Using the Geochemistry of Hydrothermal Fluids to Understand Geothermal Systems
Geothermal Exploration and Conceptual Modeling
DEDICATED TO MY FRIEND, MENTOR AND A PIONEER IN USING GEOCHEMISTRY TO UNDERSTAND GEOTHERMAL SYSTEMS

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Using Geochemistry to Understand Hydrothermal Systems

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

- Reservoir temperature estimate (and if the temperature gradient is known depth)
- Fluid type (steam±gas, hot water-NaCl brine or other)
- Possible outflow and upflow zones
- Multiple reservoirs
- Degree of water/rock interaction
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
  - Equilibration with observed mineralogy

- Processes: mixing/groundwater intrusion, conductive heating/cooling, boiling
- Scaling and corrosion
- Possible environmental issues
- Baseline for monitoring reservoir during operation
Water: meteoric (1 or 2?) ± magmatic ± sea water ± connate ± metamorphic

Rock: reservoir and cap

Heat source: volcanic/magmatic ↔ deeply circulating in high heat flow zone

Permeability: fracture, primary porosity, formation enhanced permeability, sealed or open

WHY GEOCHEMISTRY?
IT CAN PROVIDE SOME OF THE BASIC COMPONENTS OF A CONCEPTUAL MODEL OF A GEOTHERMAL SYSTEM
The Geochemistry 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).

\[
\text{temperature}
\]

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

\[
\text{water/rock (permeability)}
\]

\[
time, \text{closed/open}
\]

\[
\text{equilibrium}
\]

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

- The geochemist, if lucky, will get to see a piece of the final water (water\(_f\))
- We try and assess the reservoir conditions that produced the changes from initial to final.
- Need to constrain some of the variables
To understand the chemistry constrain Variables and Conditions

- Build on previous work using analogies
- Develop a Preliminary Conceptual Model based on Geologic setting
  - Volcanic/Magmatic
  - Deeply Circulating Non-volcanic
  - Regional basement rocks
  - Tectonic setting…
- Estimate the Input Variables
  - Water Source (s)
  - Rock-Reservoir and Cap, $\text{rock}_{i,f}$
  - Heat/Temperature
  - Permeability-Water/Rock Interaction
From the geologic setting and previous work, identify likely input parameters and reservoir conditions

*Silicic Magmatic/Intrusive*

- **Reservoir**: granite, pre-volcanic basement cap: volcanic sediments, alteration
- **Heat**: age of intrusion
- **Permeability**: fractures-structure/intrusion
- **Fluids**: meteoric±gas

From Henley et al., 1984, reproduced from Henley and Ellis, 1983
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
Hot Spring Chemistry?
Hydrothermal Reservoir Chemistry? From Moeck, 2013

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

Fluids: meteoric,
Permeability fault controlled
Reservoir rock: brittle basement, cap: fine grained sediments
Heat: deeply circulating water in mod heat flow region: ~60°C/km.
Permeability: ?
Fluids: Meteoric water: hot springs Bicarbonate warm springs

From Moeck, 2013
What kind of hot springs here?
Geochemistry and Structure: Surface Manifestations and Faulting in Geothermal Systems Nicholas C. Davatzes Temple Univ., 2008/12

Association of Hot Springs and Faults
(Worldwide—All rock types & Tectonic Settings)

Not everywhere on the Earth sustains the same heat flow. The variation is largely due to variations in the presence of large, vertically extensive zones of permeability.

Advective heat transport quickly exceeds conductive heat flow even at fluid flow rates of as little as 1 cm/year.

Curewitz and Karson (1997)
Chemistry of a Geothermal System

Initial
- 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
- 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
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\(_2\)O + CO\(_2\)
  or
  \[ +\text{H}_2\text{O} = \text{prehnite} + \text{CO}_2 \]
- Pyrite + pyrrhotite + prehnite + water = epidote + H\(_2\)S
  or pyrite + H\(_2\)O = Fe-Al-silicate + H\(_2\)S
  + dissolution
  + magmatic volatiles
Noncondensible Gas

- **Magmatic Influx**
  - CO$_2$, SO$_2$, H$_2$, HCl, HF and H$_2$O

- **Mineral/Gas reactions**
  - Epidote, prehnite, garnet, clinozoisite, Pyrite, pyrohtite, magnetite, etc. controlling CO$_2$/H$_2$S/H$_2$

- **Gas-gas reactions**
  - CO$_2$ + 4H$_2$ = CH$_4$ + 2H$_2$O

- **Vapor-Liquid Distribution, Distribution Coefficients, B=Cv/Cl**
  - C$_{tot}$=Cv(y) +Cl(1-y)
Reservoir processes transform original geothermal fluids

Even after \( \text{water(s)} + \text{gas} + \text{rock} \) 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
- Influx of hot fluid and/or gas
So how do we solve this puzzle?
Geochemical Exploration Tricks of the Trade (1)

Field Work (assuming surface manifestations)

- Sample surface manifestations carefully and as many as possible
- 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
Sample Everything!
Interpretation

- Use field observations and input from the geologists and geophysicists to understand the geologic setting and the likely reservoir rocks and minerals and recharge areas.
- 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.
Next section

- Address some interpretation methods one by one
- Focus on exploration, defining components of the conceptual model to further understand the system
- Talk about the well chemistry data later—many techniques are the same, just more added and more other data
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\textsubscript{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>$T = 53.500 + 0.11236C - 0.5559 \times 10^{-4} C^2 + 0.1772 \times 10^{-7} C^3 + 88.390 \log C$</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

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

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

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)
Silica and Mixing from Fournier 1991
Cation Geothermometers

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

\[ \text{NaAlSi}_3\text{O}_8 + \text{K}^+ = \text{KAlSi}_3\text{O}_8 + \text{Na}^+ \text{ where } K_{eq} = \left[ \frac{[\text{KAlSi}_3\text{O}_8][\text{Na}^+]}{[\text{NaAlSi}_3\text{O}_8][\text{K}^+]} \right] \]

(activity) of solids = 1, so \( K_{eq} = [\text{Na}^+]/[\text{K}^+] \) and 

\[ \log K_{eq} = \Delta H^o/2.303RT + C \]

change in heat of solution, \( \Delta H^o \), doesn’t change much 0-300°C, [Na\(^+\)]/[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:

\[ t^\circ C = \left\{ \frac{876.3}{\log(\text{Na/K})} \right\} + 0.087750 - 273.15 \]
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 \( \log (Ca^{1/2}/Na) + 2.06 < 0 \), \( \beta = 1/3 \), 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
Trilinear Diagrams from Powell and Cumming, 2010
From Dr. Spycher at last year’s GRC course on Exploration

Example

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

![Graph showing saturation indices and mineral compositions](image-url)

- Measured 181°C

(from Reed & Spycher, 1984)
From Dr. Spycher at last year’s GRC course on Exploration

http://esd.lbl.gov/research/projects/geot/
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
- \( 3\text{FeS}_2 + 2\text{H}_2 = \text{Fe}_3\text{S}_4\text{H}_2\text{O} \)
- \( \text{FeS}_2 + \text{H}_2 = \text{FeS} + \text{H}_2\text{S} \)
- \( \text{CaCO}_3 + \text{K-mica} = \text{CaAl-silicate} + \text{Kspar} + \text{CO}_2 \)
- 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
\( C_{tot} = C_l \ (1-y) + C_0 \ (y) \) or \( C_{tot}/C_l = (1-y) + By \)
### Table 1: Gas geothermometer equations

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
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</tr>
</thead>
<tbody>
<tr>
<td>FT&lt;sup&gt;1&lt;/sup&gt;</td>
<td>$\log P_{CO_2} + 4 \log P_{H_2} - \log P_{CH_4} - 2 \log P_{H_2O} = 10.76 - 9323/T$</td>
<td>Giggenbach (1980)</td>
</tr>
<tr>
<td>NAH&lt;sup&gt;1&lt;/sup&gt;</td>
<td>$\log P_{N_2} + 3 \log P_{H_2} - 2 \log P_{NH_3} = 11.80 - 5400/T$</td>
<td>Giggenbach (1980)</td>
</tr>
<tr>
<td>HSH&lt;sup&gt;1&lt;/sup&gt;</td>
<td>$3 \log P_{H_2S} - \log P_{H_2} = 15.71 - 10141/T$ (py-mag)</td>
<td>Giggenbach (1980)</td>
</tr>
<tr>
<td></td>
<td>$\log P_{H_2S} - \log P_{H_2} = 4.94 - 2874/T$ (py-pyh)</td>
<td>Giggenbach (1980)</td>
</tr>
<tr>
<td>DAP&lt;sup&gt;2&lt;/sup&gt;</td>
<td>$T = \frac{24775}{2 \log (CH_4/CO_2) - 6 \log (H_2/CO_2) - 3 \log (H_2S/CO_2) - 7 \log P_{CO_2} + 36.05}$</td>
<td>Giggenbach (1980)</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;S&lt;sup&gt;3&lt;/sup&gt;</td>
<td>$\log P_{H_2S} = 6.05 - 3990/T$</td>
<td>Giggenbach (1980)</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;4&lt;/sup&gt;</td>
<td>$\log P_{CO_2} = -8.366 + 0.0168T$</td>
<td>Giggenbach (1980)</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;-H&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;5&lt;/sup&gt;</td>
<td>$\log P_{CO_2} + 2 \log P_{H_2} = 16.298 - 8982/T$</td>
<td>Giggenbach (1980)</td>
</tr>
<tr>
<td>CO&lt;sub&gt;6&lt;/sub&gt;</td>
<td>$\log \left( \frac{P_{CO_2}}{P_{CO_2}} \right) - \log \left( \frac{P_{H_2}/P_{H_2O}}{} \right) = 2.485 - 2248/T$</td>
<td>Giggenbach (1980)</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O&lt;sup&gt;1&lt;/sup&gt;</td>
<td>$\log P_{H_2O} = 5.51 - 2048/T$</td>
<td>Giggenbach (1980)</td>
</tr>
<tr>
<td>z factor&lt;sup&gt;7&lt;/sup&gt;</td>
<td>$\log z = \log P_{H_2O} - 3.041 + 2118/T - \log T$</td>
<td>Giggenbach (1980)</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
Chemical geothermometers: equilibrium controlling CO₂ concentration in fluids at Reykjaness, SW Iceland

\[
\text{CO}_2,_{\text{aq}} \text{ (ppm)} \\
\begin{array}{c}
\text{CO}_2 \text{ buffer reaction} \\
2 \text{ clinozoisite} + 2 \text{ calcite} + 3 \text{ quartz} + 2 \text{ H}_2\text{O} \\
= 3 \text{ prehnite} + 2 \text{ CO}_2
\end{array}
\]

\[
a_{\text{czo}} = 1 \\
a_{\text{pre}} = 1
\]

\[
a_{\text{czo}} = 0.17 \\
a_{\text{pre}} = 0.80
\]
Helium Isotopes

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

- Source water: meteoric, sea water, metamorphic
- Water/rock interaction
- Boiling-fractionation between liq and vapor
  - Single step
  - Multi-step
  - Continuous
- Evaporation
Origin of geothermal fluids: mostly meteoric + O-18 shift from water/rock interaction

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).
Basic Processes Affecting Oxygen and Hydrogen Isotopes in Geothermal Water

- Equilibrium fractionation of water vapor (steam) with respect to water
- In geothermal waters, \( ^{18}O \) increases by \(~0\) to \(>15\) o/oo due to rock-water isotope exchange. Deuterium changes very little, because rocks contain little H.
Oxygen-18 v Deuterium in a producing geothermal system

Fractionation makes tracing fluids with isotopes difficult in active geothermal systems.
Hot spring temperature << Reservoir temperatures

Hot spring temperatures are maximum of 100°C (or less at high elevation), how did they cool on the way from the reservoir?

- Conductive
  - Low flow
  - Long flow path
- Boiling
- Mixing with cold meteoric water (s)
Boiling

The following equations constrain distribution of deep (tot) fluid components between liquid, $l$, and vapor, $v$, on boiling:

- $H_{tot} = H_l (1-y) + H_v (y)$
- $C_{tot} = C_l (1-y) + C_v (y)$

Used to calculate reservoir fluids from separated steam and brine samples, and to understand chemistry of boiling springs and fumaroles, understand boiling in the system.
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
Unmixing mixed fluids
Data Integration/Modeling

- “mature” vs “immature”
- Minerals in equilibrium with geothermal fluids
- Partitioning based on boiling
- Speciation and activity coefficients
- WATCH, iTough2, etc.

Requires extensive and thorough analysis
Depends on thermodynamic data
What if there are no surface manifestations?

- Call the geophysicist?
- Soil Gas?
- Used extensively in mineral exploration
  - Locating leakages from blind geothermal systems
    - Blind systems have no surface manifestations, but may leak gases
  - Mapping structure in geothermal systems
    - Gasses will leak in zones of permeability
    - faults

Success rate?
- Has identified fault leakage and distinguished between deep magmatic gas in a few studies
- Requires relatively simple structures not overwhelmed by organic material
Possible Analytes

- Carbon Dioxide (CO$_2$)
- Radon (Rn)
- Helium (He)
- Mercury (Hg)
- Nitrogen (N$_2$), Oxygen (O$_2$)
- Isotopes (C, He, Rn)
**CO₂**
- In situ, flux measurements
- Isotopes can be used to differentiate between geothermal and biogenic

From Chiodini et al (2008)
Statistical tools

- Delineating background from anomalous can be challenging.
- Cumulative probability plots can be used to identify populations (Sinclair 1986)

Chiodini et al 2008
Soil diffuse CO$_2$ flux at Reykjanes, SW Iceland

Results of soil diffuse degassing survey were used to site a directionally drilled well.

The well, RN-23, is now the best, by far, in the area.
OK, so now we can say something about the fluids and under what conditions were they generated.

What does this tell us about the geothermal system?
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.

26 September 2014 GRC Workshop
GEOLOGICA INC.
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
Hot springs too immature for application of Na/K waters?
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
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<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>
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<tr>
<td>Shallow well</td>
<td>185</td>
<td>139</td>
<td>62</td>
<td>232</td>
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<td>108</td>
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<tr>
<td>Shallow well</td>
<td>147</td>
<td>180</td>
<td>-61</td>
<td>230</td>
<td>204</td>
<td>105</td>
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<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>
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<tr>
<td>Hot Spring</td>
<td>147</td>
<td>148</td>
<td>-175</td>
<td>203</td>
<td>170</td>
<td>85</td>
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<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.
If a geothermal system sufficient for power generation appears likely, a well (or 2 or 3) will be drilled and tested

- What can the geochemist learn from these wells?
- Physical conditions and fluid chemistry from one or more feed zones
- Lithology and (maybe) alteration mineralogy
Sampling
Sample Analysis and Evaluation

2-phase sampling requires careful separation and documentation of separator conditions

- **Brine**
  - 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

- **Reservoir Properties from Geochemical Evaluation**
  - Temp, mixing, fluid influx, boiling

- **Operational/Design Issues:**
  - Scaling and corrosion
  - Steam Purity

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

- **Reservoir Properties**

- **Noncondensible Gas Loading**

- **Toxic Emissions** - H$_2$S, B,
Sample Analysis and Evaluation

2-phase sampling requires careful separation and documentation of separator conditions

- **Brine**
  - 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

- **Reservoir Properties from Geochemical Evaluation**
  - Temp, mixing, fluid influx, boiling

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  - Scaling and corrosion
  - Steam Purity

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

- **Reservoir Properties**
- **Noncondensible Gas Loading**
- **Toxic Emissions-H$_2$S, B**
Interpretation of well test data

- One or more reservoir fluids? Potential for coldwater influx? Lateral variations?
- Boiling in the reservoir? Excess steam
- Temperatures relative to downhole measured temperatures?
- Gas loading, scaling, corrosion for project design
- Baseline for reservoir monitoring
Summary: Inputs to conceptual models from exploration geochemistry

- Temperature
- Water
- Heat
- Permeability
Sampling during Flow Testing

- Sampling separator
- Flow line
- Cooler/condenser
Sample Set-up
Fahlquist & Janik, 1992
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
Brine + steam samples

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
Sample Analysis for Laboratory Analysis

2-phase sampling requires careful separation and documentation of separator conditions

- **Brine**
  - 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
  - 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
Field Measurements

- Brine
- pH
- Conductivity
- Sometimes, alkalinity

- Steam
- G/S
- Condensate pH and conductivity
Data Interpretation

- $H_{tot} = H_l (1-y) + H_v (y)$
- $C_{tot} = C_l (1-y) + C_v (y)$
- $y = (H_{tot} - H_l)/(H_v - H_l)$
- $H_{tot}$ = 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):
$C_{tot} = C_v \times y$

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

For semi-volatile components where $B = C_v/C_l$
$C_l = C_{tot}/((1-y) + By)$ 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 \(C_{L\text{res}}\) is:

\[
C_L \times \{(1 - Y_{\text{TD}}) / (1 - Y_{\text{exs}})\} = C_{L\text{res}}.
\]

For non-excess steam or just brine wells,

\[
Y_{\text{TD}} = H_{\text{TD}} - H_{\text{Lsep}} / H_{\text{vsep}} - H_{\text{Lsep}}
\]

And the correction is:

\[
C_L \times (1 - Y_{\text{TD}}) = C_{L\text{res}}.
\]

(\text{equations become the same as } Y_{\text{exs}} \text{ goes to 0.})
So now that we have reservoir chemistry

- Water type?
  - Na, K, Ca, Mg? Cl, HCO$_3$, SO$_4$, pH, etc
- Geothermometers on total flow
- Silica, cation, gas, isotope geothermometers
- Mineral saturation relative to observed mineraology
- Changes with production rates
- Comparison with other wells
- Gas Pressures
- Scaling potential

26 September 2014 GRC Workshop
Weighted average Total Fluid: As delivered to the plant. To calculate steam and brine, use reverse of calculation to combine samples, Calculate Cv and Cl from Ctot

<table>
<thead>
<tr>
<th>Substance</th>
<th>Weighted Average</th>
<th>Corrected to Reservoir (mg/kg)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>555.9</td>
<td>351897</td>
</tr>
<tr>
<td>K</td>
<td>78.7</td>
<td>117</td>
</tr>
<tr>
<td>Ca</td>
<td>2.53</td>
<td>386</td>
</tr>
<tr>
<td>Mg</td>
<td>0.05</td>
<td>630</td>
</tr>
<tr>
<td>Fe</td>
<td>0.02</td>
<td>4.71</td>
</tr>
<tr>
<td>Al</td>
<td>0.34</td>
<td>9.84</td>
</tr>
<tr>
<td>SiO2</td>
<td>398.7</td>
<td>8.94</td>
</tr>
<tr>
<td>B</td>
<td>103.9</td>
<td>40.93</td>
</tr>
<tr>
<td>Li</td>
<td>6.73</td>
<td>0.01</td>
</tr>
<tr>
<td>Cl</td>
<td>154.38</td>
<td>92</td>
</tr>
<tr>
<td>CO2</td>
<td>351897</td>
<td></td>
</tr>
<tr>
<td>HCO3</td>
<td>1351.98</td>
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<tr>
<td>H2S</td>
<td>117</td>
<td></td>
</tr>
<tr>
<td>NH4</td>
<td>21.53</td>
<td></td>
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<tr>
<td>N2</td>
<td>386</td>
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<td>CH4</td>
<td>630</td>
<td></td>
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<tr>
<td>Cl</td>
<td>154.38</td>
<td></td>
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<tr>
<td>H2</td>
<td>8.94</td>
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<tr>
<td>SO4</td>
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<tr>
<td>C2H6</td>
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</tr>
<tr>
<td>C3H8</td>
<td>0.09</td>
<td></td>
</tr>
</tbody>
</table>

*Values corrected to reservoir conditions
Partial Equilibration

Immature Waters

Granite
Sandstone
Diorite Basalt
Ultramafic
Limestone
Seawater
Deep well

10 K

Na

1000 Mg^0.5
Is one of the wells on the edge of the field mixed with cooler groundwater or does it have drilling?
Measured vs Geothermometer Temperatures
Are the temperatures higher than measured?
Is fluid from below the bottom of the well?

5 deep wells, Measured versus geothermometer temperatures

- Quartz
- Na/K Truesdell
- Na/K Fournier
- Chalcedony
- Linear (Quartz)
Silica Scaling Potential
# Total Noncondensible gas

<table>
<thead>
<tr>
<th>WHP (bara)</th>
<th>T$_{sep}$ (°C)</th>
<th>P$_{sep}$ (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$_2$O (kg/kg)</th>
<th>Well Average g/H$_2$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>
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<td>0.036</td>
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<td>10.9</td>
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<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>
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<tr>
<td>45.9</td>
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<td>2.8</td>
<td>193</td>
<td>820.8</td>
<td>584</td>
<td>2731.9</td>
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<td>0.1390</td>
<td>0.340</td>
<td>0.0375</td>
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<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>0.036</td>
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<tr>
<td>6.2</td>
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<td>4.5</td>
<td>188.5</td>
<td>800.8</td>
<td>632.2</td>
<td>2745.9</td>
<td>0.08</td>
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<td>37.0</td>
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<td>198</td>
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<td>2741.8</td>
<td>0.12</td>
<td>0.084</td>
<td>0.21</td>
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<tr>
<td>28.1</td>
<td>159.6</td>
<td>7.9</td>
<td>198</td>
<td>843</td>
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<td>2756</td>
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<td>0.066</td>
<td>0.16</td>
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<td>40.0</td>
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<td>4.30</td>
<td>202.5</td>
<td>863.6</td>
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<td>2744.7</td>
<td>0.11</td>
<td>0.103</td>
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<td>2.88</td>
<td>187.2</td>
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<td>2731.1</td>
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<td>0.112</td>
<td>0.27</td>
<td>0.027</td>
<td>0.027</td>
</tr>
<tr>
<td>12</td>
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<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>
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<td>35.9</td>
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<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>

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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, $P_{\text{tot,meas or sim}}$

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

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

Where $K_H$ = Henry’s law constant at the reservoir temperature and $X_{\text{gas}}$ 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.
## Reservoir Parameters

<table>
<thead>
<tr>
<th></th>
<th>WELL X</th>
<th>WELL Y</th>
<th>Well Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoir Temperature (°C)</td>
<td>219</td>
<td>242</td>
<td>237</td>
</tr>
<tr>
<td>Noncondensible Gas (NCG) kg/kg</td>
<td>0.024</td>
<td>0.0415</td>
<td>0.03</td>
</tr>
<tr>
<td>Mole Fraction NCG assuming 100% CO2, Xg</td>
<td>0.0098</td>
<td>0.017</td>
<td>0.0123</td>
</tr>
<tr>
<td>Henry’s Law Constant, Kh</td>
<td>5968</td>
<td>5493</td>
<td>5563</td>
</tr>
<tr>
<td>Pgas (bar)</td>
<td>58.6</td>
<td>93.4</td>
<td>68.3</td>
</tr>
<tr>
<td>Pliq (bar)</td>
<td>23.2</td>
<td>33.5</td>
<td>31.7</td>
</tr>
<tr>
<td>Ptotal ,BP(bar)</td>
<td>81.8</td>
<td>126.9</td>
<td>100.0</td>
</tr>
<tr>
<td>Depth of Ptotal@low flow survey measurements (m)</td>
<td>980</td>
<td>1790</td>
<td>1100</td>
</tr>
<tr>
<td>Low (survey) flow (tonnes per hour, tph)</td>
<td>200</td>
<td>166</td>
<td>145</td>
</tr>
<tr>
<td>Casing Depth (m)</td>
<td>1550</td>
<td>1750</td>
<td>1080</td>
</tr>
<tr>
<td>Depth of major entry (m)</td>
<td>1740</td>
<td>2300</td>
<td>1700</td>
</tr>
</tbody>
</table>
Well Y Calculated Gas Breakout Pressure Compared to Measured Dynamic Total Pressure VS Depth

At 166.3 tph, NCG=0.019 (mol fraction), Gas Breakout pressure of 127 bar occurs at 1787m bgs
Wellbore Simulation of Gas Breakout Pressure

- A steady-flow wellbore model (Garg et al., 2004) was used to model the dynamic pressure and temperature profiles in wells X and Y.
- The dynamic pressure and temperature profiles were obtained at relatively low discharge rates.
- The constrained wellbore models were then employed to forecast the response of the wells under various discharge rates.
Well Y

<table>
<thead>
<tr>
<th>Discharge rate (tph)</th>
<th>Wellhead pressure (bars)</th>
<th>Wellhead temperature (°C)</th>
<th>Bubble point depth (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>144</td>
<td>33.39</td>
<td>218.0</td>
<td>1880</td>
</tr>
<tr>
<td>216</td>
<td>29.37</td>
<td>215.5</td>
<td>2018</td>
</tr>
<tr>
<td>288</td>
<td>25.21</td>
<td>210.8</td>
<td>2156</td>
</tr>
<tr>
<td>360</td>
<td>20.48</td>
<td>203.3</td>
<td>2282</td>
</tr>
</tbody>
</table>
Depth to Casing Shoe and Feedzone
Bubble Point vs Mass Flow Well Y

- Simulated Well Y
- Well Y Estimated with Dynamic Survey

casing shoe
Feedzone
Thank you

Please e-mail me at jhaizlip@geologica.net if you would like a copy of this presentation