Using the Geochemistry of Hydrothermal Fluids to Understand and Manage Geothermal Resources

Exploration, Assessment, Development and Operations

Jill Haizlip
GEOLOGICA Geothermal Group, Inc.

USC CGS
Distinguished Lecture Program
GEOTHERMAL 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 GEOTHERMAL SYSTEMS AND MANAGE GEOTHERMAL 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

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

\[
\text{water}(s)_i \pm \text{gas}_i + \text{rock}_i \quad \rightarrow \quad \text{water}(s)_f \pm \text{gas}_f + \text{rock}_f
\]

**water/rock (permeability)**

**time, closed/open**

**equilibrium**

where \( i = \text{initial} \) and \( f = \text{final} \)

- 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

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

9 April 2015 USC CGS Distinguished Lecture Program
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+ H\text{H}_2\text{O}+\text{CO}_2
  or +H\text{H}_2\text{O} = \text{prehnite} + \text{CO}_2
- pyrite + pyrrhotite +prehnite + water =epidote + H\text{H}_2\text{S}
  or pyrite + H\text{H}_2\text{O}=Fe-Al-silicate+ H\text{H}_2\text{S}
- + dissolution
- + magmatic volatiles
NONCONDENSIBLE GAS-SOURCES AND REACTIONS

- Magmatic Influx
  - $CO_2, SO_2, H_2, HCl, HF$ and $H_2O$

- Mineral/Gas reactions
  - Epidote, prehnite, garnet, clinozoisite, Pyrite, pyrhotite, magnetite, etc. controlling $CO_2/H_2S/H_2$

- Gas-gas reactions
  - $CO_2 + 4H_2 = CH_4 + 2H_2O$
  - Vapor-Liquid Distribution, Temperature Dependent Distribution Coefficients, $B=C_v/C_l$
  - $C_{tot}=C_v(y) + C_l(1-y)$
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 GEOTHERMAL SYSTEMS

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

CONVERSELY

HOW CAN FLUID CHEMISTRY CONSTRAIN GEOTHERMAL 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?

- What do acid-sulfate springs suggest?
- What do sodium-chloride springs suggest?
- What do neutral pH boiling springs vs acid boiling springs suggest?
- 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?

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

From Henley et al., 1984 reproduced from Henley and Ellis, 1983
Scheme of Andesitic Volcanic Hydrothermal System
What chemistry of surface manifestations might we expect? What are the surface manifestations telling us?

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).

GEOLOGICA GEOTHERMAL GROUP INC.
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, SO$_4$, HCO$_3$, pH, TDS, NH$_3$, Na, K, Ca, Mg, Li, B, As, Hg, F, B, Al, SiO$_2$
  - Oxygen-18 and deuterium

- Field measurements
  - Temperature, pH, conductivity
  - Alkalinity, et

- Fumaroles/Steam from boiling springs
  - Ar, O$_2$, N$_2$, CH$_4$, H$_2$, CO$_2$, NH$_3$, H$_2$S, Total NCG, B
  - Oxygen-18 and deuterium

- Other isotopes:
  - He$^3$/He$^4$, carbon on HCO$_3$ (water), CH$_4$ and CO$_2$ or sulfur on SO$_4$ (water), and H$_2$S
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, SO$_4$, HCO$_3$, pH, TDS, NH$_3$, Na, K, Ca, Mg, Li, B, As, Hg, F, Sr, B, Al, SiO$_2$,
  - Oxygen-18 and deuterium
  - Etc.

- Steam
  - Ar, O$_2$, N$_2$, CH$_4$, H$_2$, CO$_2$, NH$_3$, H$_2$S, Total NCG, B
  - Oxygen-18 and deuterium
  - Etc.

- Field Measurements - pH, conductivity, etc.
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
Steamp

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

- $H_{tot} = H_{l} (1-y) + H_{v} (y)$
- $C_{tot} = C_{l} (1-y) + C_{v} (y)$
- $y = \frac{H_{tot} - H_{l}}{H_{v} - H_{l}}$
- $H_{tot}$ = enthalpy of liquid at reservoir temperature
- $H_{l}$ = enthalpy of liquid at sampling P,T
- $H_{v}$ = enthalpy of steam at sampling P,T
- $C_{tot}$ = concentration in the total fluid or reservoir
- $C_{v}$ = 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 $B = \frac{C_{v}}{C_{l}}$
- $C_{l} = \frac{C_{tot}}{(1-y)+By}$ 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

\[ Y_{\text{meas}} = H_{\text{tot}} - \frac{H_{\text{Lsep}}}{H_{\text{vsep}}} - H_{\text{Lsep}} \]
\[ Y_{\text{exs}} = H_{\text{TD}} - \frac{H_{\text{Lqa}}}{H_{\text{vqa}}} - H_{\text{Lqa}} \]

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 \( C_{L_{\text{res}}} \) is:
\[ C_L \ast \frac{(1 - Y_{\text{TD}})/(1 - Y_{\text{exs}})}{C_{L_{\text{res}}}} \]
For non-excess steam or just brine wells,
\[ Y_{\text{TD}} = H_{\text{TD}} - \frac{H_{\text{Lsep}}}{H_{\text{vsep}}} - H_{\text{Lsep}} \]
And the correction is:
\[ C_L \ast (1 - Y_{\text{TD}}) = C_{L_{\text{res}}} \]
(\( \text{equations become the same as } Y_{\text{exs}} \text{ goes to 0.} \)
EXPLORATION

- Temperature dependent water/rock reactions → Chemical geothermometers
- Variations in chemistry: fluid flows, inflows and outflows → 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
<table>
<thead>
<tr>
<th>Geothermometer</th>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz-no steam loss</td>
<td>$T = \frac{1309}{(5.19 - \log C)} - 273.15$</td>
<td>Fournier (1977)</td>
</tr>
<tr>
<td>Quartz-maximum steam loss at 100 °C</td>
<td>$T = \frac{1522}{(5.75 - \log C)} - 273.15$</td>
<td>Fournier (1977)</td>
</tr>
<tr>
<td>Quartz</td>
<td>$T = \frac{42.198 + 0.28831C - 3.6686 \times 10^{-4} C^2 + 3.1665 \times 10^{-7} C^3 + 77.034 \log C}{5.19 - \log C} - 273.15$</td>
<td>Fournier and Potter (1982)</td>
</tr>
<tr>
<td>Quartz</td>
<td>$T = \frac{53.500 + 0.11236C - 0.5559 \times 10^{-4} C^2 + 0.1772 \times 10^{-7} C^3 + 88.390 \log C}{5.19 - \log C} - 273.15$</td>
<td>Arnorsson (1985) based on Fournier and Potter (1982)</td>
</tr>
<tr>
<td>Chalcedony</td>
<td>$T = \frac{1032}{(4.69 - \log C)} - 273.15$</td>
<td>Fournier (1977)</td>
</tr>
<tr>
<td>Chalcedony</td>
<td>$T = \frac{1112}{(4.91 - \log C)} - 273.15$</td>
<td>Arnorsson et al. (1983)</td>
</tr>
<tr>
<td>Alpha-Cristobalite</td>
<td>$T = \frac{1000}{(4.78 - \log C)} - 273.15$</td>
<td>Fournier (1977)</td>
</tr>
<tr>
<td>Opal-CT (Beta-Cristobalite)</td>
<td>$T = \frac{781}{(4.51 - \log C)} - 273.15$</td>
<td>Fournier (1977)</td>
</tr>
<tr>
<td>Amorphous silica</td>
<td>$T = \frac{731}{(4.52 - \log C)} - 273.15$</td>
<td>Fournier (1977)</td>
</tr>
</tbody>
</table>

From Guler, 2012
Silica and pH

\[ \text{SiO}_{2,\text{min}} + \text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4 \]

\[ \text{H}_4\text{SiO}_4 \rightleftharpoons \text{H}_3\text{SiO}_4^- + \text{H}^+ \]

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:
  \[ \text{NaAlSi}_3\text{O}_8 + \text{K}^+ = \text{KAlSi}_3\text{O}_8 + \text{Na}^+ \]
  where \( K_{eq} = \frac{[\text{KAlSi}_3\text{O}_8][\text{Na}^+]}{[\text{NaAlSi}_3\text{O}_8][\text{K}^+]} \)
  [activity] of solids = 1, so \( K_{eq} = \frac{[\text{Na}^+]}{[\text{K}^+]} \) and
  \[ \log K_{eq} = \frac{\Delta H^\circ}{2.303RT} + C \]
  change in heat of solution, \( \Delta H^\circ \), doesn’t change much 0-300°C, \( \frac{[\text{Na}^+]}{[\text{K}^+]} \) and log \( K_{eq} \) ~ 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:

\[ t^\circ C = \frac{876.3}{\{\log(Na/K)\} + 0.087750} - 273.15 \]
Other cations:

- **Na-K-Ca**
  \[ \log K_{eq} = \left\{ \frac{1647}{\log (Na/K) + \beta \{\log \ (Ca^{1/2}/Na) + 2.06\} + 2.47} \right\} - 273.15; \]

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

  If \( t^\circ C > 100^\circ C \), 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)

- \( K/Mg^{1/2} \) – fast acting, seeps most appropriate in volcanic systems (Giggenbach, 1988)

- \( Li/Na, Li/Mg^{1/2} \) - 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

Example

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

![Graph showing saturation indices of multiple minerals](image_url)
A similar approach by Arnorsson (2000)
Noncondensible 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**
  - $3\text{FeS}_2 + 2\text{H}_2 = \text{Fe}_3\text{Si}_4\text{H}_2\text{O}$
  - $\text{FeS}_2 + \text{H}_2 = \text{FeS} + \text{H}_2\text{S}$
  - $\text{CaCO}_3 + \text{K-mica} = \text{CaAl-silicate} + \text{Kspar} + \text{CO}_2$
  - 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.

$C_{\text{tot}} = C_l (1-y) + C_0 (y)$ or $C_{\text{tot}}/C_l = (1-y) + By$
Table 1: Gas geothermometer equations

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$FT^1$:</td>
<td>$\log P_{CO2} + 4\log P_{H2} - \log P_{CH4} - 2\log P_{H2O} = 10.76 - 9323/T$</td>
</tr>
<tr>
<td>$NAH^1$:</td>
<td>$\log P_{N2} + 3 \log P_{H2} - 2 \log P_{NH3} = 11.80 - 5400/T$</td>
</tr>
<tr>
<td>$HSH^1$:</td>
<td>$3 \log P_{H2S} - \log P_{H2} = 15.71 - 10141/T$ (py-mag)</td>
</tr>
<tr>
<td></td>
<td>$\log P_{H2S} - \log P_{H2} = 4.94 - 2874/T$ (py-pyh)</td>
</tr>
<tr>
<td>$DAP^2$:</td>
<td>$T = 24775/(2 \log (CH4/CO2) - 6 \log (H2/CO2) - 3 \log (H2S/CO2) - 7 \log P_{CO2} + 36.05)$</td>
</tr>
<tr>
<td>$H2S^3$:</td>
<td>$\log P_{H2S} = 6.05 - 3990/T$</td>
</tr>
<tr>
<td>$CO2^4$:</td>
<td>$\log P_{CO2} = -8.366 + 0.0168 T$</td>
</tr>
<tr>
<td>$CO2-H2^5$:</td>
<td>$\log P_{CO2} + 2\log P_{H2} = 16.298 - 8982/T$</td>
</tr>
<tr>
<td>$CO^6$:</td>
<td>$\log (P_{CO}/P_{CO2}) - \log (P_{H2}/P_{H2O}) = 2.485 - 2248/T$</td>
</tr>
<tr>
<td>$H2O^1$:</td>
<td>$\log P_{H2O} = 5.51 - 2048/T$</td>
</tr>
<tr>
<td>$z$ factor$^7$:</td>
<td>$\log z = \log P_{H2O} - 3.041 + 2118/T - \log T$</td>
</tr>
</tbody>
</table>

All temperatures in degrees Kelvin

References:
4. Adapted from Giggenbach & Goguel (1989)
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

- $^{3}\text{He}/^{4}\text{He}$ can be used to detect mantle-derived volcanic gases
- Difficult to sample (Kennedy 2006)
Evaporation trends
(kinetic, non-equilibrium)
Slopes of:
-2 (lowest humidity) to
-5 (highest humidity)

δ-D changes
-1 to -4 o/oo
per 100 m
elevation rise

Global Meteoric Water Line
δ-D = 8.13 + 8.18O + 10.8

Equilibrium fractionation
of water vapor (steam)
with respect to water

In geothermal waters, 18O increases by ~0 to >15 o/oo
due to rock-water isotope exchange. Deuterium
changes very little, because rocks contain little H.

Basic Processes Affecting Oxygen and Hydrogen Isotopes
in Geothermal Water
Origin of geothermal fluids: mostly meteoric + O-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
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

![Diagram showing mixing of waters](image)

- **Enthalpy (j/gm)**
- **Chloride (mg/kg)**

- **Steam**
- **Aquifer fluid (265°C)**
- **Cold water mixing**
- **Steam loss**
- **Aquifer fluid flashed to 100°C**
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

<table>
<thead>
<tr>
<th>Weighted average of chemistry, corrected to reservoir (mg/kg)*</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Na</strong> 555.9</td>
<td>As 0.18</td>
</tr>
<tr>
<td><strong>K</strong> 78.7</td>
<td><strong>HCO3</strong> 1351.98</td>
</tr>
<tr>
<td><strong>Ca</strong> 2.53</td>
<td><strong>NH4</strong> 21.53</td>
</tr>
<tr>
<td><strong>Mg</strong> 0.05</td>
<td><strong>Cl</strong> 154.38</td>
</tr>
<tr>
<td><strong>Fe</strong> 0.02</td>
<td><strong>F</strong> 3.92</td>
</tr>
<tr>
<td><strong>Al</strong> 0.34</td>
<td><strong>Ba</strong> 0.66</td>
</tr>
<tr>
<td><strong>SiO2</strong> 398.7</td>
<td><strong>Br</strong> 0.66</td>
</tr>
<tr>
<td><strong>B</strong> 103.9</td>
<td><strong>B</strong> 103.93</td>
</tr>
<tr>
<td><strong>Li</strong> 6.73</td>
<td><strong>SO4</strong> 11.40</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Scaling Potential-Silica

[Diagram showing the solubility of amorphous silica at different pH levels and temperatures.]
Total Noncondensible gas corrected to reservoir conditions

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

$P_{\text{gas}}$ can be estimated using Henry’s Law and the minimum single-phase water pressure, $P_{\text{liq}}$, can be estimated using steam tables:

- $P_{\text{gas}} = X_{\text{gas}} \times K_{H}$
- $P_{\text{liq}} = P_{\text{water@sat T}}$
- $P_{\text{tot, BP}} = P_{\text{gas}} + P_{\text{liq}}$
- $P_{\text{tot, BP}} = P_{\text{tot, meas or sim}}$

Where $K_{H}$ = Henry’s law constant at the reservoir temperature and $X_{\text{gas}}$ 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.
At 166.3 tph, NCG=0.019 (mol fraction), Gas Breakout pressure of 127 bar occurs at 1787m bgs

How determined?
Working with a reservoir engineer
Use wellbore simulation to extrapolate depth to bubble point at different (Wellbor, Garg et al., 2004)
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, $H_{NKC}$
- 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

<table>
<thead>
<tr>
<th>Kizildere Reservoir Layer</th>
<th>TDS in reservoir (mg/kg)</th>
<th>Depth to Gas Breakout (m)</th>
<th>Depth to top of reservoir (m)</th>
<th>Total Pressure $P_{tot}$ (bara)</th>
<th>Gas Pressure $P_{CO2}$ (bara)</th>
<th>Temperature ($^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deep</td>
<td>4180</td>
<td>1200-1800</td>
<td>&gt;1600</td>
<td>100-160</td>
<td>67-85</td>
<td>220-242</td>
</tr>
<tr>
<td>Intermediate</td>
<td>3970</td>
<td>300-600</td>
<td>400-1000</td>
<td>40-60</td>
<td>17-36</td>
<td>190-210</td>
</tr>
</tbody>
</table>
Brine Characteristics

Kizildere Deep and Intermediate Reservoir Fluid Chemistry

- **KD-15**
- **R-1A**
- **KD-2A**
- **KD-23D**
- **KD-14**
- **KD-21**
- **KD-21**
- **R-1**

Concentration corrected to reservoir conditions mg/kg
Brine and Geothermometers

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

<table>
<thead>
<tr>
<th>Kizildere Reservoir Layer</th>
<th>Quartz (Arnórsson et al., 1983)</th>
<th>Chalcedony</th>
<th>Na/K (Fournier, 1979)</th>
<th>Na/K Truesdell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>°C</td>
<td>°C</td>
<td>°C</td>
</tr>
<tr>
<td>Deep</td>
<td>242</td>
<td>259</td>
<td>263</td>
<td>247</td>
</tr>
<tr>
<td>Intermediate</td>
<td>195</td>
<td>206</td>
<td>224</td>
<td>196</td>
</tr>
</tbody>
</table>

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 pH<2, dissolves rock, oxidizes sulfide to sulfate
- Boiling extends from Devils Kitchen to South Pool
- Travertine-<200°C liquid dominated
- Scinter>200°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°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
<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Quartz adiabatic</th>
<th>Na-K-Ca</th>
<th>Na-K-Ca Mg corr</th>
<th>Na/K Fournier</th>
<th>Na/K Truesdell</th>
<th>K/Mg (Giggenbach)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deep Well (average)</td>
<td>220</td>
<td>257</td>
<td>238</td>
<td>279</td>
<td>269</td>
<td>170</td>
</tr>
<tr>
<td>Shallow well</td>
<td>185</td>
<td>139</td>
<td>62</td>
<td>232</td>
<td>207</td>
<td>108</td>
</tr>
<tr>
<td>Shallow well</td>
<td>147</td>
<td>180</td>
<td>-61</td>
<td>230</td>
<td>204</td>
<td>105</td>
</tr>
<tr>
<td>W Hot spring</td>
<td>133</td>
<td>94</td>
<td>-5</td>
<td>234</td>
<td>209</td>
<td>78</td>
</tr>
<tr>
<td>W Hot spring</td>
<td>163</td>
<td>206</td>
<td>-32</td>
<td>236</td>
<td>212</td>
<td>109</td>
</tr>
<tr>
<td>W Hot spring</td>
<td>164</td>
<td>216</td>
<td>-68</td>
<td>233</td>
<td>208</td>
<td>111</td>
</tr>
<tr>
<td>W Hot spring</td>
<td>151</td>
<td>182</td>
<td>-301</td>
<td>233</td>
<td>208</td>
<td>84</td>
</tr>
<tr>
<td>Hot Spring</td>
<td>147</td>
<td>148</td>
<td>-171</td>
<td>203</td>
<td>170</td>
<td>85</td>
</tr>
<tr>
<td>W Deep well</td>
<td>168</td>
<td>227</td>
<td>227</td>
<td>236</td>
<td>211</td>
<td></td>
</tr>
<tr>
<td>W Deep well</td>
<td>150</td>
<td>201</td>
<td>190</td>
<td>173</td>
<td>134</td>
<td>161</td>
</tr>
</tbody>
</table>

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 ~200°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

Hot Spring and shallow well Na/K temperatures more closely predicted deep temperatures. Silica Appears to have re-equilibrated.
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
Cooler/condenser

Steam/gas samples

Fahlquist and Janik, 1992 USGS OFR-92-211