 200^\circ\text{C}$ liquid dominated
- Scinter $> 200^\circ\text{C}$ liquid dominated

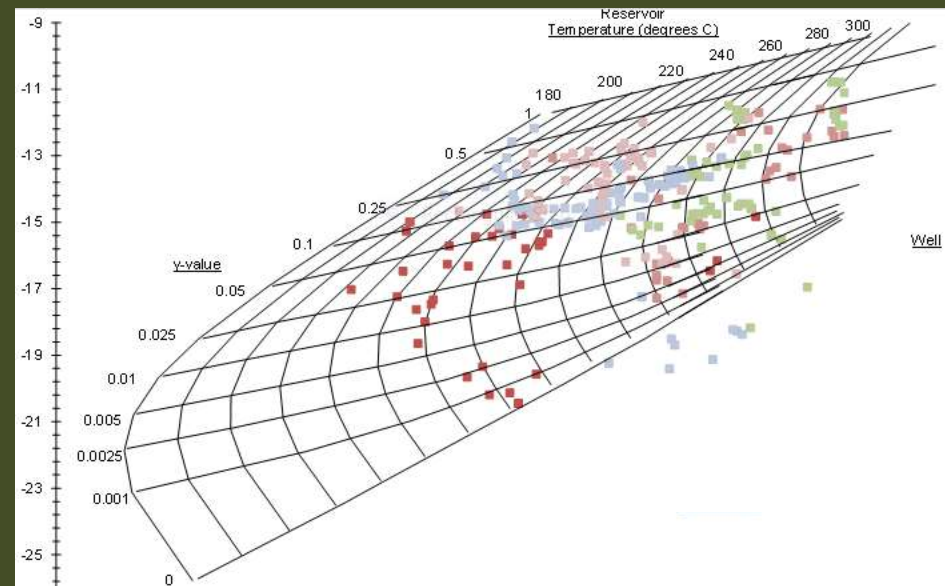
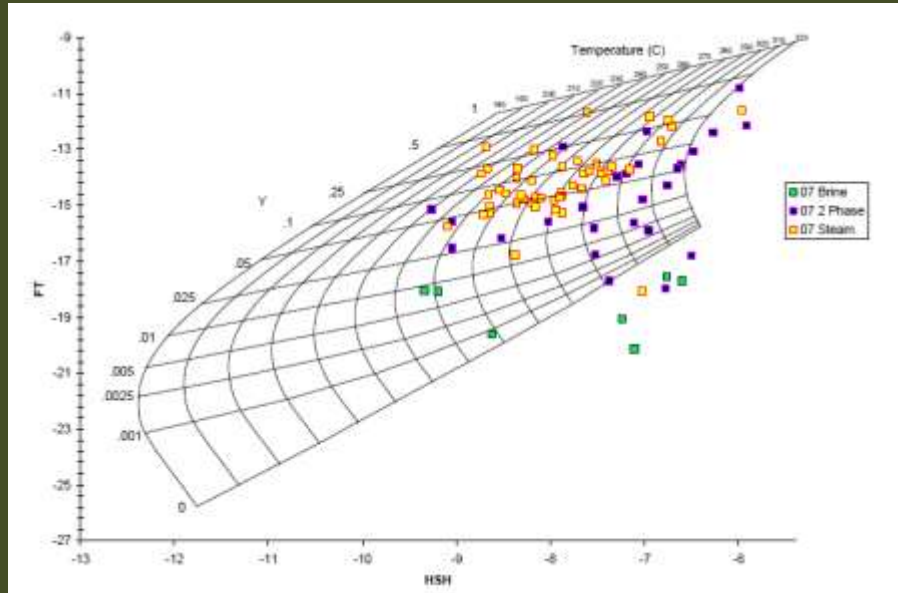
Can't say?

- ⦿ Vapor dominated or liquid dominated or two-phase?
- ⦿ Liquid geothermometers do not apply.
- ⦿ Gas geothermometers might, but no gas data from the fumaroles.

How'd it go?

- Shallow holes drilled near the hot spring identified NaCl brine and temperatures from geothermometers, followed after another 10 years of nearly 100 wells
- Coso is a $>250^{\circ}\text{C}$ two-phase geothermal system producing 200 MW power since 1987
- Extensive literature on its origin, model etc.
- Fluid chemistry is now part of reservoir monitoring and understanding, but it played a very limited role in the discovery of the field

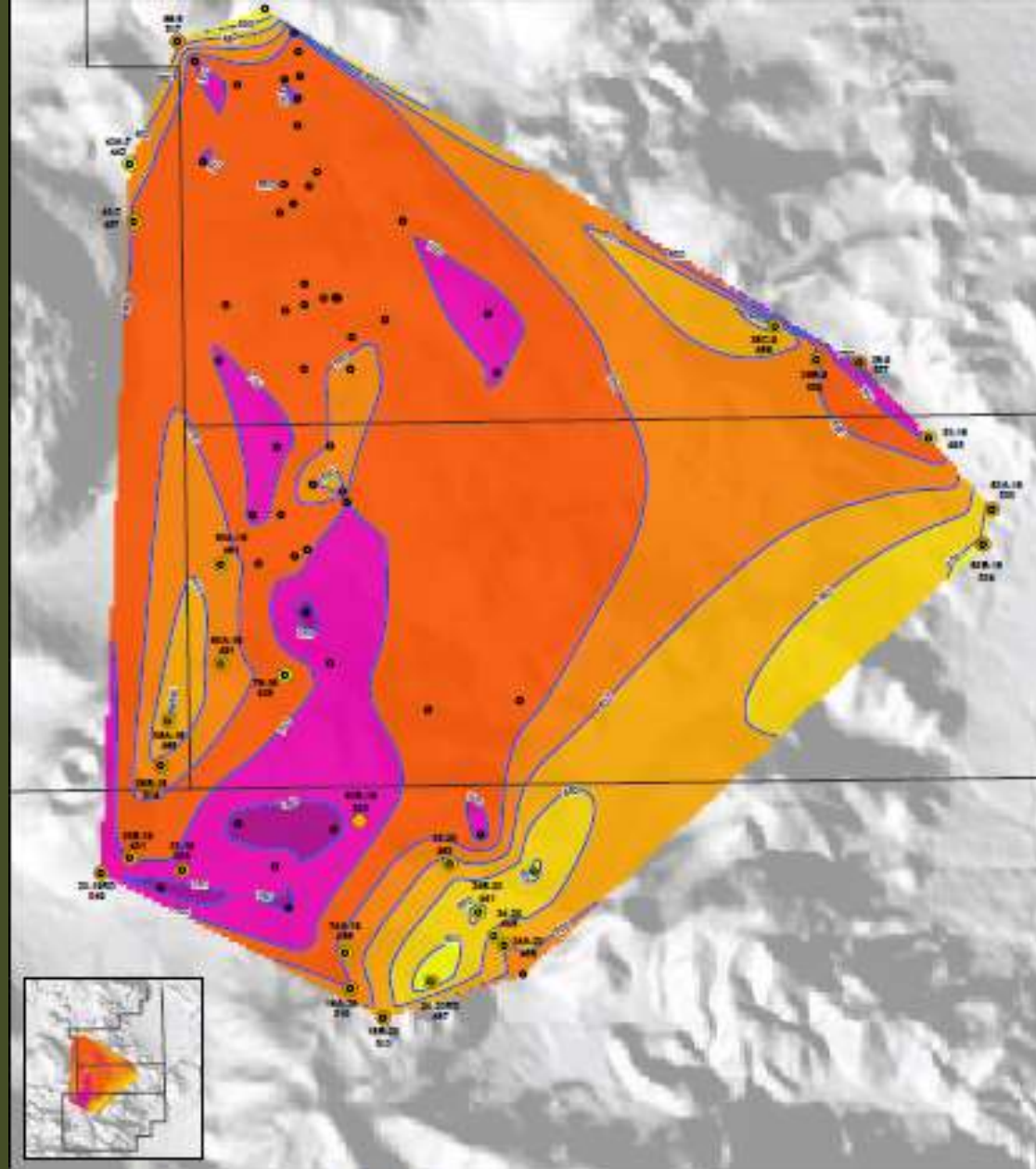
Using chemistry to monitor the reservoir especially reservoir boiling



Steam fractions in steam,
2-phase and liquid wells

Steam fractions by area

Differences in liquid and gas geothermometer temperatures suggesting different provenance of steam and brine



Different types of “Excess Steam”

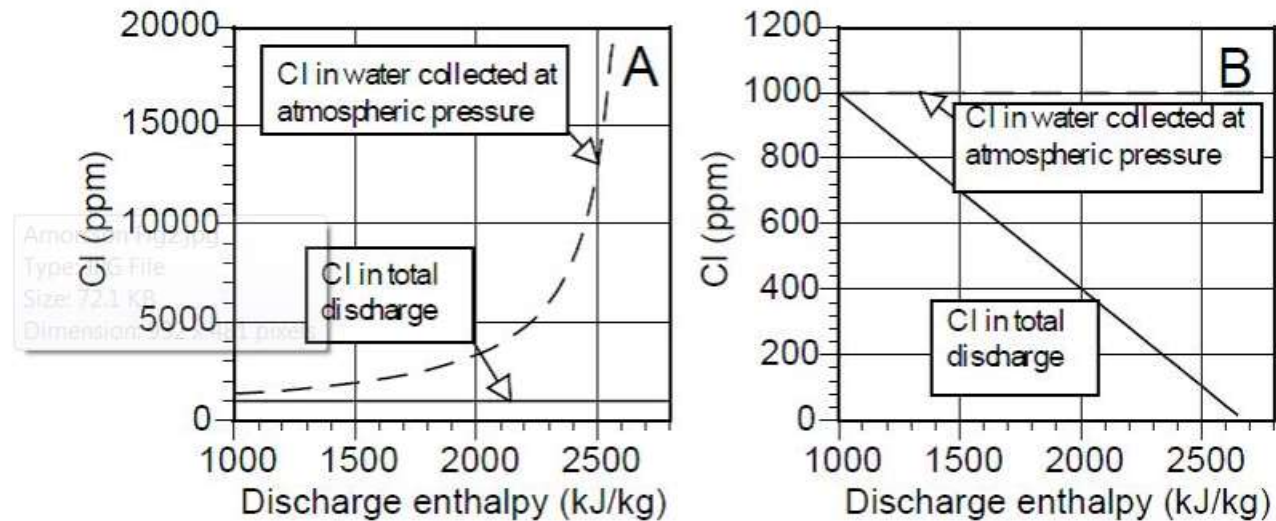
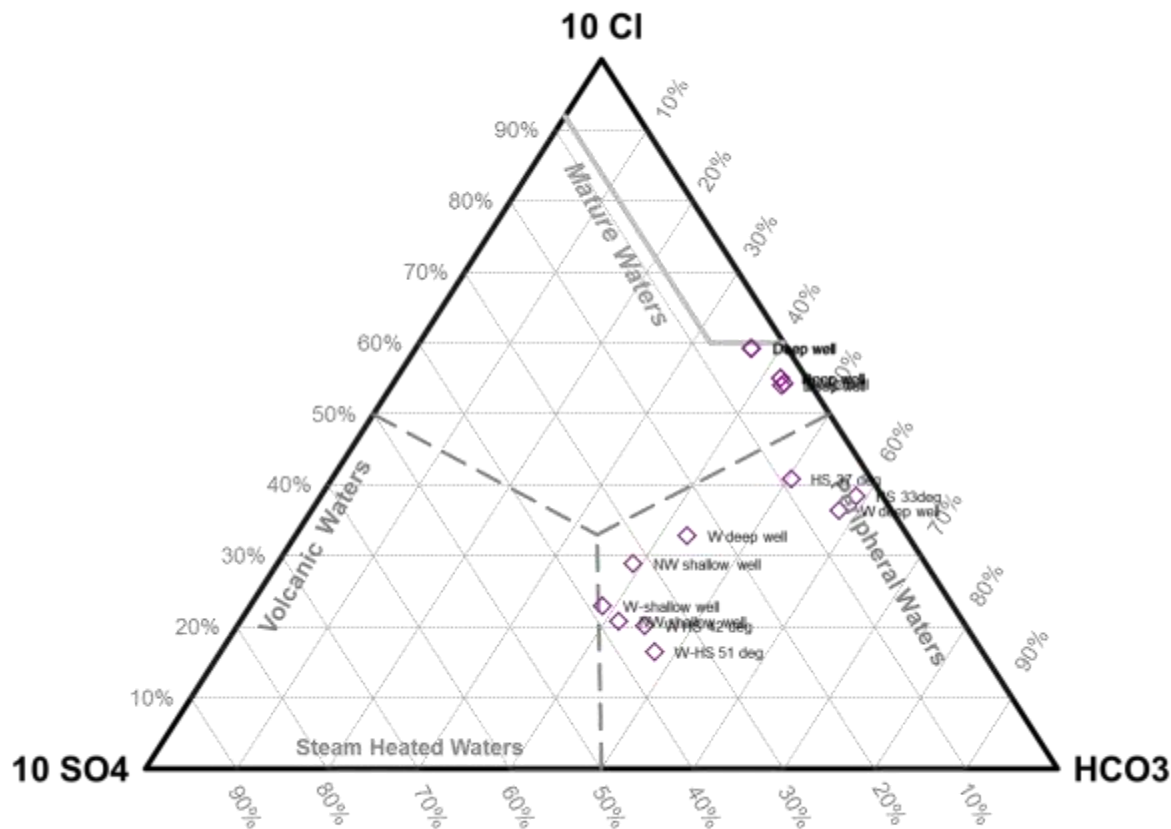


Figure 11. Relation between Cl and discharge enthalpy. A: Excess enthalpy is due to conductive heat transfer from aquifer rock to fluid flowing into well (closed system). B: Excess enthalpy is caused by phase segregation in the producing aquifer (open system).

Extensional Tectonic System in Turkey-Early Exploration

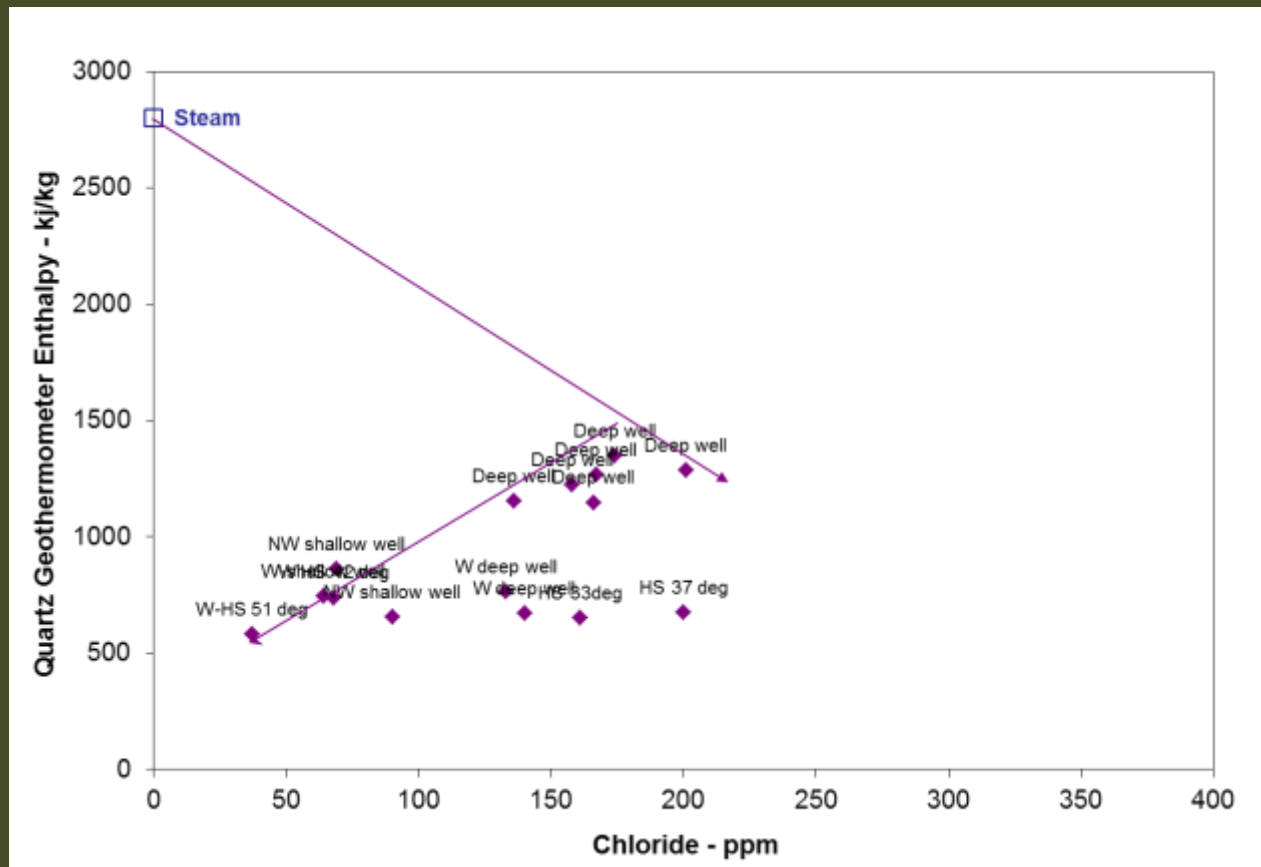
- In an actively extensional graben with steeper graben bounding faults transforming into low angle faults
- Cross faults generating potential for structural dilation
- Regional high heat flow evidenced as elevated temperatures in oil and gas exploration wells within the basin
- Basement rock is metamorphic with quartzite, gneiss, schists and marbles
- Basin filled with younger sediments, some fine grained-potential cap
- Hot springs and shallow thermal wells.

Surface Manifestations and Nearby Shallow and deep Wells



- 33-51°C Hot Springs along a fault zone~ perpendicular to the graben
- Travertine but no, color , odor, etc.
- Bicarbonate waters
- Nearby wells have higher SO4
- Deep wells more Cl, still low

Surface Manifestations and Nearby Shallow and deep Wells



- Hot Springs not clearly deep well water that has been cooled by mixing
- Range of silica independent of Cl

Geothermometer Temperatures in deg C						
Sample Name	Quartz adiabatic	Na-K-Ca	Na-K-Ca Mg corr	Na/K Fournier	Na/K Truesdell	K/Mg (Giggenbach)
Deep Well (average)	220	257	238	279	269	170
Shallow well	185	139	62	232	207	108
Shallow well	147	180	-61	230	204	105
W Hot spring	133	94	-5	234	209	78
W Hot spring	163	206	-32	236	212	109
W Hot spring	164	216	-68	233	208	111
W Hot spring	151	182	-301	233	208	84
Hot Spring	147	148	-175	203	170	85
W Deep well	168	227	227	236	211	
W Deep well	150	201	190	173	134	161

Temperature from HS >160, from deep well >220.
Hot springs cooled conductively from low flow and other wells which are farther away just may be cooler.

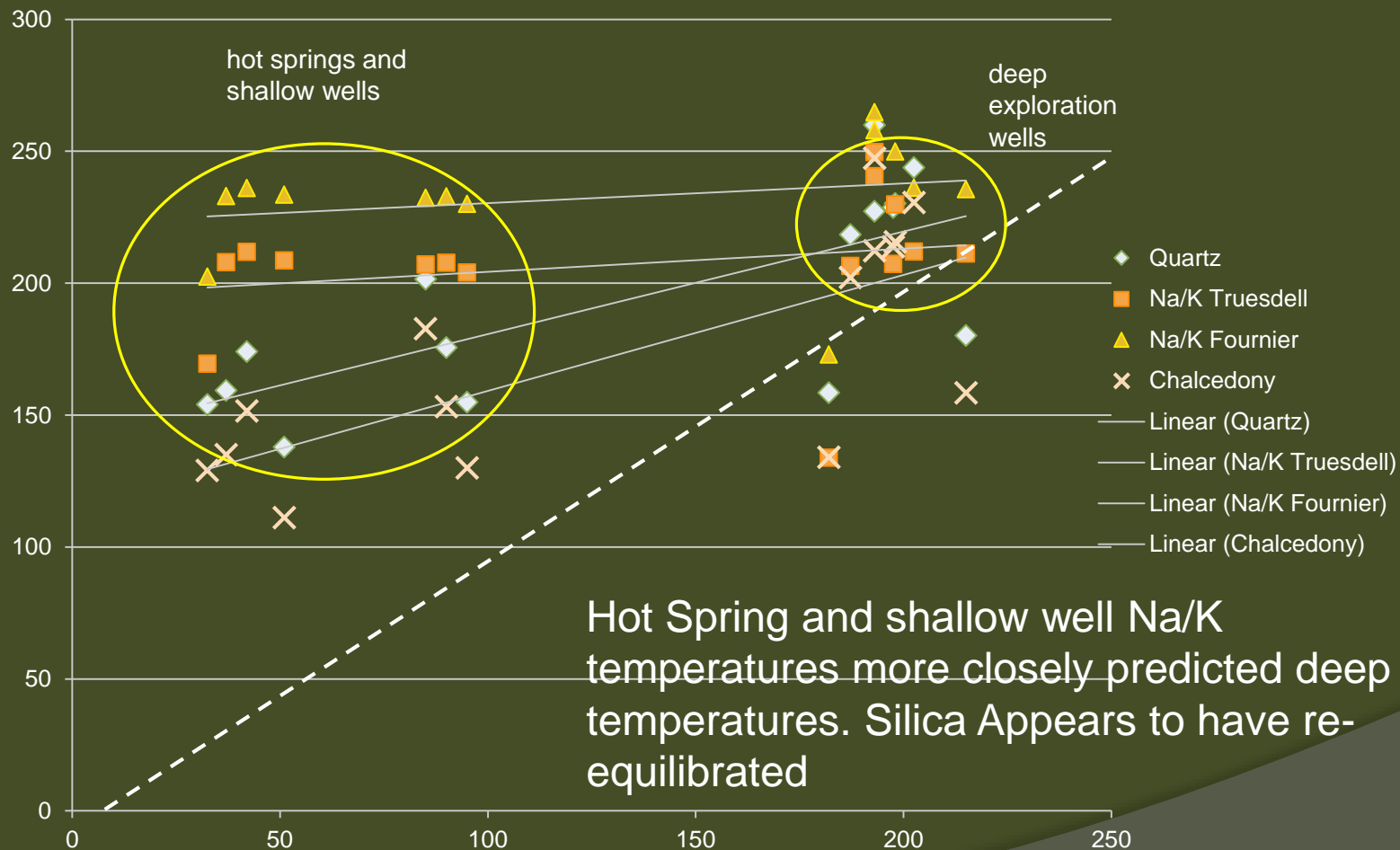
What could we have said from pre-drilling chemistry?

- ⦿ There is a geothermal system within temperatures suitable for power generation, but Na/K cation geothermometers probably too high and Ca is affected by carbonate precipitation
- ⦿ Size may be significant as indications of hot water in shallow wells over a large area
- ⦿ High bicarbonate and low chloride imply relatively immature waters
- ⦿ Meteoric water source from mountains to the south
- ⦿ High B and low Cl/B ratios indicate metamorphic host rocks which have already lost Cl

How'd it go?

- Discovered and drilled a $\sim 200^{\circ}\text{C}$ reservoir primarily hosted in metamorphic basement overlain by fine grained younger sediments
- High permeability and low storage imply flow through fractures
- High carbon dioxide gas concentrations support artesian flow

Comparison of Geothermometers and Measured temperatures

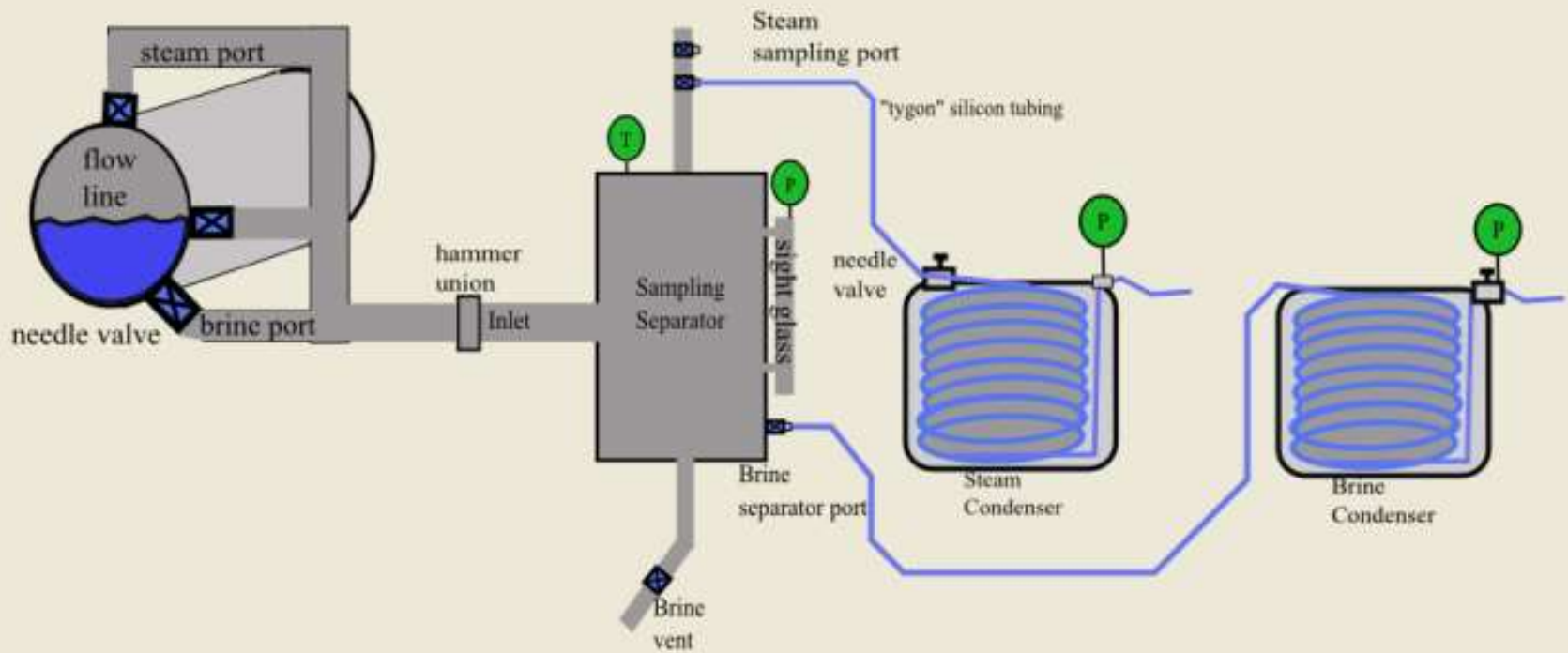


Flow Testing Equipment

- Sampling separator
- Flow line
- Cooler/condenser

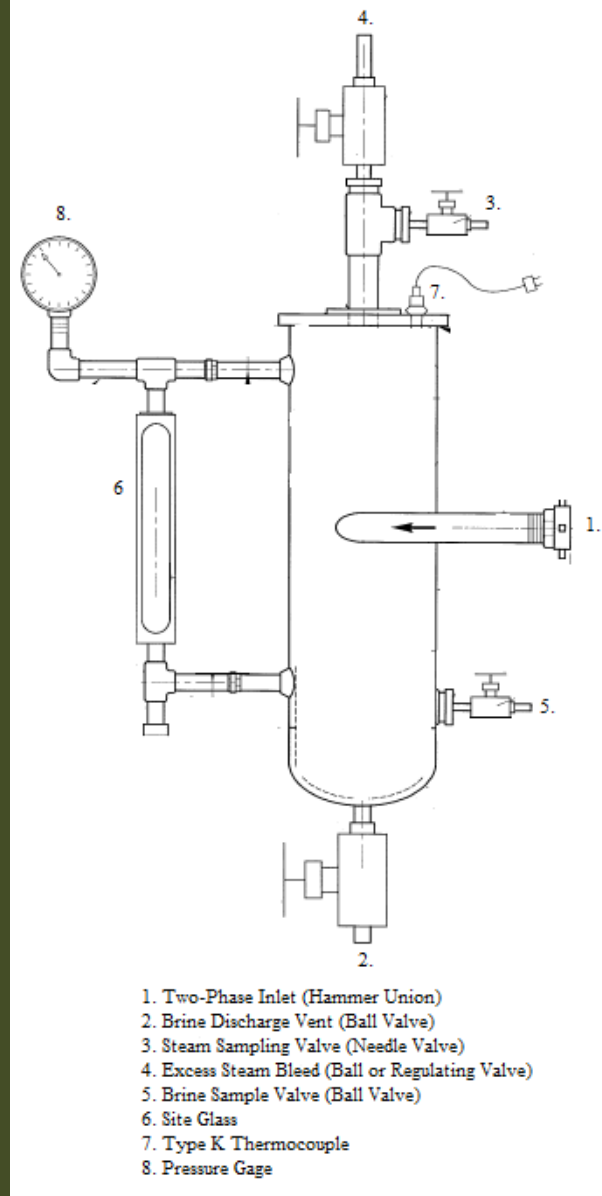


Another style



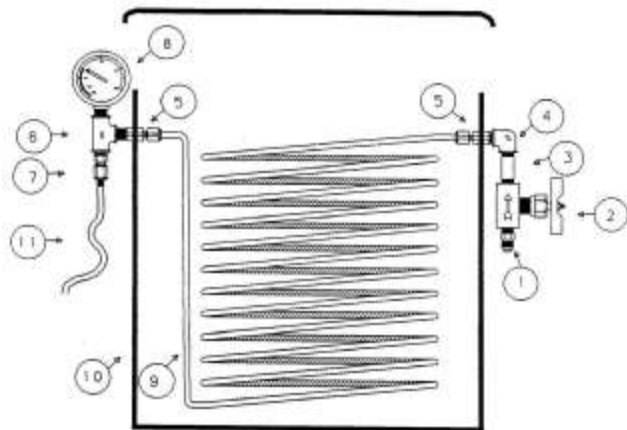
Sampling Separator Sketch Design by Veizades

- 1-attached to the 2-phase flow line with valve-open and equilibrate P
- 2-Open steam vent and level
- 3- brine sampled from below the level and steam from top.
- 4-Maintain level above brine drain when sampling brine and below steam when sampling steam
- 5-connect with coolers/condensers after achieving level
- 6- use conductivity to make sure you have good separation



VA VEIZADES & ASSOCIATES, INC.
CONSULTING ENGINEERS
5 THIRD STREET - SUITE 400 - SAN FRANCISCO - CA 94103
TEL: 415. 394.8866 FAX: 415. 394.8866

Cooler/condenser



- 1.) JIC Fitting (1/4" NPT x S.A.E. 37°)
- 2.) Marsh Needle Valve (1/4" NPT)
- 3.) S.S. Nipple (3" x 1/4" NPT)
- 4.) S.S. Elbow (1/4" NPT)
- 5.) Bulkhead Fitting (1/4" NPT x 1/4" Swagelok)
- 6.) S.S. Tee (1/4" NPT)
- 7.) Swagelok to Tygon (1/4" NPT x 1/4" hosebarb)
- 8.) 30" Hg x 30 Psi Vacuum/Pressure Gauge
- 9.) 20' 1/4" O.D. S.S. Tubing (0.035" wall)
- 10.) 8 - 20 Gallon Drum with Lid
- 11.) Tygon Tubing (size 15, 3/16" I.D.)

Figure 3 Two-Phase Flow Testing Sampling Condenser (ASTM E 1675-95 Figure 3)

Steam/gas samples

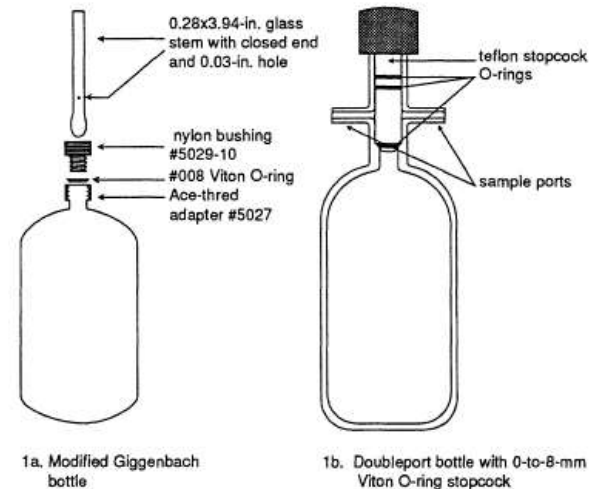


Figure 1. Two types of gas sample bottles used by this laboratory. 1a. Gas sample bottle modified from Giggenbach (Nehring and Truesdell, 1978a). 1b. Doubleport sample bottle with 0-to-8-mm Viton O-ring stopcock.

Fahlquist and Janik, 1992 USGS OFR-92-211

