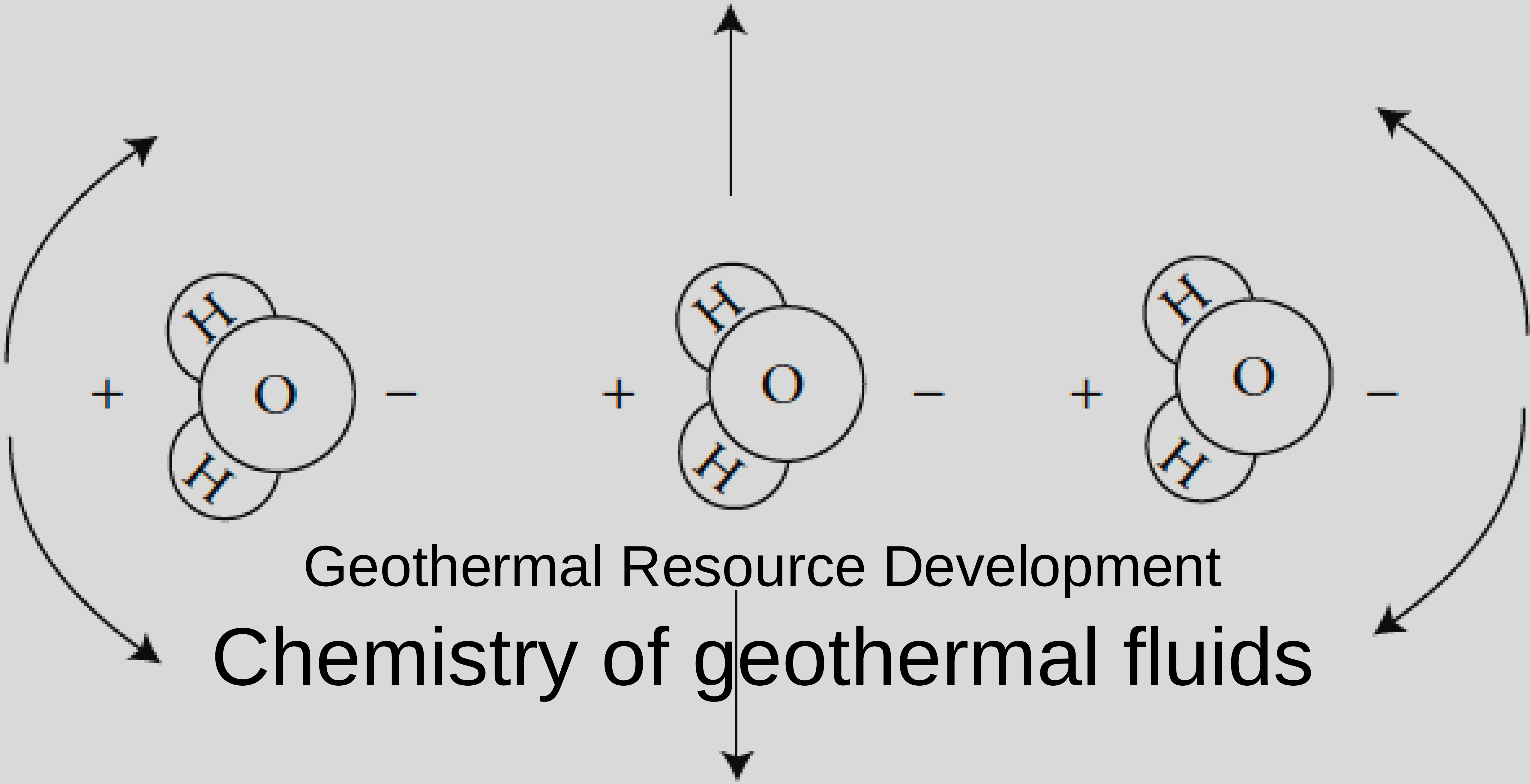


Geothermal Resource Development

Chemistry of geothermal fluids

Why we care about geochemistry

The composition of geothermal waters gives us important information about:

- The characteristics of a reservoir including, temperature, mineralogy, and flow history
- Potential impacts on operation of machinery in the geothermal plant

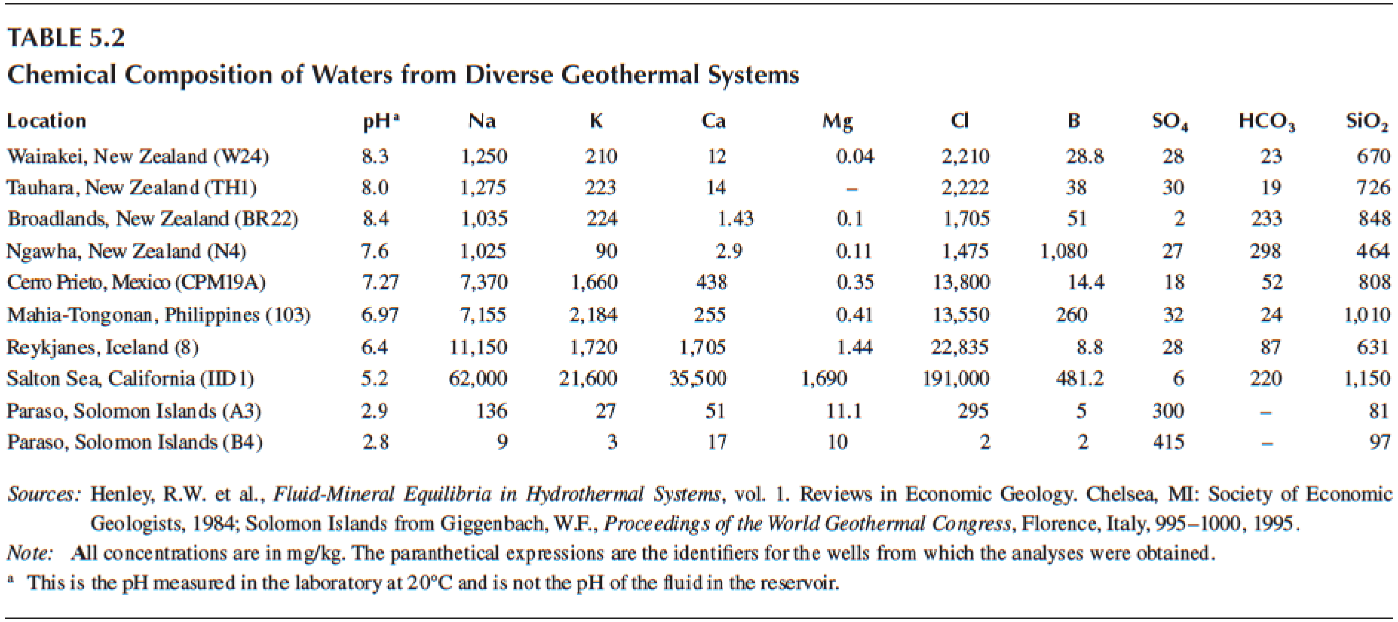


TABLE 5.2

Chemical Composition of Waters from Diverse Geothermal Systems

Location	pH[a]	Na	K	Ca	Mg	Cl	B	SO_4	HCO_3	SiO_2
Wairakei, New Zealand (W24)	8.3	1,250	210	12	0.04	2,210	28.8	28	23	670
Tauhara, New Zealand (TH1)	8.0	1,275	223	14	–	2,222	38	30	19	726
Broadlands, New Zealand (BR22)	8.4	1,035	224	1.43	0.1	1,705	51	2	233	848
Ngawha, New Zealand (N4)	7.6	1,025	90	2.9	0.11	1,475	1,080	27	298	464
Cerro Prieto, Mexico (CPM19A)	7.27	7,370	1,660	438	0.35	13,800	14.4	18	52	808
Mahia-Tongonan, Philippines (103)	6.97	7,155	2,184	255	0.41	13,550	260	32	24	1,010
Reykjanes, Iceland (8)	6.4	11,150	1,720	1,705	1.44	22,835	8.8	28	87	631
Salton Sea, California (IID1)	5.2	62,000	21,600	35,500	1,690	191,000	481.2	6	220	1,150
Paraso, Solomon Islands (A3)	2.9	136	27	51	11.1	295	5	300	–	81
Paraso, Solomon Islands (B4)	2.8	9	3	17	10	2	2	415	–	97

Sources: Henley, R.W. et al., *Fluid-Mineral Equilibria in Hydrothermal Systems*, vol. 1. Reviews in Economic Geology. Chelsea, MI: Society of Economic Geologists, 1984; Solomon Islands from Giggenbach, W.F., *Proceedings of the World Geothermal Congress*, Florence, Italy, 995–1000, 1995.

Note: All concentrations are in mg/kg. The paranthetical expressions are the identifiers for the wells from which the analyses were obtained.

[a] This is the pH measured in the laboratory at 20°C and is not the pH of the fluid in the reservoir.

Source: Glassley, W. E., *Geothermal Energy*

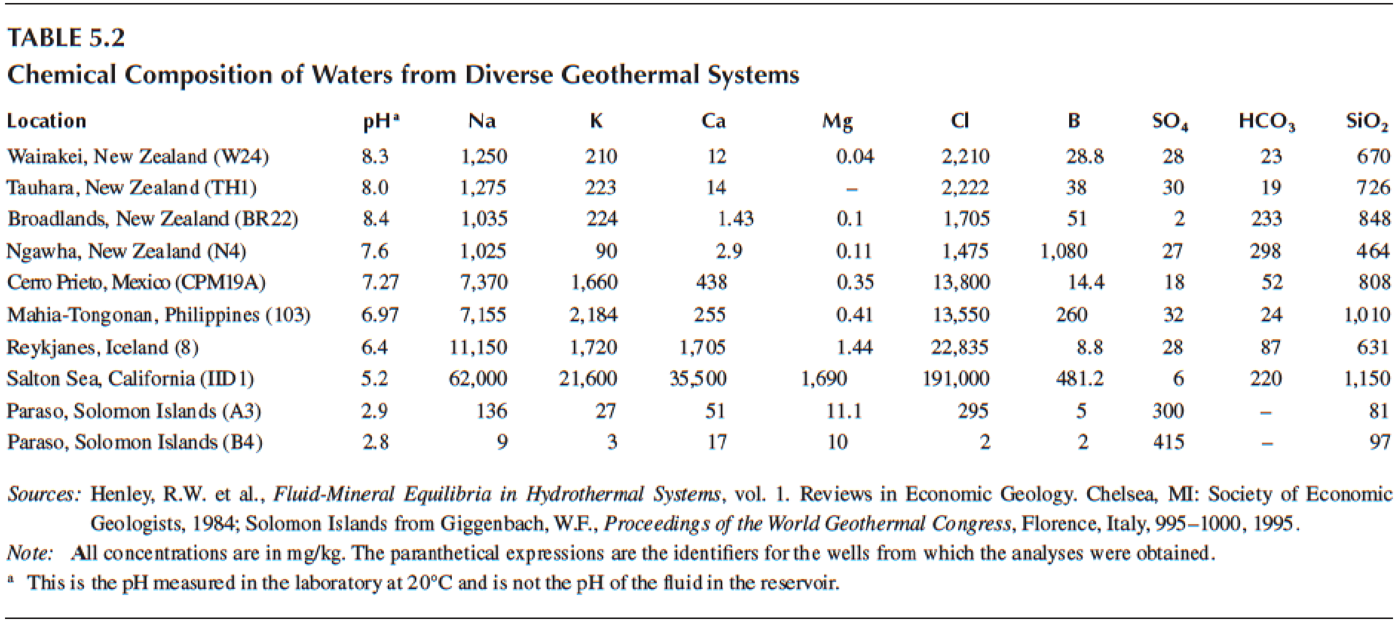
Why we care about geochemistry

The composition of geothermal waters gives us important information about:

- The characteristics of a reservoir including, temperature, mineralogy, history
- Potential impacts on operation of machinery in the geothermal plant

Geothermal waters have a broad range of chemical compositions:

- Very dilute: ppm, by weight, of dissolved constituents
- Very concentrated: 10s of %, by weight, of dissolved consisteunts



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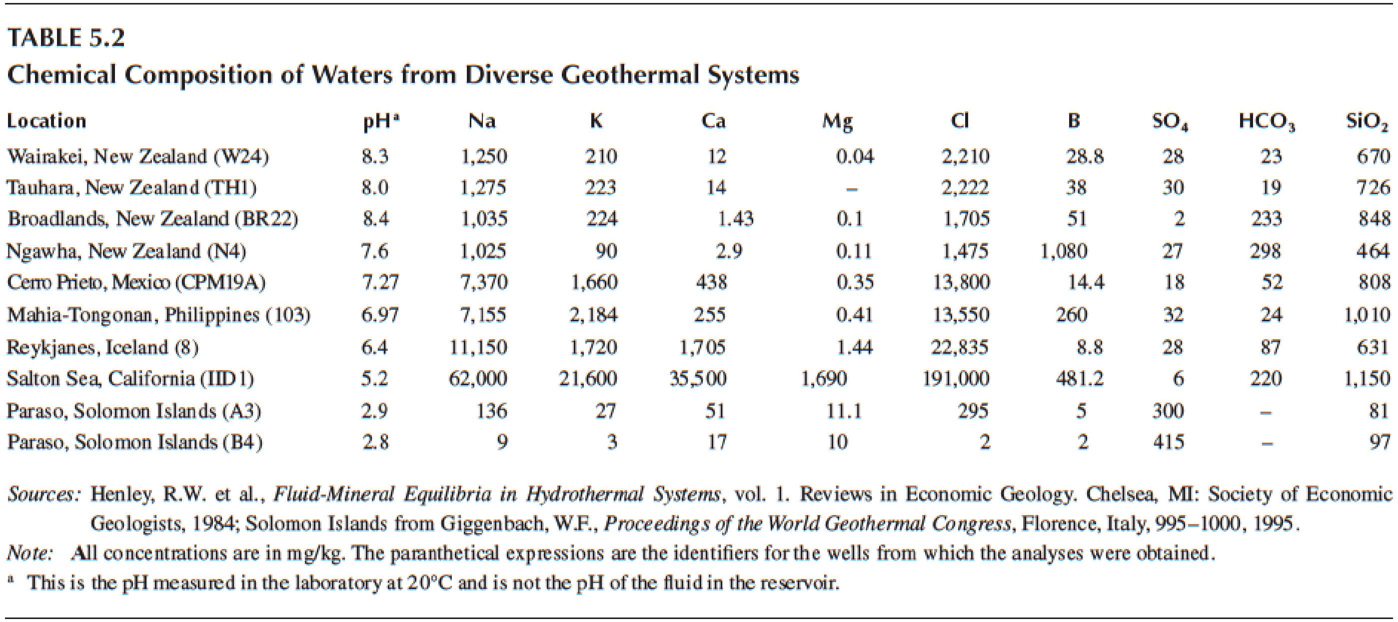
Why we care about geochemistry

Major questions:

- What are the basic chemical processes in geothermal systems?
- How do basic chemical analyses provide us with information about the geothermal resource?



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Source: Glassley, W. E., *Geothermal Energy*

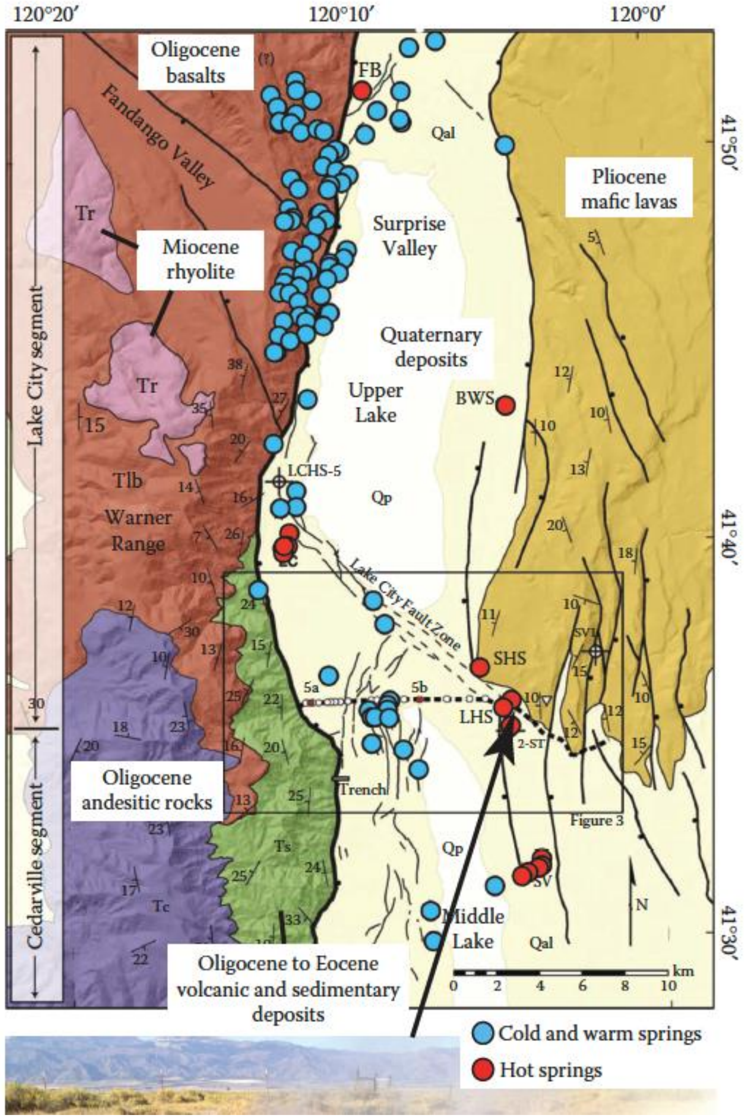
Why we care about geochemistry

Water geochemisty matters for high temperature resources:

- Waters used for direct use (e.g., heating, ventilation, air conditioning) only need a few 10s of °C for these applications: these small temperature drops are unlikley to significantly effect fluid composition
- High temerature fluids are associated with magma bodies and/or igneous activity
- **Temperatures >120°C results in extensive rock-water interactions, which influences fluid chemistry**

Surface water can act as tracers for subsurface resources:

- Chemical markers might point to heat anomalies
- Spatial distribution of elements/isotopes/compounds



Source: Glassley, W. E., *Geothermal Energy*

Topics covered today...

1. Water as a chemical agent
2. Components and chemical systems
3. Saturation and the law of mass action
4. Kinetics of geothermal reactions
5. Gases in geothermal fluids
6. Fluid flow and mixing in natural systems

Water as a chemical agent

Water as a chemical agent

Water molecules are polar.

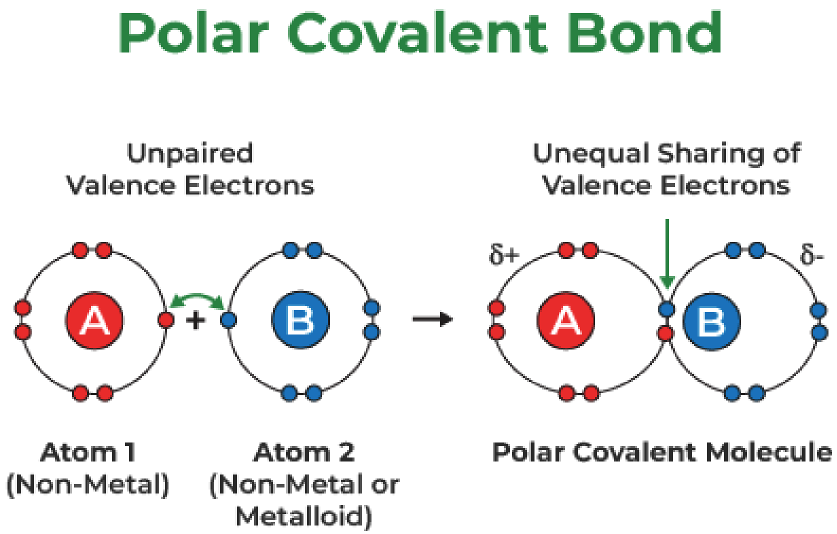
Polarity is due to the orientation of H atoms, which are covalently bound to a central O atom.

Covalent (molecular) bonds:

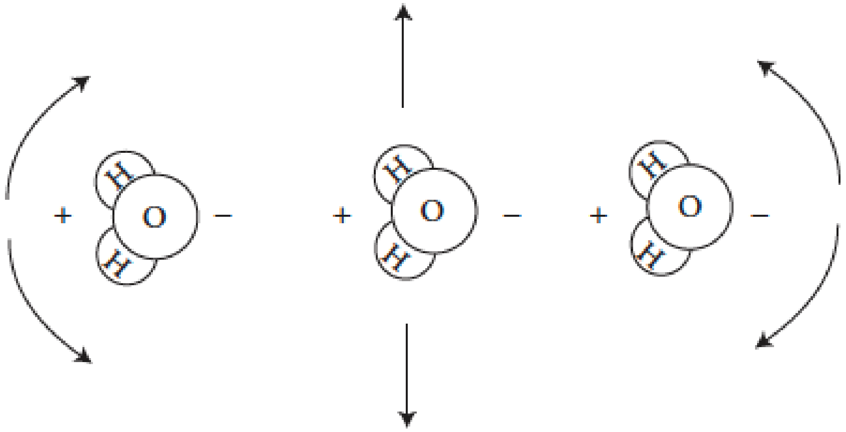
- Atoms share electrons to form electron pairs between them, thereby filling both valence shells.

Polar covalent bonds:

- Electronegativity between atoms differs, resulting in unequal electron sharing.
- Electrons are drawn to the more electronegative atoms, so that they become closer to that atom.
- **In water, O is more electronegative than H, and the water molecule inherits polarity.**



Source: geeksforgeeks.org



Source: Glassley, W. E., *Geothermal Energy*

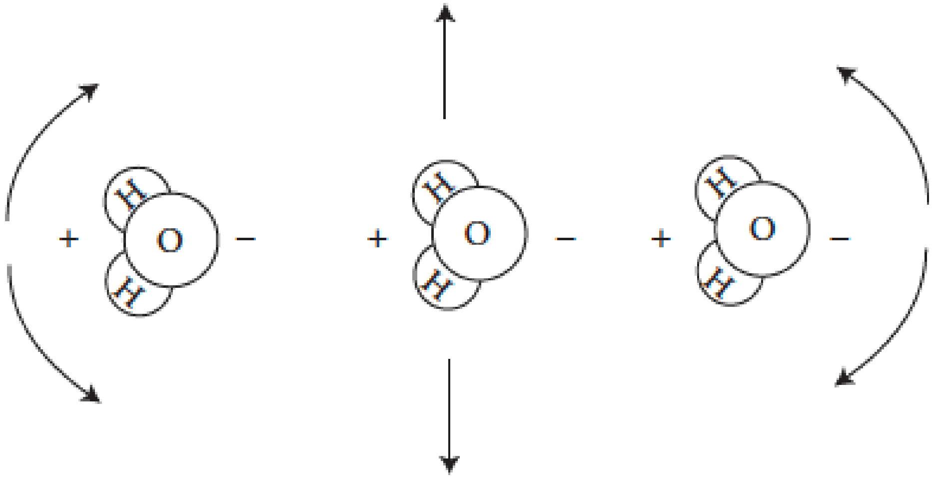
Water as a chemical agent

Compounds – including **minerals** – have exposed atoms and associated electrical charges on the surface.

This means that minerals and water molecules can interact.

Water is a solvent:

- It can dissolve consituents (solutes) and carry them as dissolved load.
- Polarity has a strong influence on how internal energy of water changes with temperature: influences solubility.

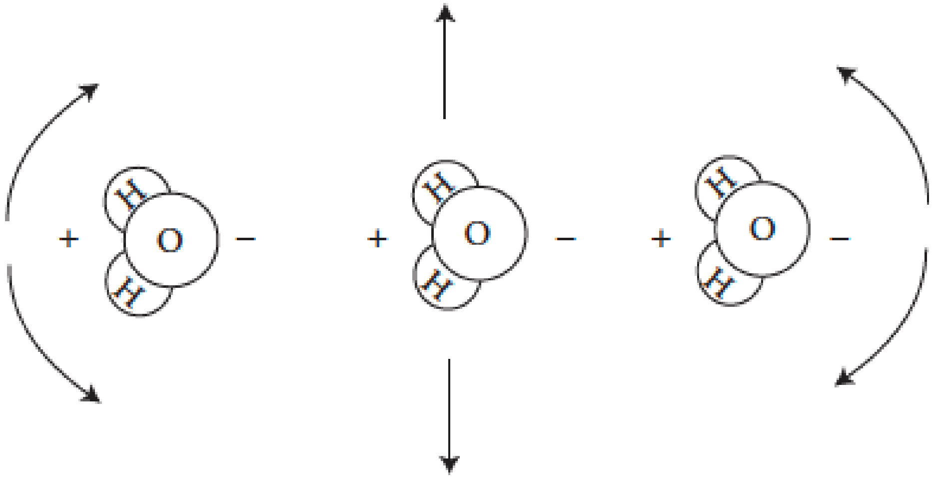


Source: Glassley, W. E., *Geothermal Energy*

Water as a chemical agent

Water molecules are polar **but water, itself, is not electrically charged.**

Therefore, the dissolved load must be electrically balanced.



Source: Glassley, W. E., *Geothermal Energy*

Components and chemical systems

Components and chemical systems

Chemical components:

- The minimum number of chemical constitutents needed to fully describe the collection of substances in a **system**

Phases:

- Entities that make up a system: minerals, gases, liquids

An example chemical system:

- The three-phase silica (SiO_2) system containing **quartz, tridymite, chalcedony**
- Each of these ***polymorphs*** is a phase because it has a different crystal stucture, even though the chemical composition is the same.

Source: mindat.org

Components and chemical systems

The **quartz-tridymite-chalcedony** system can be completely described the following chemical reactions:

Quartz ⟺ Tridymite

Tridymite ⟺ Chalcedony

Chalcedony ⟺ Quartz

2 ways of defining the system components:

1. 2 component system: Si and O
   - Useful for tracking individual elements and isotopes
   - Dissociation of the minerals
   - Isotopic behaviour
2. 1 component system: SiO_2
   - useful for understanding the behaviour of the mineral


quartz


tridymite


chalcedony

Source: mindat.org

Chemical potential and Gibbs Energy

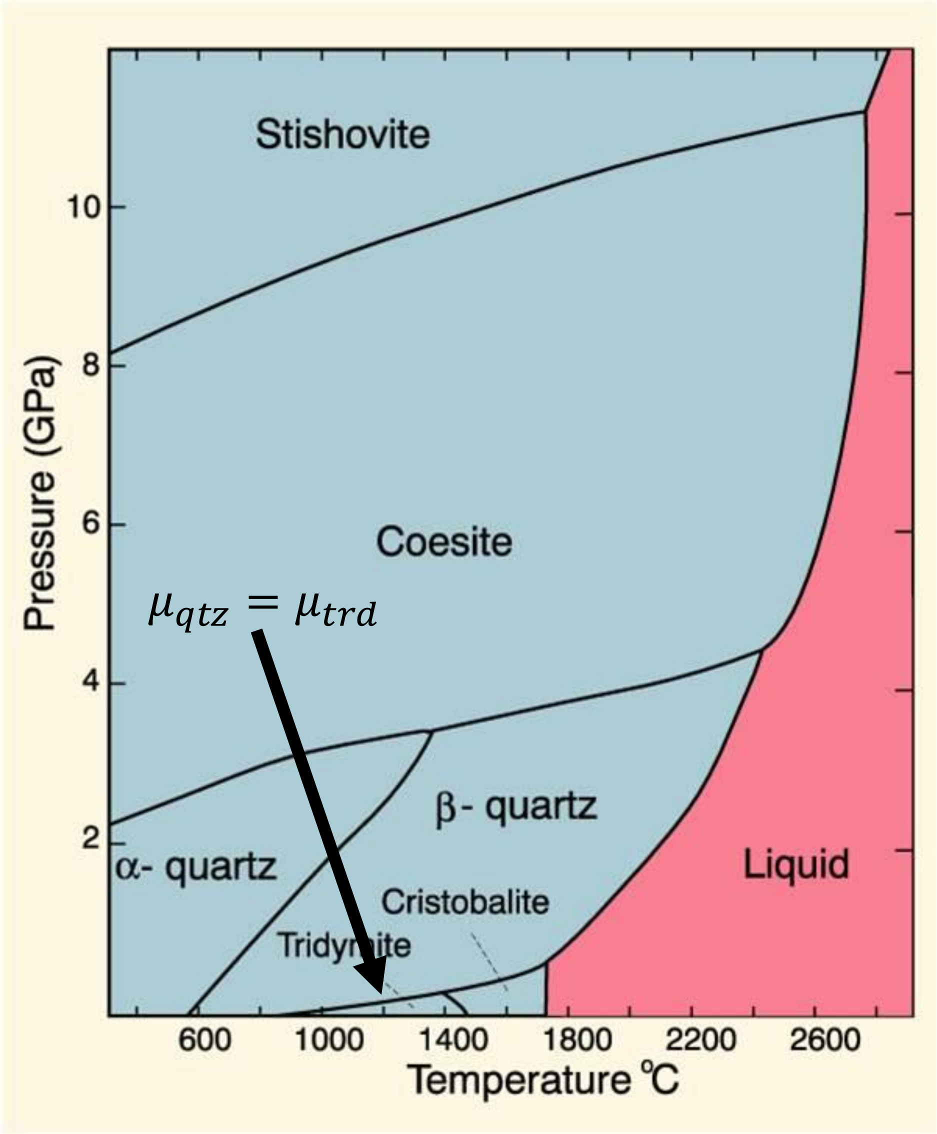
Once we have identified the components of a system:

- Describe which minerals or collections of minerals are stable phases under a given set of P-T conditions
- Each component has a ***chemical potential:*** $\boldsymbol{\mu}\ \left[\frac{\boldsymbol{J}}{\boldsymbol{mole}}\right]$

Chemical potential, $\boldsymbol{\mu}$:

- Energy that is absorbed or released during chemical reaction or phase transition.
- **The most stable energy state is the lowest.**

e.g., the most stable SiO_2 polymorph will be the one with the lowest chemical potential at any given P-T condition



Source: https://serc.carleton.edu/details/images/8743.html

Chemical potential and Gibbs Energy

SiO2 is a simple system!

What do we do when the system becomes increasingly complex (i.e., contains lots of components)?

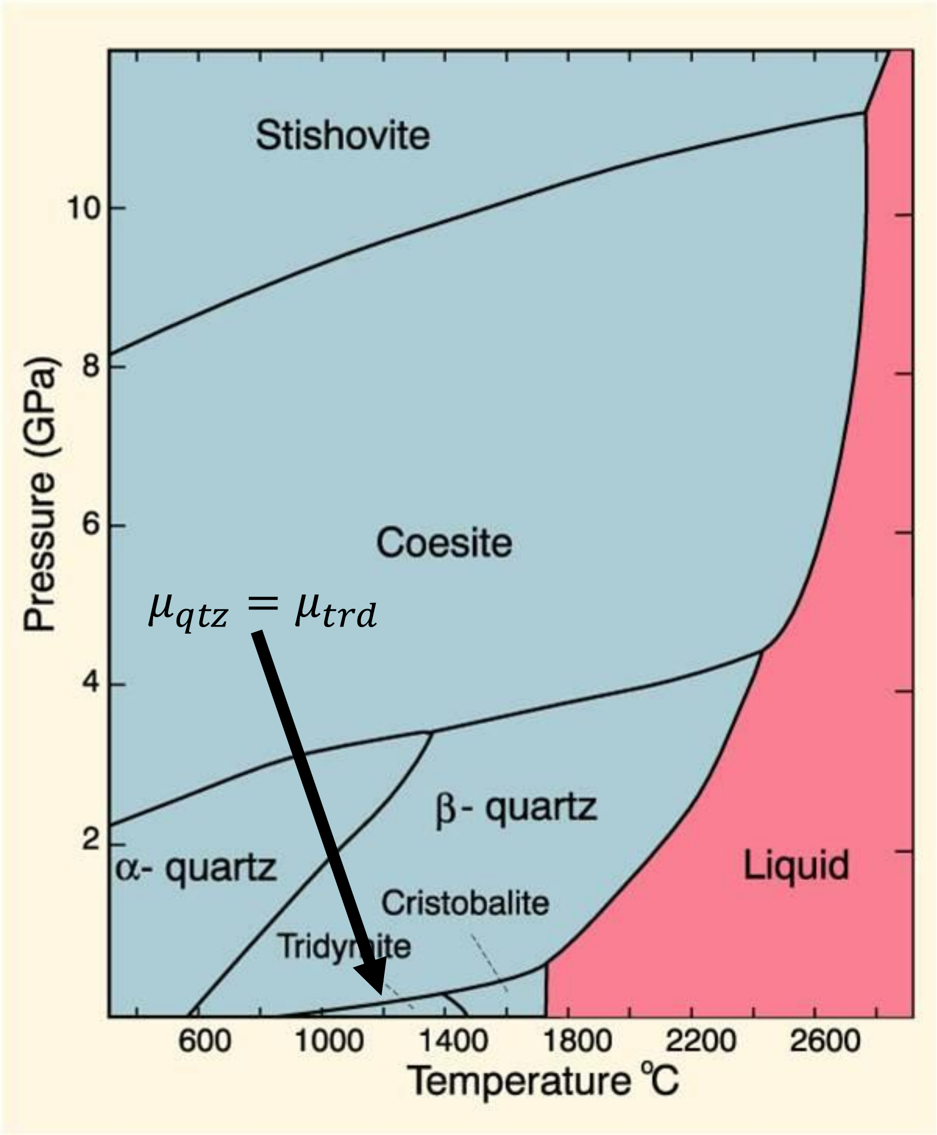
It’s too complicated to keep track of every individual component in complex systems.

So, we use the Gibbs energy function:

$$\Delta G_j = \sum \mu_j^i$$

Where ΔG_j is the Gibbs energy function of phase j

μ_j^i is the chemical potential of component i in phase j



$\mu_{qtz} = \mu_{trd}$

Source: https://serc.carleton.edu/details/images/8743.html

Chemical potential and Gibbs Energy

So, we use the Gibbs energy function:

$$\Delta G_j = \sum \mu_j^i$$

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Remember:

The Gibbs function expresses the changes in enthalpy, entropy, and pressure-volume work that occur when a phase is affected by evolving physical (P-T-x) conditions.

Chemical potential and Gibbs Energy

So, we use the Gibbs energy function:

$$\Delta G_j = \sum \mu_j^i$$

Where ΔG_j is the Gibbs energy function of phase j

μ_j^i is the chemical potential of component i in phase j

If $\Delta\mu_j^i$ is sufficiently large to make a phase unstable – relative to some other arrangement of the components – then a reaction will occur, forming a new assemblage of phases.

Therefore:

$$\Delta G_{rx} = \sum \Delta G_j,$$

Where ΔG_{rx} is the Gibbs energy function of the reaction, at some specificed P-T.

Chemical potential and Gibbs Energy

So, we use the Gibbs energy function:

$$\Delta G_j = \sum \mu_j^i$$

Where ΔG_j is the Gibbs energy function of phase j

μ_j^i is the chemical potential of component i in phase j

How do we calculate the chemical potential - $\boldsymbol{\mu_i^{T,P,x}}$ - of any component in a phase at any P-T-x condition?

Activity, a

The activity of a component is a thermodynamic measure of the difference between the chemical potential of that component from one set of conditions (e.g., pressure, temperature, or other variables of state) to another:

$$\mu_i^{T,P,x} = \mu_i^0 + R \times T \times \ln a_i$$

Where:

$\mu_i^{T,P,x}$ is the chemical potential of component i at some P, T, and composition (x) of the phase being considered

μ_i^0 is the chemical potential of component i at some standard state

Activity, a

The chemical potential of a component at any P-T-x conditions is:

$$\mu_i^{T,P,x} = \mu_i^0 + R \times T \times \ln a_i$$

The energy needed for a reaction to occur is given by:

$$\Delta G_j = \sum \mu_j^i = \sum \mu_j^{iT,P,x} = \sum [\mu_j^{i0} + R \times T \times \ln a_j^i]$$

and

$$\Delta G_{rx} = \sum \Delta G_j$$

These relationships allow us to determine the chemical state of a system from the chemical compositions of the phases in the system.

Gibbs function and activity

Why is this important for geothermal systems?

- If we know the how P-T conditions change with respect to a reference frame for any system, we can predict the chemical evolution of that system.
- If we know the chemical composition of phases in a system, then we can extract information about the P and T conditions within the system.

The latter point, especially, is critical for geothermal exploration!

Saturation and the Law of Mass Action

Question

Consider a pot of boiling water.

Once the water has boiled, the pot is removed and placed in a perfectly insulated location, so that it does not lose nor gain heat.

Pour in 10g of NaCl and 10g of SiO_2, each with a grain size of 10μm.

What happens to the water composition after:

- 10 minutes?
- 1 hour?
- 1 day?
- 1 year?

Question

Question 1:

How much NaCl and SiO2 will dissolve into the water?

Or: What is the equilibrium state of the system?

Question 2:

How long does it take for these amounts of NaCl and SiO_2 to dissolve?

Or: How long does it take for the system to reach its equilibrium state?

Equilibrium constants and the Law of Mass Action

Dissolution of halite (NaCl, salt):

$$\mathrm{NaCl} \leftrightarrow \mathrm{Na}^{+} + \mathrm{Cl}^{-}$$

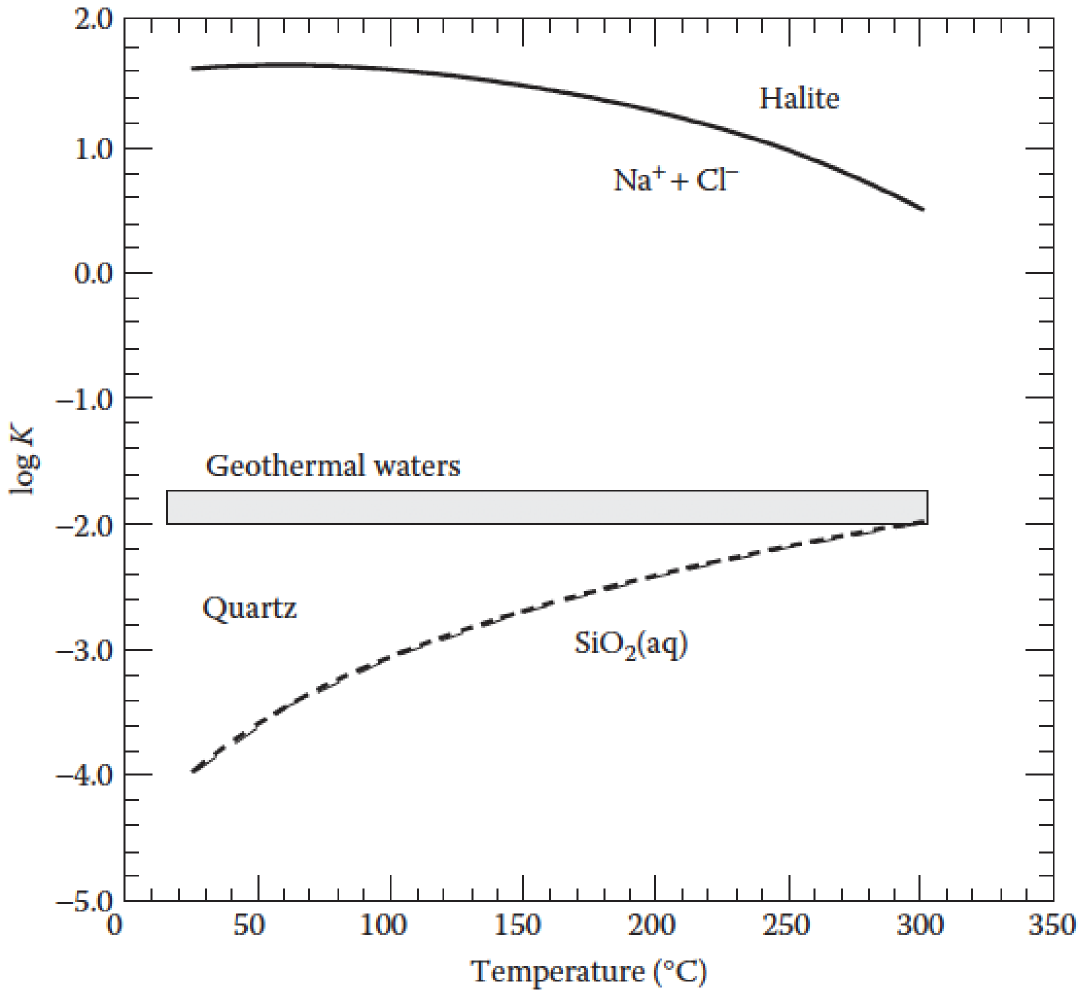
reactant products (solutes)

Equilibrium occurs when the rate of the forward reaction euqals the rate of the reverse reaction.

All reactant and product concentrations are constant at equilibrium.

At equilibrium, the water is saturated in halite, for the given P-T conditions.

Equilibrium constants and the Law of Mass Action



For a **reversible reaction**, $\boldsymbol{aA + bB \leftrightarrow cC + dD}$, the equilibrium constant is defined:

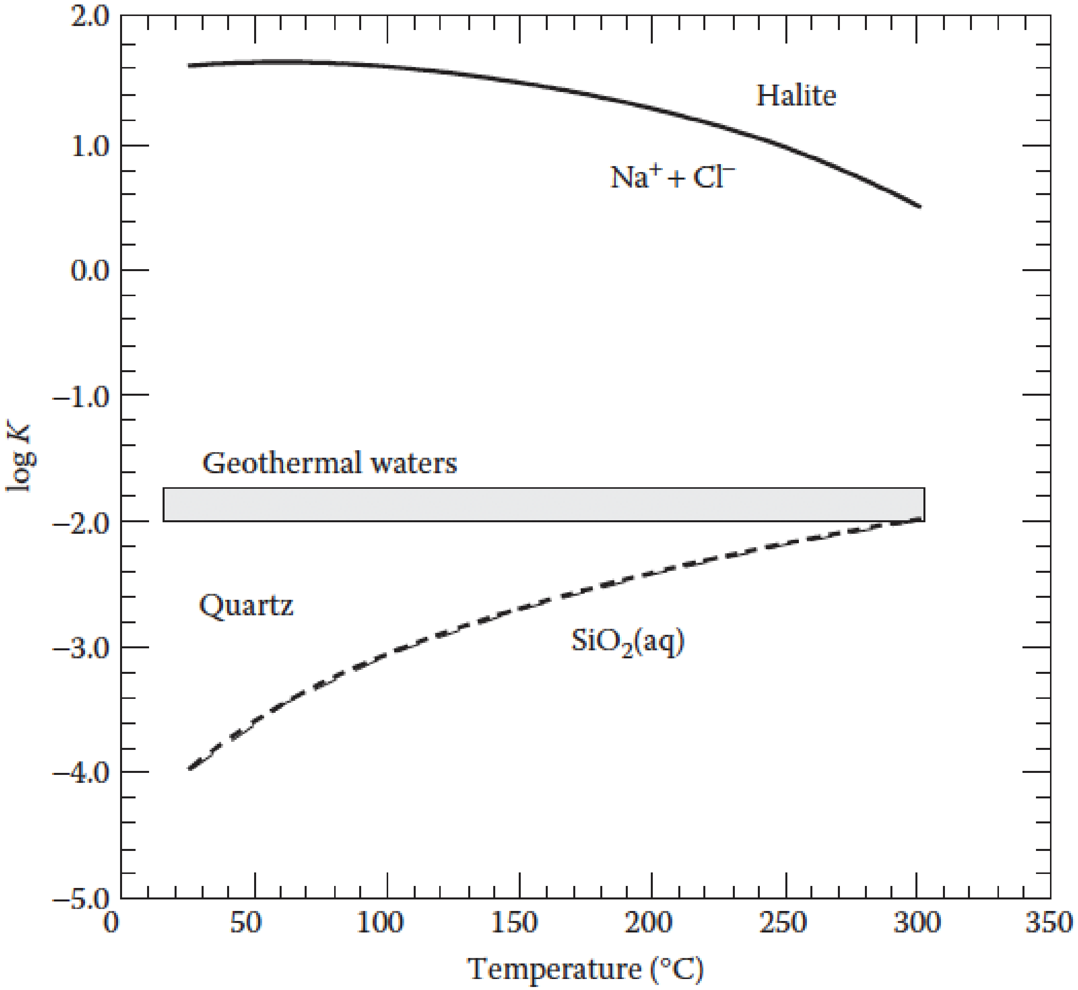
$$K = \frac{{a_C}^{c} \times {a_D}^{d}}{{a_A}^{a} \times {a_B}^{b}}$$

Where *a* is the activity

Note: *a* of pure solids and pure liquids is 1, by convention.

Source: Glassley, W. E., *Geothermal Energy*

Equilibrium constants and the Law of Mass Action



For our salt dissolution reaction:

$$\mathrm{NaCl} \leftrightarrow \mathrm{Na}^{+} + \mathrm{Cl}^{-}$$

So:

$$K = \frac{a_{Na^{+}} \times a_{Cl^{-}}}{a_{NaCl}}$$

Note: *a* of pure solids and liquids is 1, by convention.

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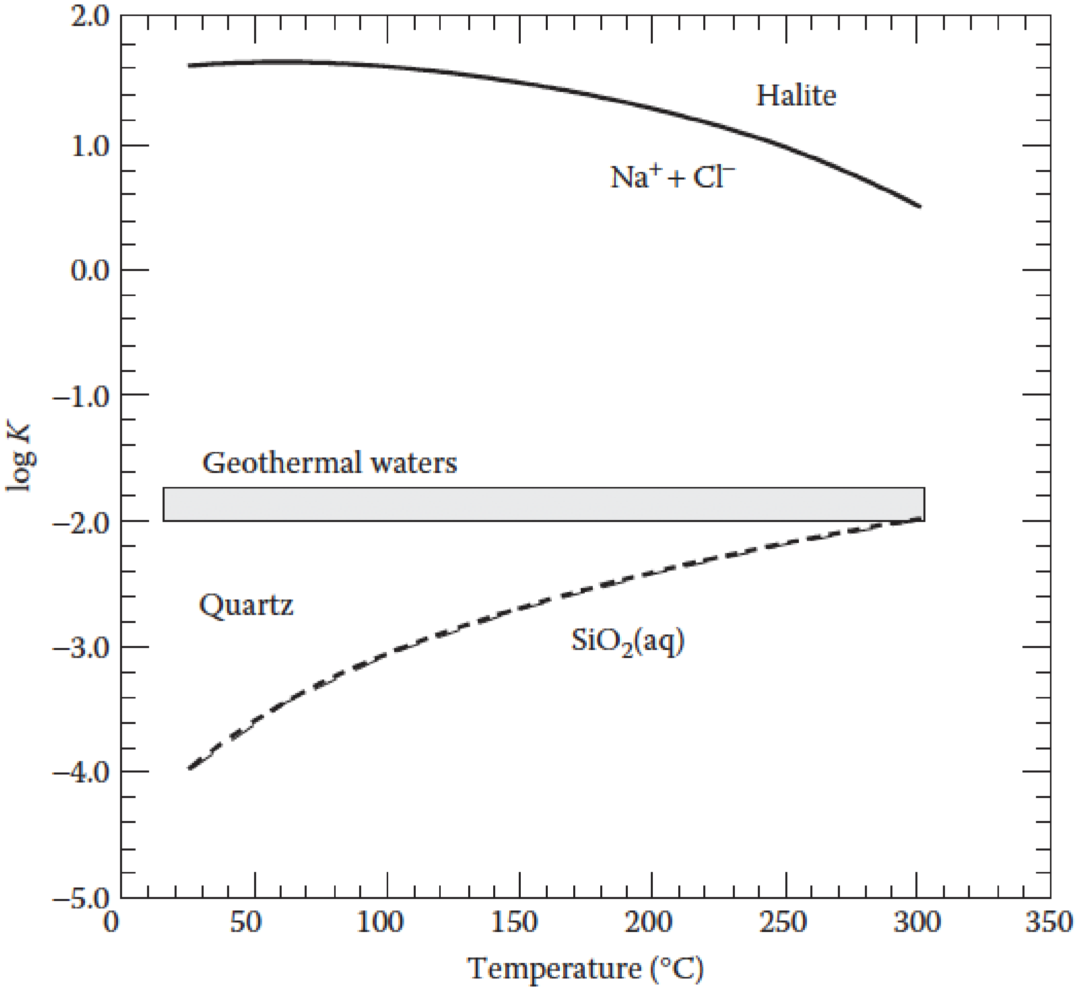
Activity, a



Source: Glassley, W. E., *Geothermal Energy*

For a dissolved species, $\boldsymbol{a_i = \gamma_i \times m_i}$,

where γ_i is the activity coefficient

m_i is the molality (mol/kg) of the species in solution

For dilute solutions, the activity coefficient is 1.

***a* is an effective concentration.**

For our generic reversible reaction,

$\boldsymbol{aA + bB \leftrightarrow cC + dD}$**:**

$$K = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

Will a reaction take place?

You need to determine if a reaction is at equilibrium:

$$A = R \times T \times \ln\left(\frac{Q}{K}\right),$$

Where: A is affinity (J/mole)

R is the universal gas cosntant (8.314 J/mole.K)

T is temperature (K)

Q is the reaction quotient

K is the equilibrium constant for that reaction

Reaction quotient, Q

Relative amount of products and reactants present in a reaction **at any given time.**

Recall: $\boldsymbol{aA + bB \leftrightarrow cC + dD}$

$$Q = \frac{{a_C}^c \times {a_D}^d}{{a_A}^a \times {a_B}^b} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$

Q = K when the reaction is at equilibrium.

Will a reaction take place?

$$A = R \times T \times \ln\left(\frac{Q}{K}\right)$$

If Q = K, **A = 0** and the solution is at equilibrium.

For our salt dissolution system: $\mathrm{NaCl} \leftrightarrow \mathrm{Na^+} + \mathrm{Cl^-}$

If **Q > K and A > 0**, the concentration of the products exceeds the equilibrium value: the solution will precipitate a solid.

This is call **supersaturation.**

If **Q < K and A < 0**, the reactant will continue to dissolve until it is all dissolved or Q = K (solution reaches equilibrium).

Affinity, A

Affinity, A, has units of J/mole and is mathematically equivalent to The Gibbs energy function:

$$A = G_{products} - G_{reactants} = \left(H_{products} - \ H_{reactants}\right) - T \times \left(S_{products} - \ S_{reactants}\right)$$

Therefore:

$$\Delta G = -R \times T \times \ln \frac{Q}{K}$$

This statement relates the activities of the species (included in K and Q) involved in a reaction and the conditions under which they will coexist in thermodynamic equilibrium.

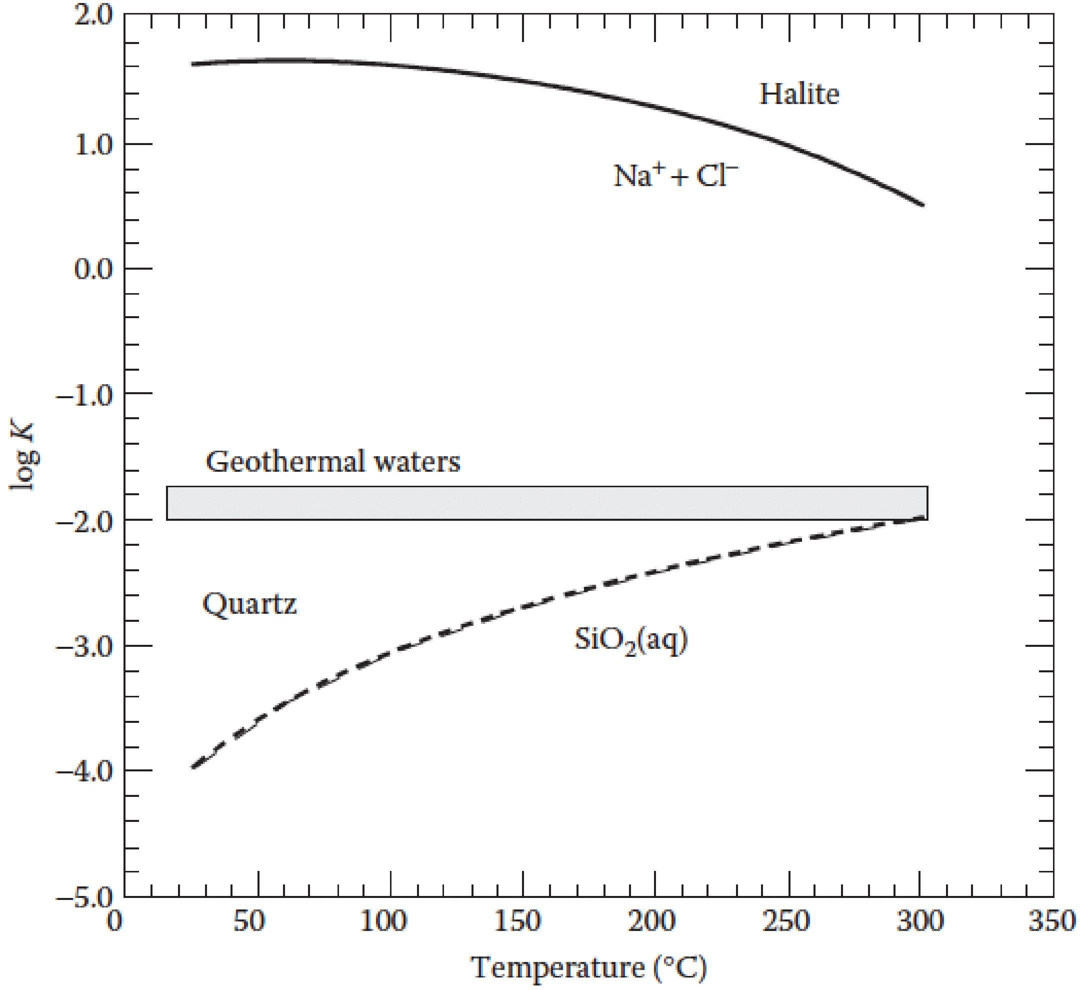
Exercise

Consider a pot of boiling water.

Once the water has boiled, the pot is removed and placed in a perfectly insulated location, so that it does not lose nor gain heat.

Pour in 10g of NaCl and 10g of SiO_2, each with a grain size of 10μm.

Exercise



How much halite will dissolve in 1L of water at 100°C?

Recall:

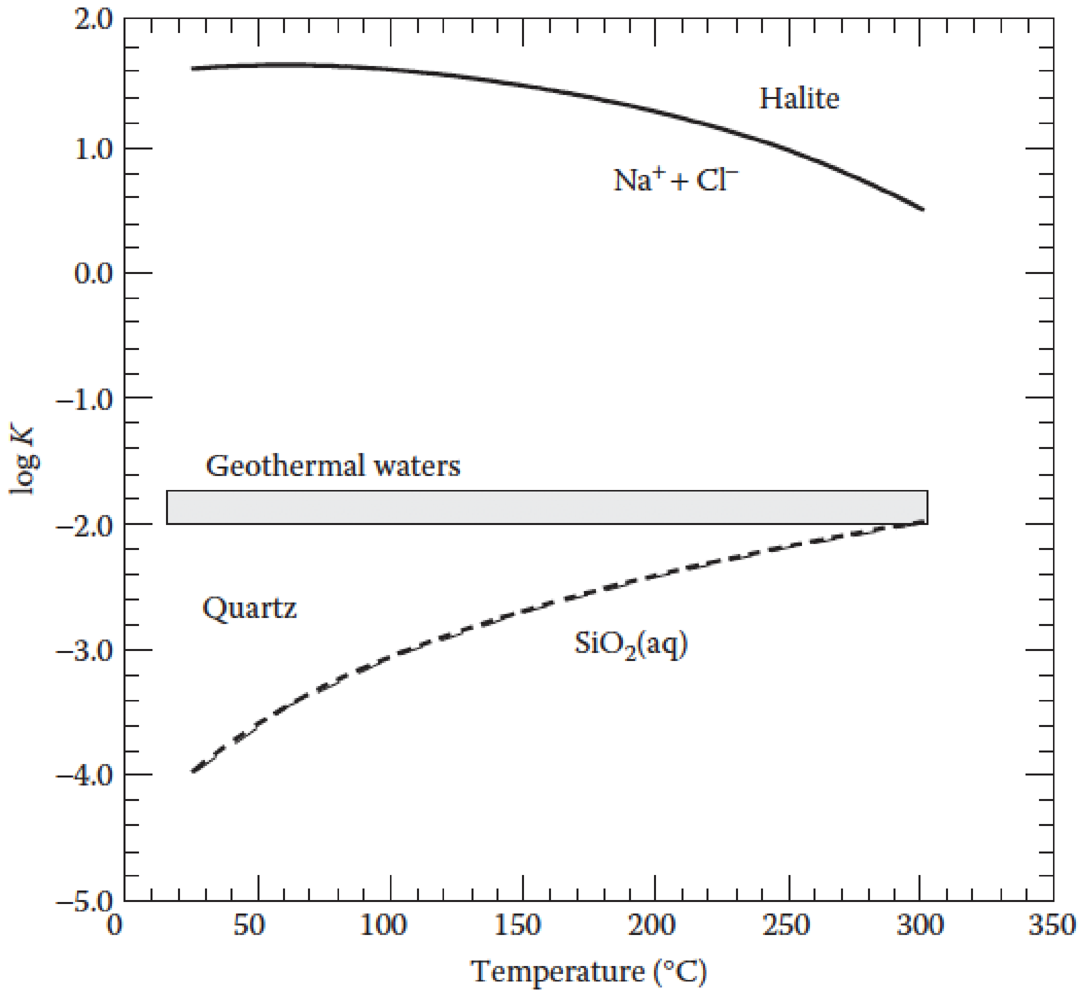
$$K = \frac{[a_{Na^+}] \times [a_{Cl^-}]}{[a_{NaCl}]}$$

Molecular weight of Na^+: 22.99 g/mole

Molecular weight of Cl^-: 35.39 g/mole

Source: Glassley, W. E., *Geothermal Energy*

Exercise



What about SiO_2?

$SiO_{2(solid)} \leftrightarrow SiO_{2(aq)}$

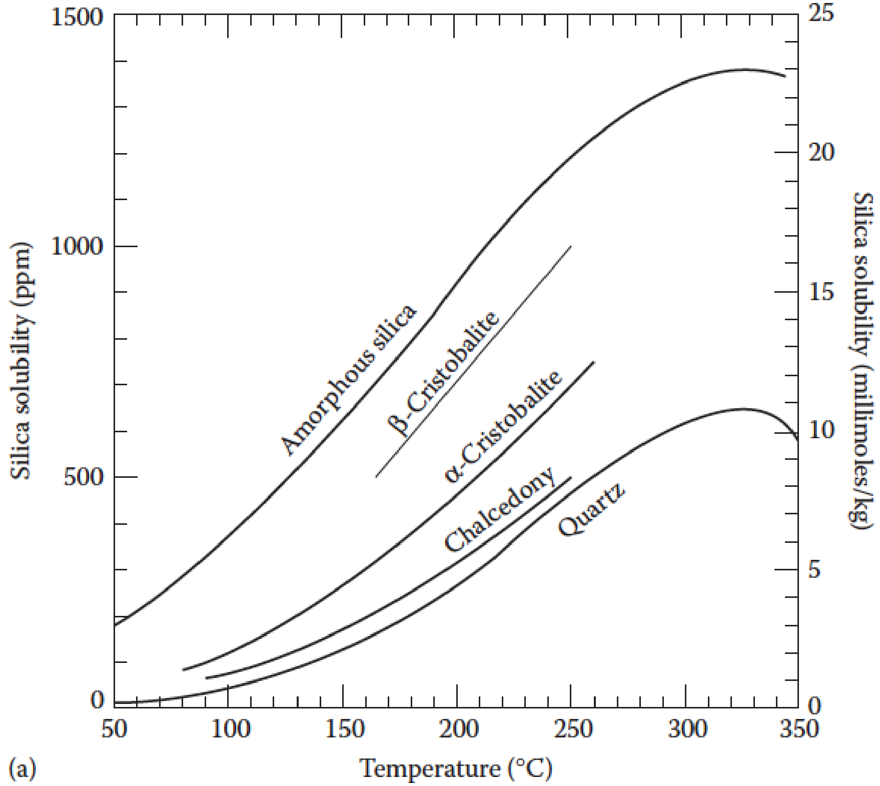
How much silica will dissolve in 1L of water at 100°C?

Molecular weight of Si^{4+}: 28.09 g/mole

Molecular weight of O^{2-}: 16.00 g/mole

Source: Glassley, W. E., *Geothermal Energy*

Solubility



Solubility: the maximum concentration of a solute that can be maintained in a solvent at a given pressure and temperature.

Units:

Mass/volume

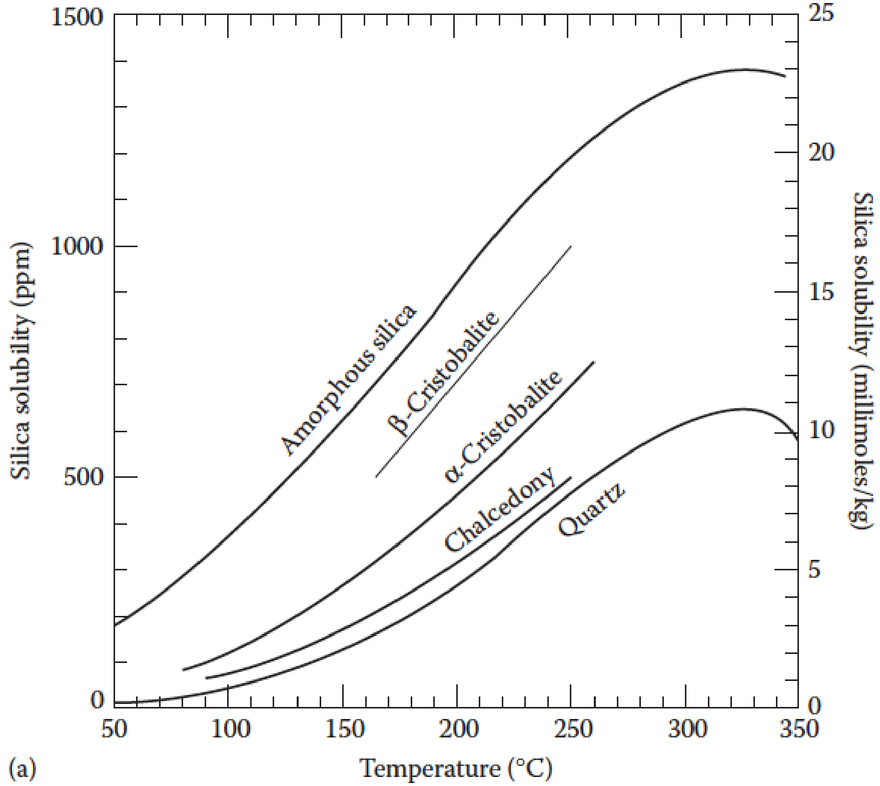
Mass/mass

Parts per million (ppm) by weight

Moles of solute per kg of solvent (molality, M)

Source: Glassley, W. E., *Geothermal Energy*

Solubility



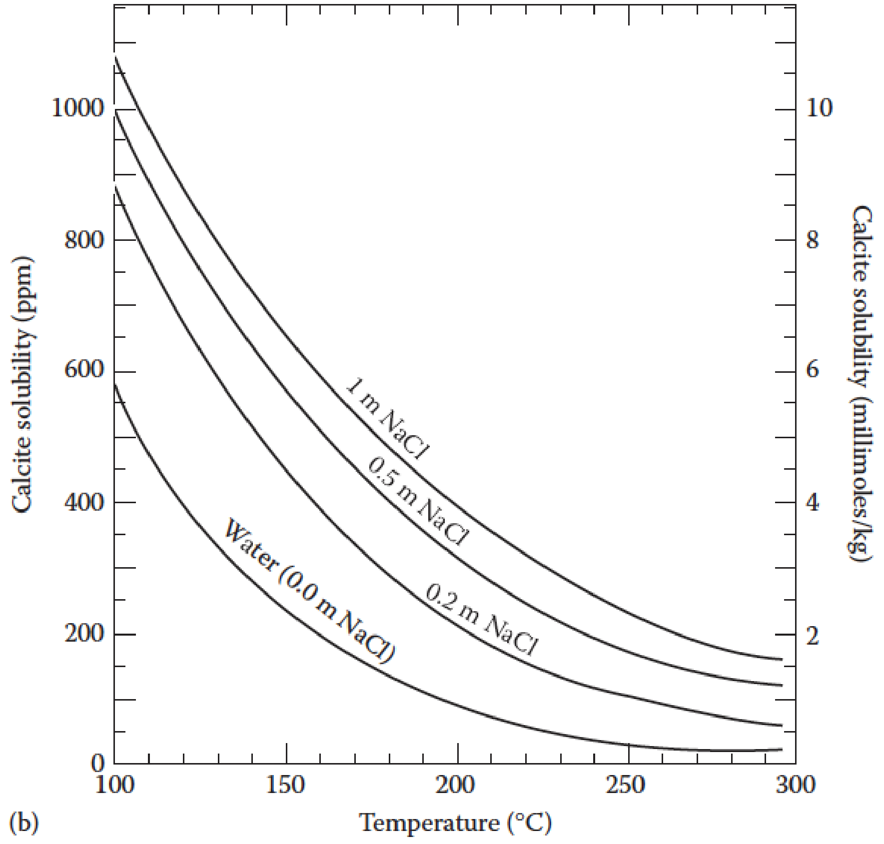
Solubility changes with temperature.

Why does the solubility of quartz decrease at 350°C?

Even simple chemical systems experience complex interactions with the solvent at the atomic scale.

Source: Glassley, W. E., *Geothermal Energy*

Solubility



Calcite solubility:

$CaCO_3$ (s) → $Ca^{2+} + CO^{2-}_3$

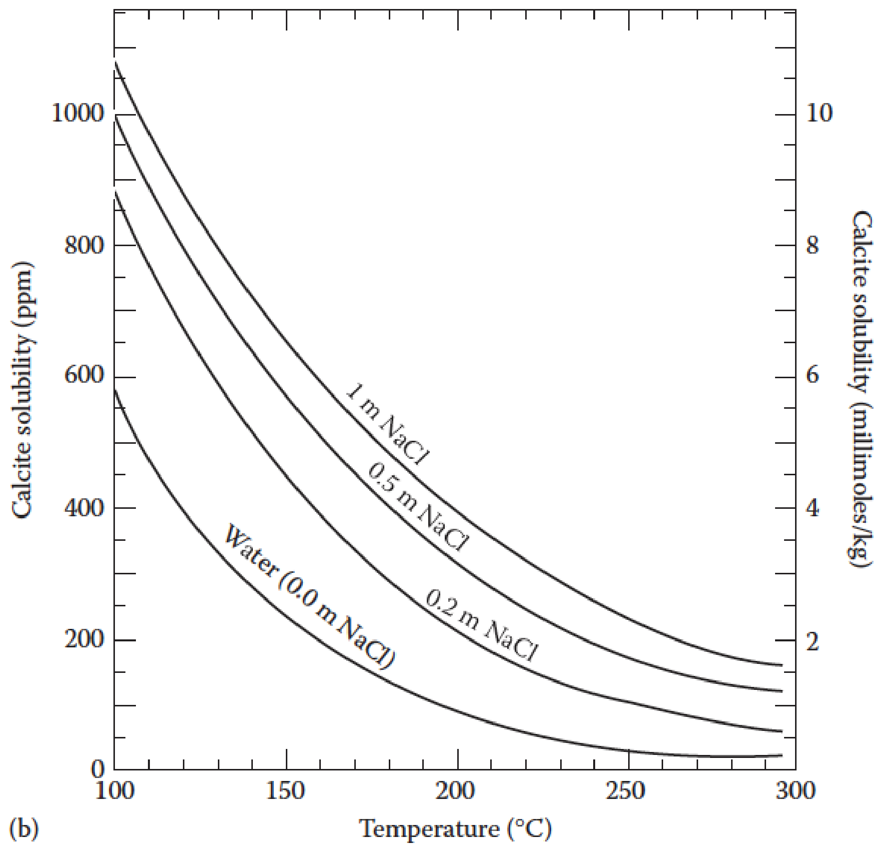
This reaction is coupled with hydrolysis of the carbonate ion to form bicarbonate:

$CO^{2-}_3 + H_2O \rightarrow HCO^-_3 + H^+$

H^+ determines the pH of the solution, which is an important control on calcite precipitation and dissolution.

Source: Glassley, W. E., *Geothermal Energy*

Solubility

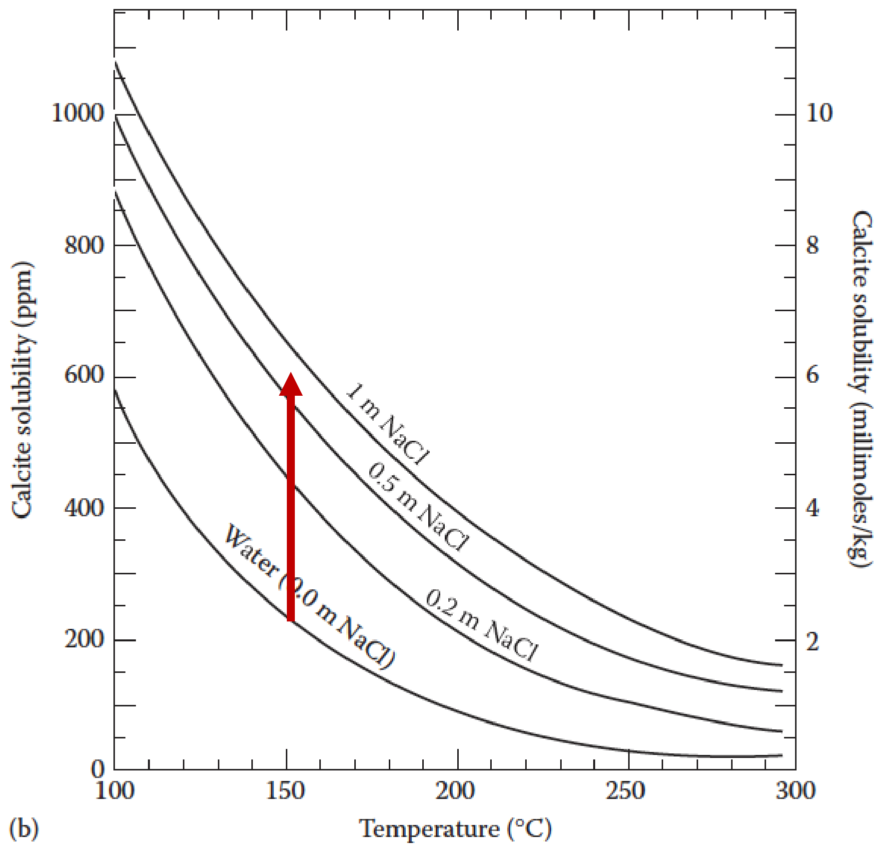


Calcite experiences *retrograde solubility.*

Retrograde solubility: decreasing solubility with increasing temperature.

Source: Glassley, W. E., *Geothermal Energy*

Solubility



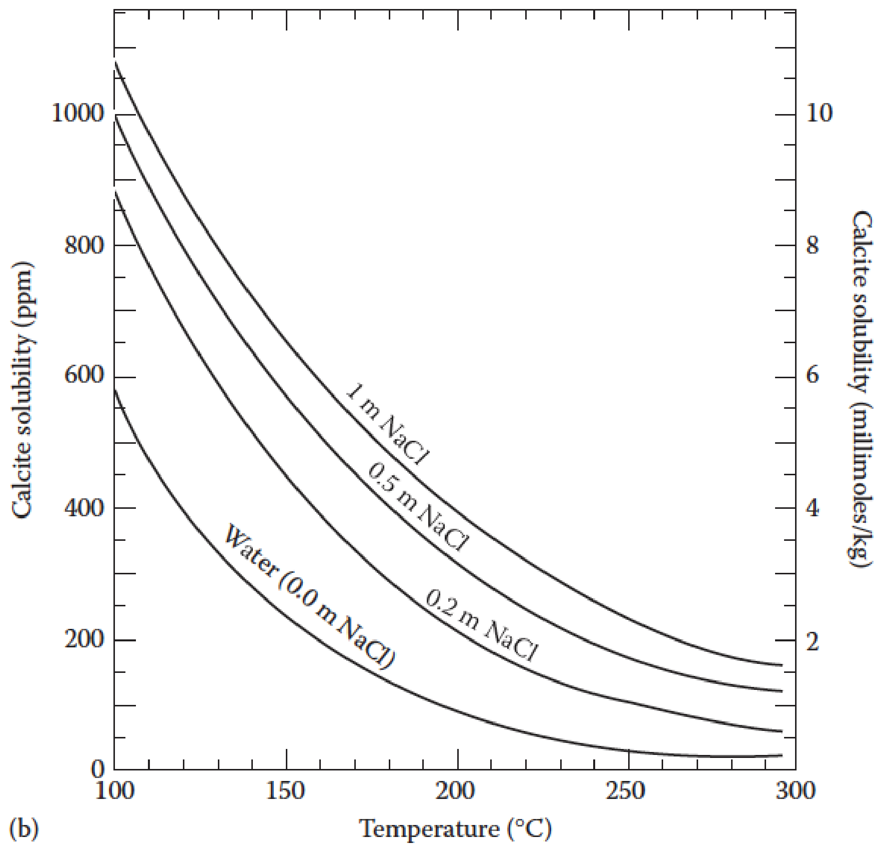
Calcite experiences *retrograde solubility.*

Retrograde solubility: decreasing solubility with increasing temperature.

Calcite solubility is also influenced by the concentration of other solutes, including halite.

Source: Glassley, W. E., *Geothermal Energy*

Solubility



Rock-fluid interactions matter!

So far, we've only talked about simple, closed systems.

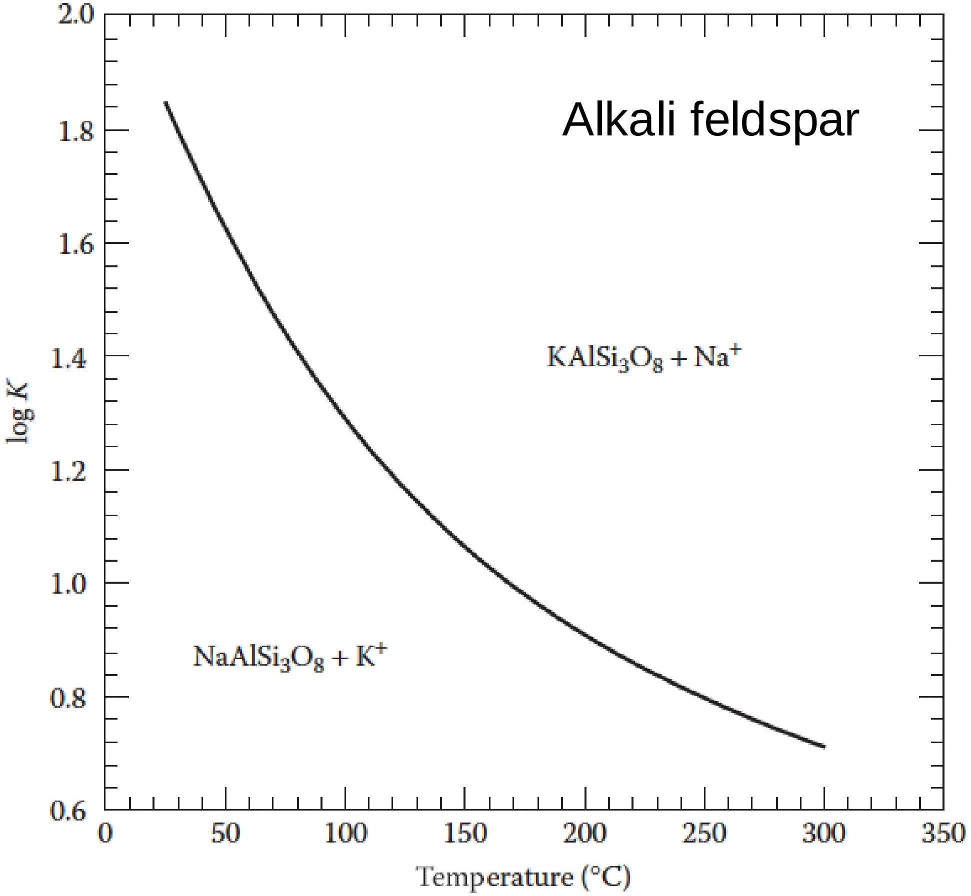
Geological systems contain several types of minerals.

The complex rock-fluid interactions mean that precipitation and dissolution of different minerals can happen at the same time!

Geological systems are also not closed chemical systems…

Source: Glassley, W. E., *Geothermal Energy*

Ion Exchange



Quartz has a fixed chemical composition: SiO_2

Some minerals can accommodate a variety of ions in their structure.

Example: alkali feldspar, one of the most common minerals in the Earth's crust, which can accommodate sodium and potassium in its crystal structure:

$$\mathbf{NaAlSi_3O_8 + K^+ \leftrightarrow KAlSi_3O_8 + Na^+}$$

At any given temperature, the alkali feldspar system has a fixed Na^+:K^+ ratio: potential geothermometer!

Source: Glassley, W. E., *Geothermal Energy*

Kinetics of geothermal systems

Kinetics of geothermal systems

How quickly do materials dissolve or precipitate from a solution?

Depends on:

- Pressure and temperature of the system
- Effective surface area of the solid exposed to the solution
- Chemical composition of the solution
- How easily mineral components are removed from or added to the exposed surface of the solids with which the fluid is in contact

These variables influence exert an influence on the Gibbs energy function of the reaction.

Kinetics of geothermal systems

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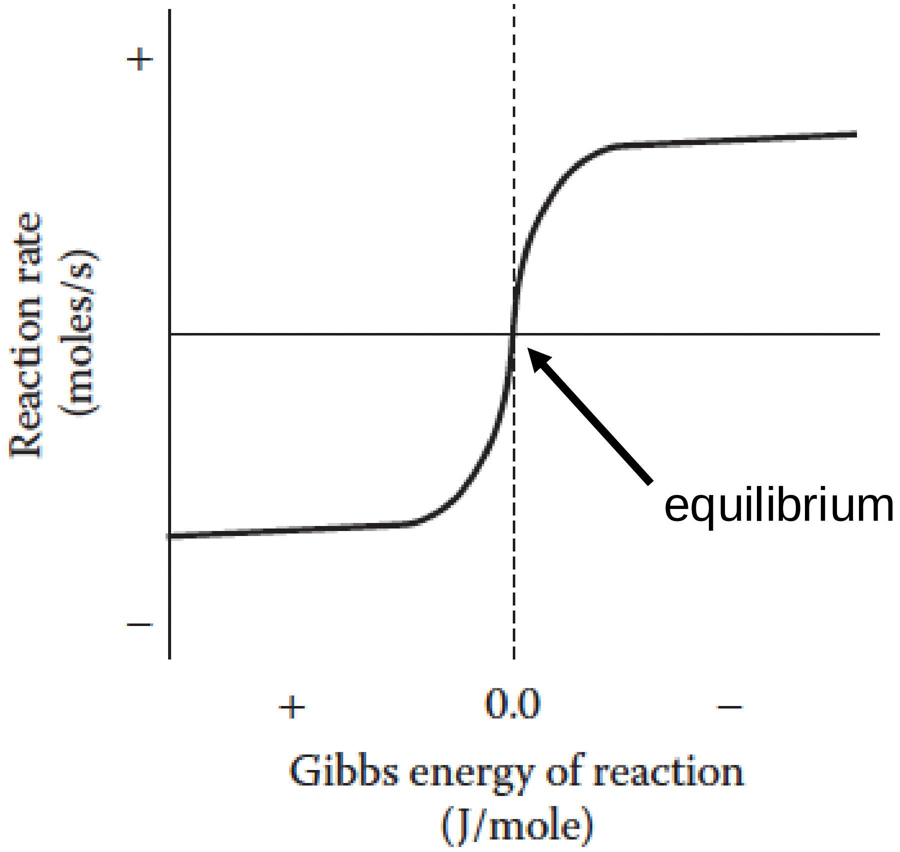
The rate at which such processes proceed is called the kinetics of the reaction.

Reaction rate laws can take into account the variables above, but often can only be applied to specific mineral systems.

Be careful when using them!

Kinetics of geothermal systems



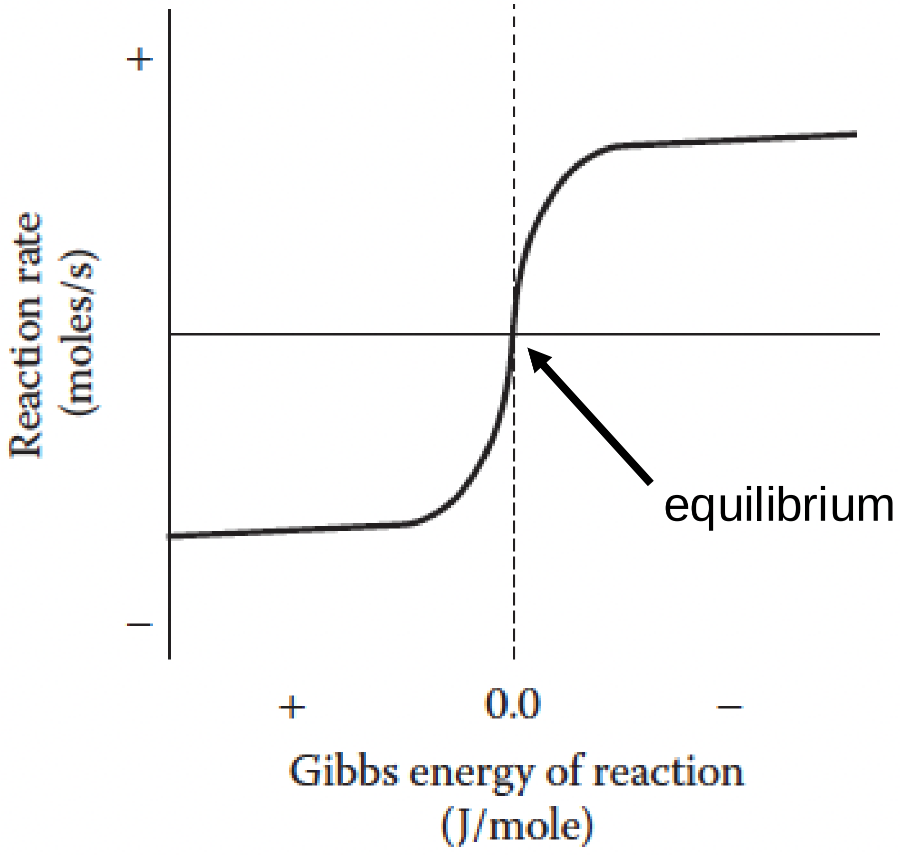
At equilibrium, the Gibbs function and reaction rate are equal to 0.

Far from equilibrium, the reaction rate is a large positive or negative number.

Any equation describing this behaviour has to account for the system behaviour close to equilibrium and far-from-equilibrium.

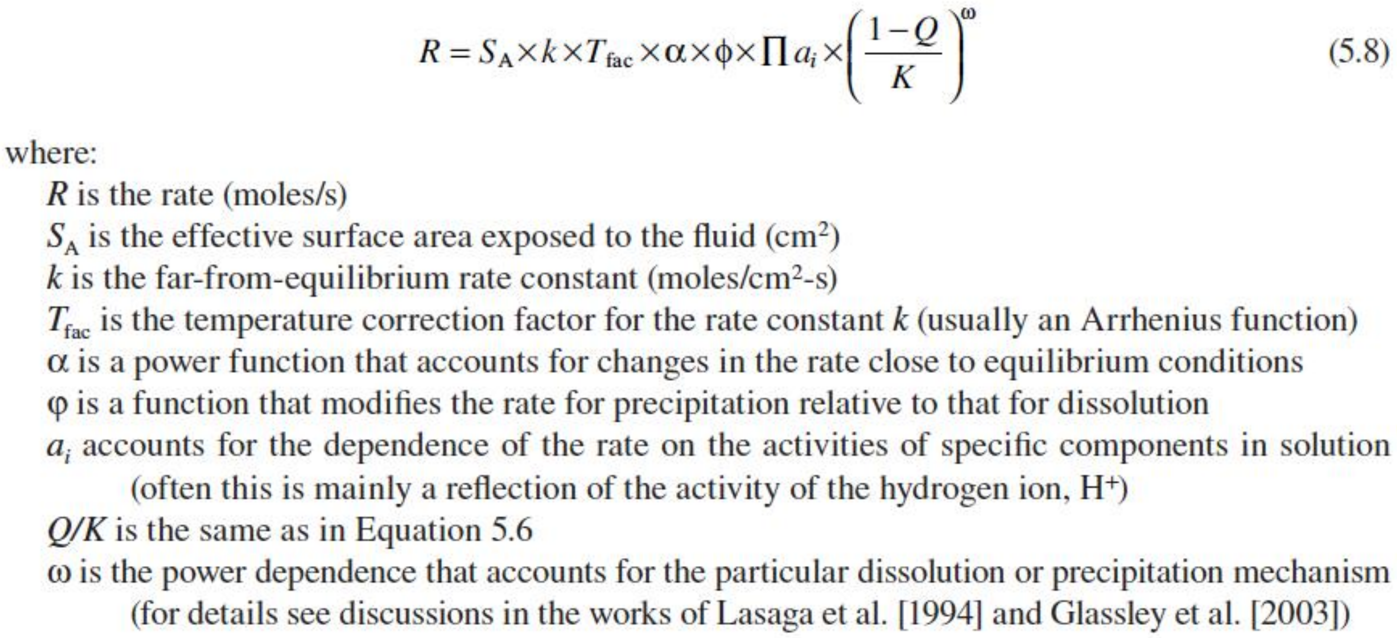
Source: Glassley, W. E., *Geothermal Energy*

Kinetics of geothermal systems



Below is an example of a reaction rate equation.

If we know the number of moles present, we can use equation 5.8 to determine the time required to dissolve a material or the time required to precipitate a given amount of material:



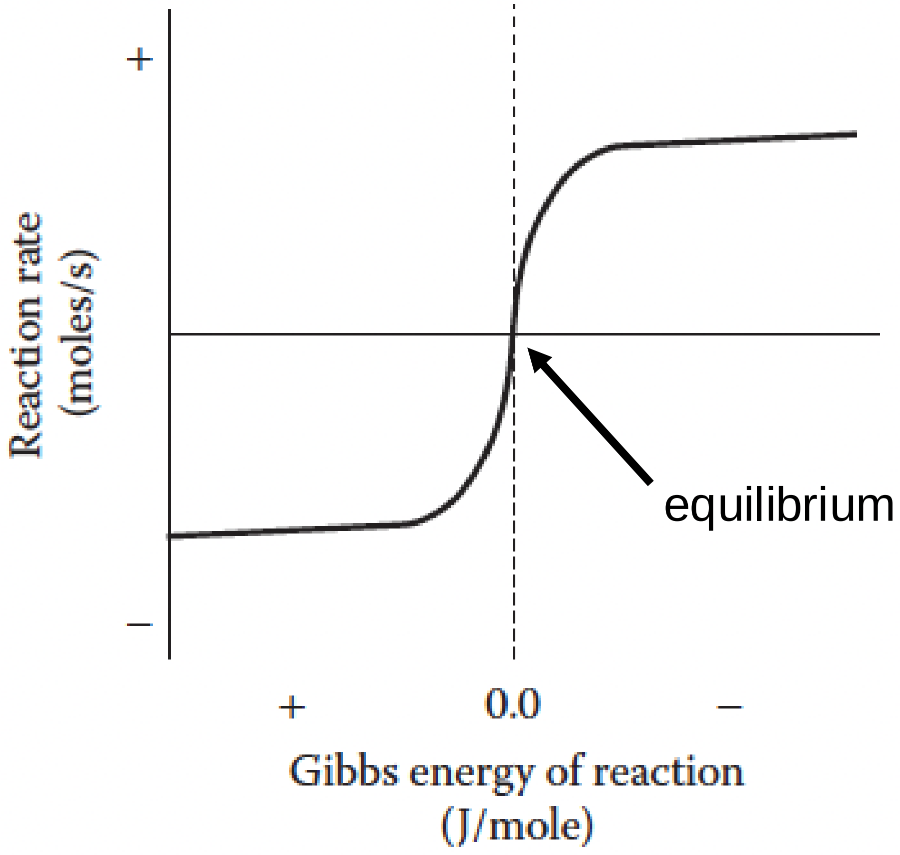
$$R = S_A \times k \times T_{fac} \times \alpha \times \phi \times \prod a_i \times \left(\frac{1-Q}{K}\right)^{\omega} \qquad (5.8)$$

where:

R is the rate (moles/s)
S_A is the effective surface area exposed to the fluid (cm^2)
k is the far-from-equilibrium rate constant ($moles/cm^2$-s)
T_{fac} is the temperature correction factor for the rate constant k (usually an Arrhenius function)
α is a power function that accounts for changes in the rate close to equilibrium conditions
φ is a function that modifies the rate for precipitation relative to that for dissolution
a_i accounts for the dependence of the rate on the activities of specific components in solution (often this is mainly a reflection of the activity of the hydrogen ion, H^+)
Q/K is the same as in Equation 5.6
ω is the power dependence that accounts for the particular dissolution or precipitation mechanism (for details see discussions in the works of Lasaga et al. [1994] and Glassley et al. [2003])

Source: Glassley, W. E., *Geothermal Energy*

Kinetics of geothermal systems



Equation 5.8 is difficult to apply, mostly because we don’t have sufficient data from natural systems or processes.

Even with simplification, descriptions of reaction kinetics in geological systems remain approximations.

$$R = S_{\mathrm{A}} \times k \times T_{\mathrm{fac}} \times \alpha \times \phi \times \prod a_i \times \left(\frac{1-Q}{K}\right)^{\omega} \qquad (5.8)$$

where:

R is the rate (moles/s)
S_{A} is the effective surface area exposed to the fluid (cm^2)
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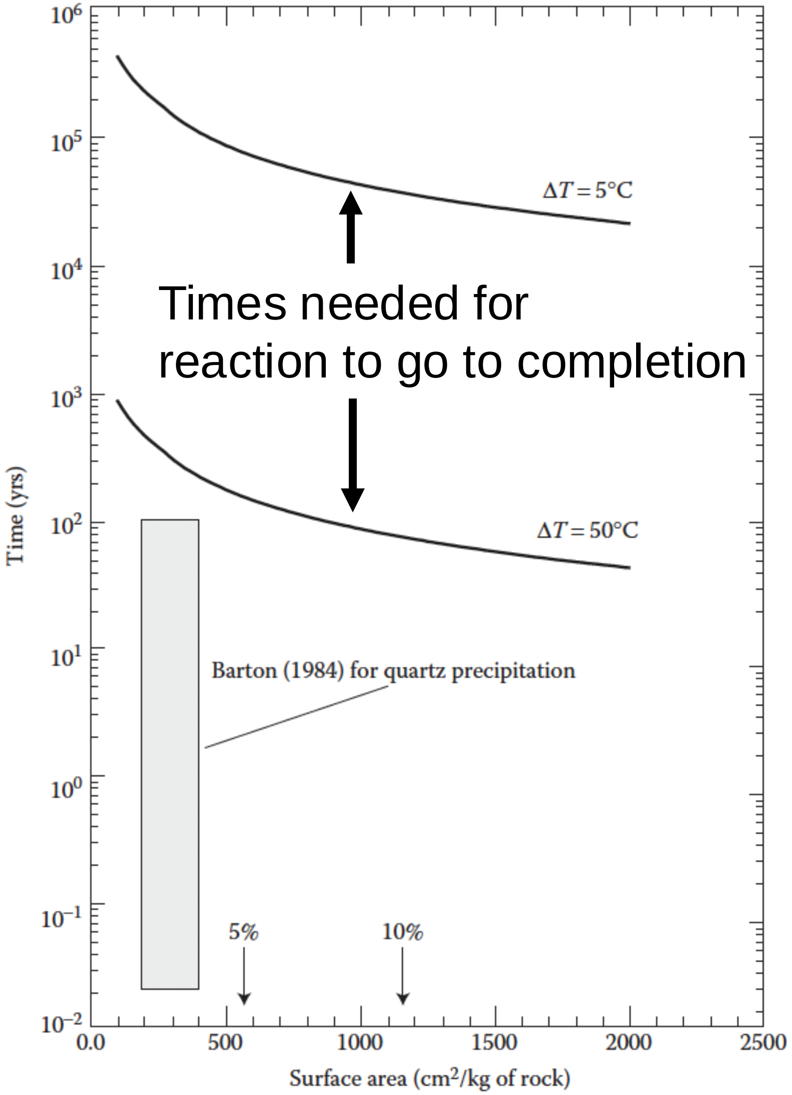
Source: Glassley, W. E., *Geothermal Energy*

Kinetics of geothermal systems



Source: Glassley, W. E., *Geothermal Energy*

How does reaction time change as a function of grain size and temperature?

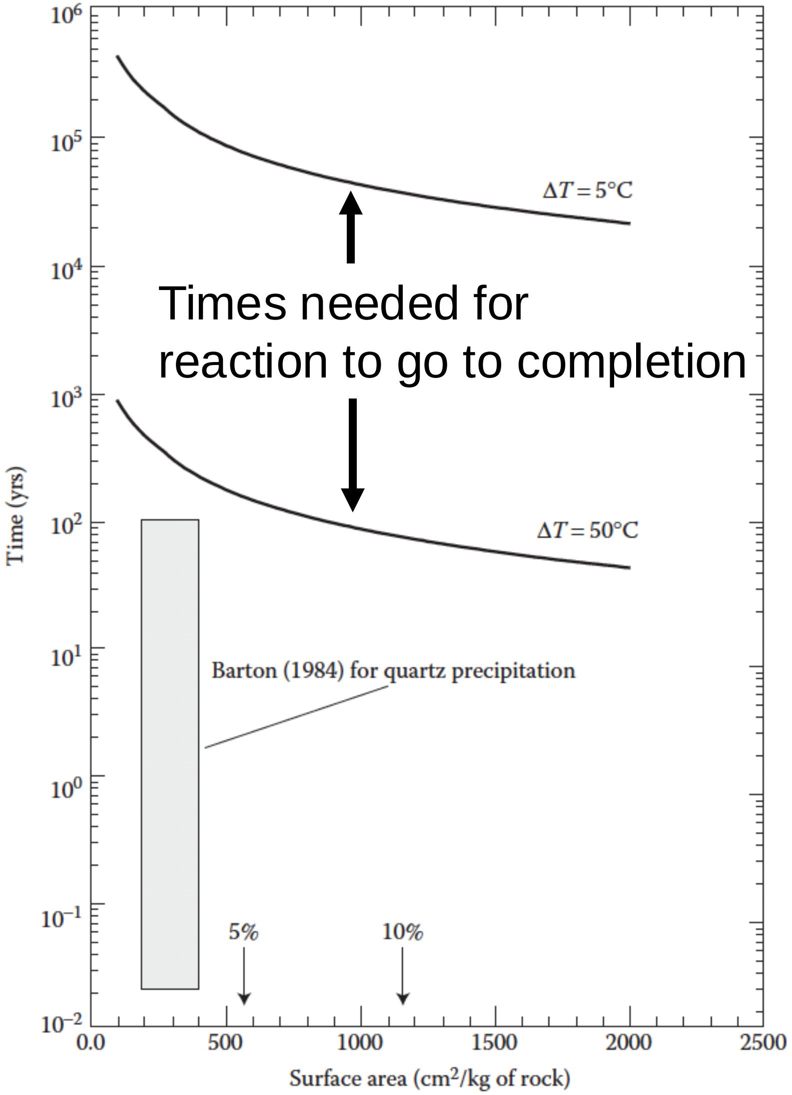
Assumptions:

- We consider a system in which a mineral has a known dissolution rate constant (measured experimentally for a given set of conditions)
- We know how the rate constant changes as temperature rises beyond the conditions for which Q/K equals 0.

Observations:

- The time needed to achieve equilibrium can vary from seconds to millions of years
- Reaction rate is very sensitive to temperature: a difference of a few degrees of temperature can change reaction rates by thousands of years
- Reaction times decrease with increasing exposed surface area

Kinetics of geothermal systems



Times needed for reaction to go to completion

Things to remember:

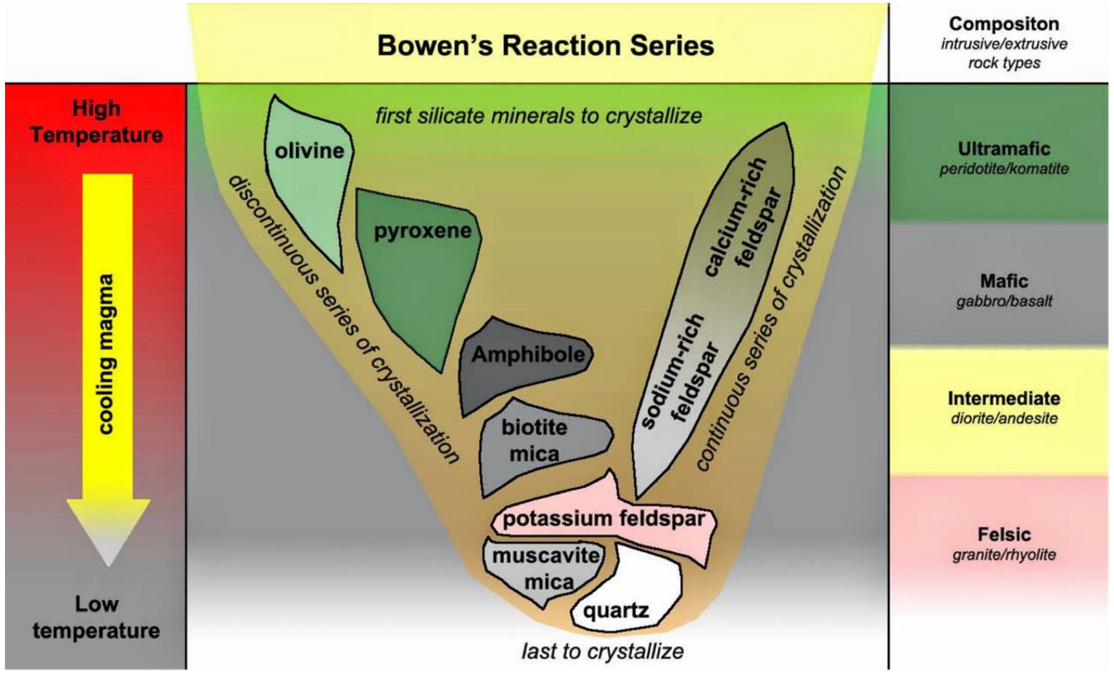
- Geothermal systems are likely not in equilibrium
- Geological systems are extremely heterogeneous
  - Mineralogy, grain size, pore volume, permeability, exposed surface area, fluid composition, etc.
- This heterogeneity means that many competing reactions will be occurring simultaneously, each approaching equilibrium at different rates

To understand the chemical characteristics of the fluids samples in a specific geothermal system, we need to know the mineralogical characteristics throughout the flow path.

Source: Glassley, W. E., *Geothermal Energy*

Gases in geothermal fluids

Where do gases come from?

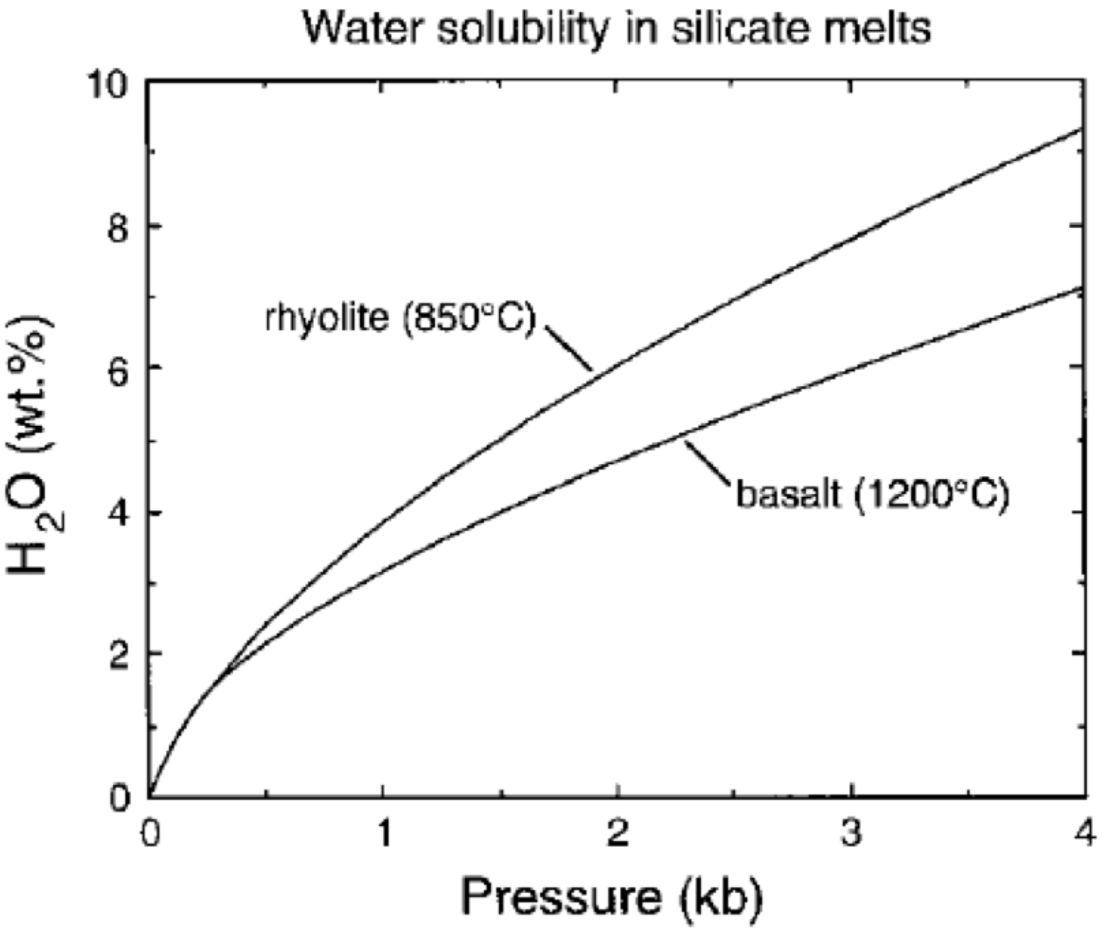


http://www.geologyin.com/2014/09/how-does-bowens-reaction-series-relate.html

As magma rises to the surface and cools, it begins to crystallise.

Some elements of the melt crystallise into minerals.

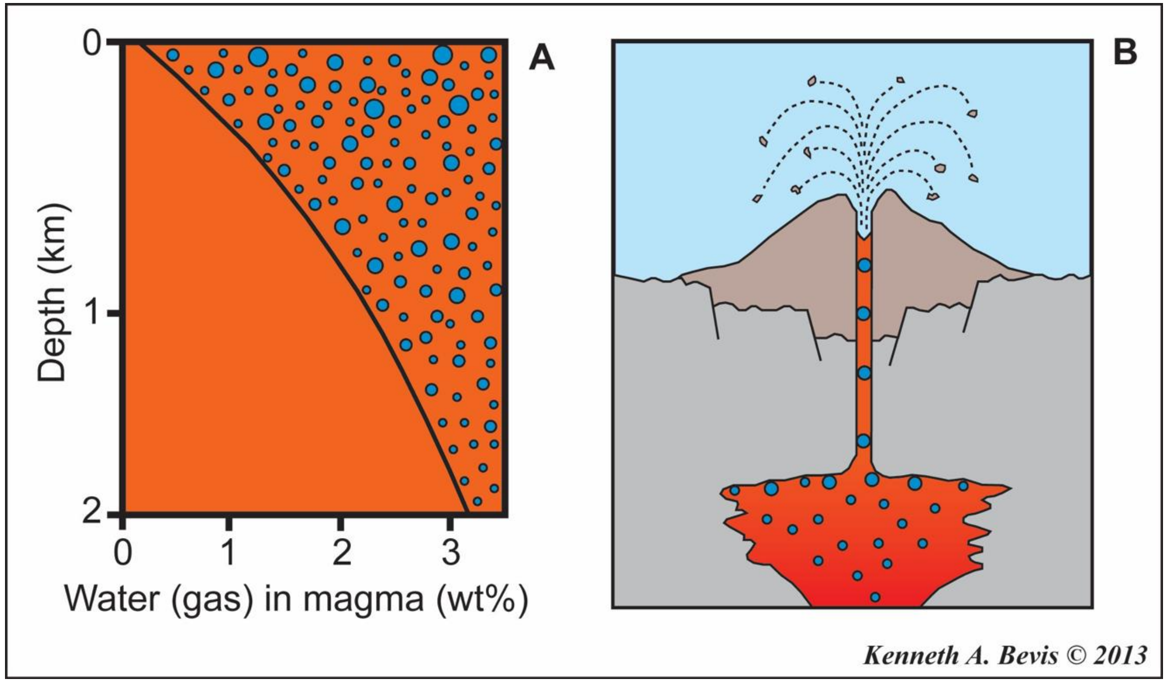
Where do gases come from?



Encyclopaedia of Volcanology

Other elements don’t fit into the crystal structures of these minerals, and tend to form volatiles: H_2O, CO_2, H_2S, O_2, CH_4…

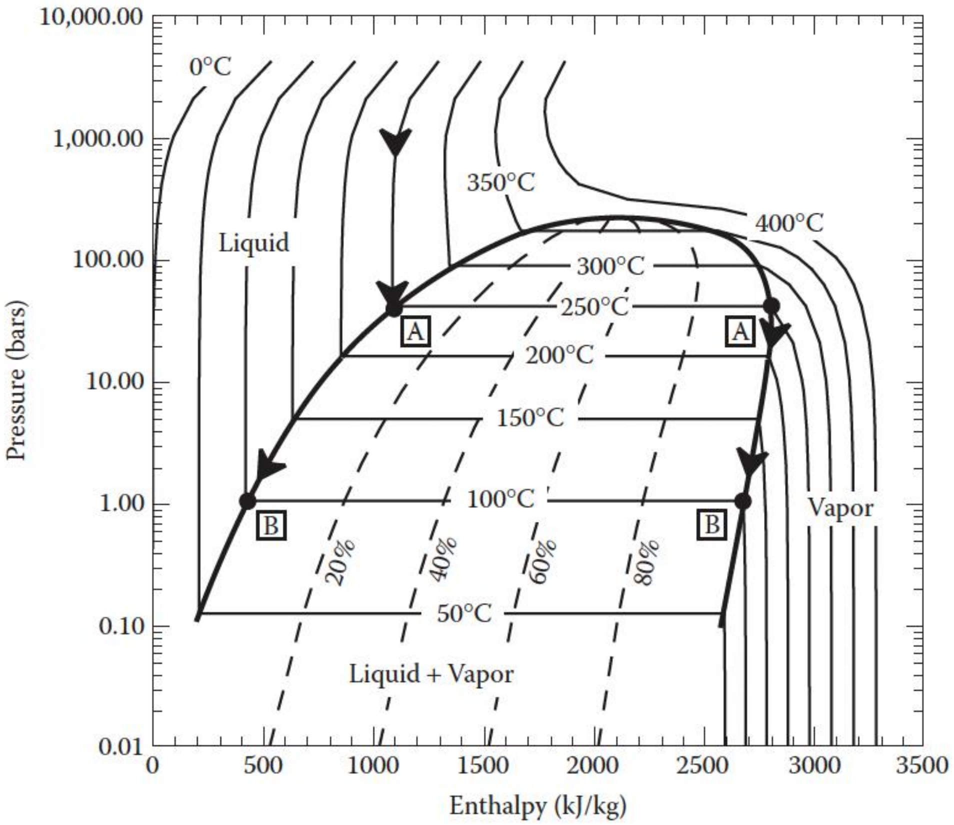
Where do gases come from?



Dissolved volatiles come out of solution as pressure decreases.

As exsolved volatiles move up through the crust, they interact with geothermal fluids, groundwater, meteoric water, etc. and change composition.

Gas partitioning between liquid and vapour



Geothermal solution from Wairakei contains dissolved gases:

Location	Enthalpy (J/g)	CO_2	H_2S	CH_4	H_2	NH_3
Wairakei, New Zealand (W24)	1135	917	44	9	8	6

At Point A, steam begins to separate.

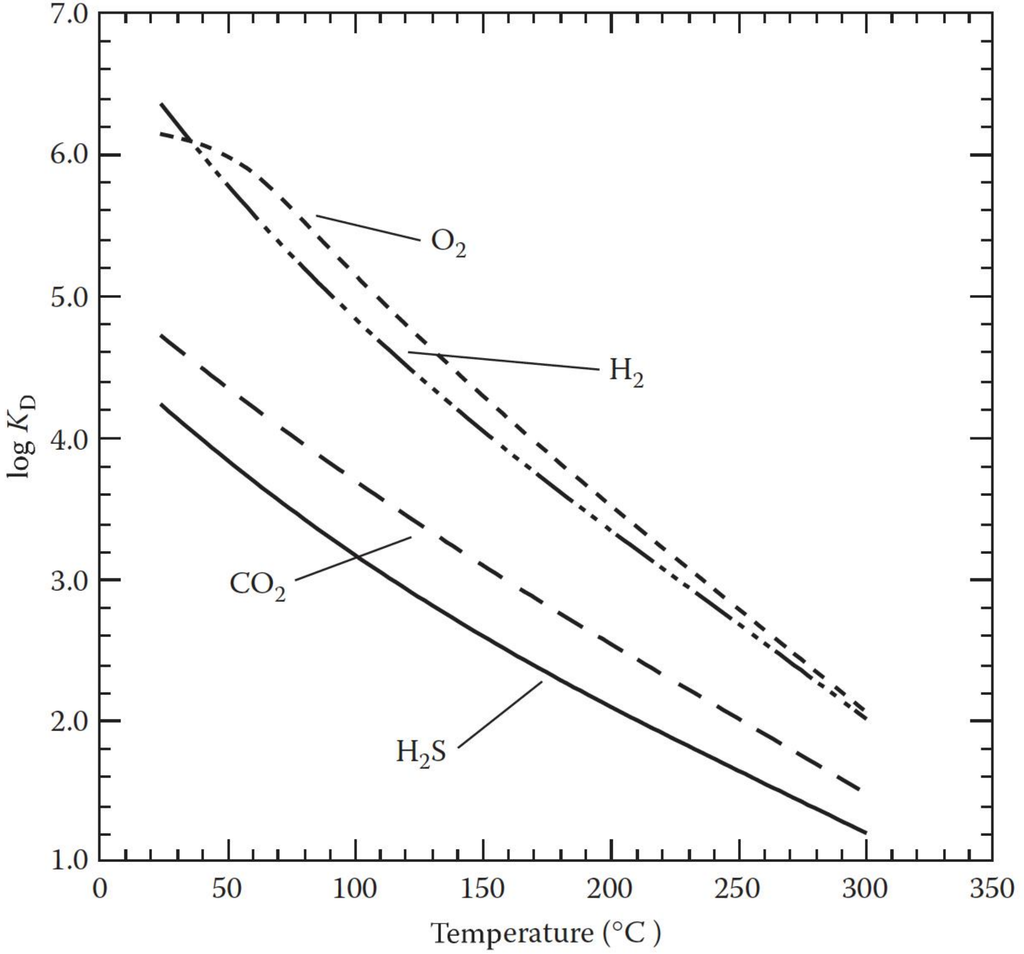
Dissolved gases have different thermodynamic properties (different log(K)):

- some gases will have come out of solution before Point A
- some will come out of the solution after Point A.

When steam forms: the total mass of each dissolved species needs to be partitioned between liquid water and water vapour.

Source: Glassley, W. E., *Geothermal Energy*

Gas partitioning between liquid and vapour



Question: How much of a compound must enter the gas phase for equilibrium to be achieved?

Liquid distribution coefficient, K_D: mass ratio between the gas and liquid phases of the species of interest

Things to note:

- Strong temperature dependence of partitioning
- At high temperature, partitioning is within an order of magnitude
- At 100°C, partitioning spans 2.5 orders of magnitude because of difference in thermodynamic properties (chemical potential!)

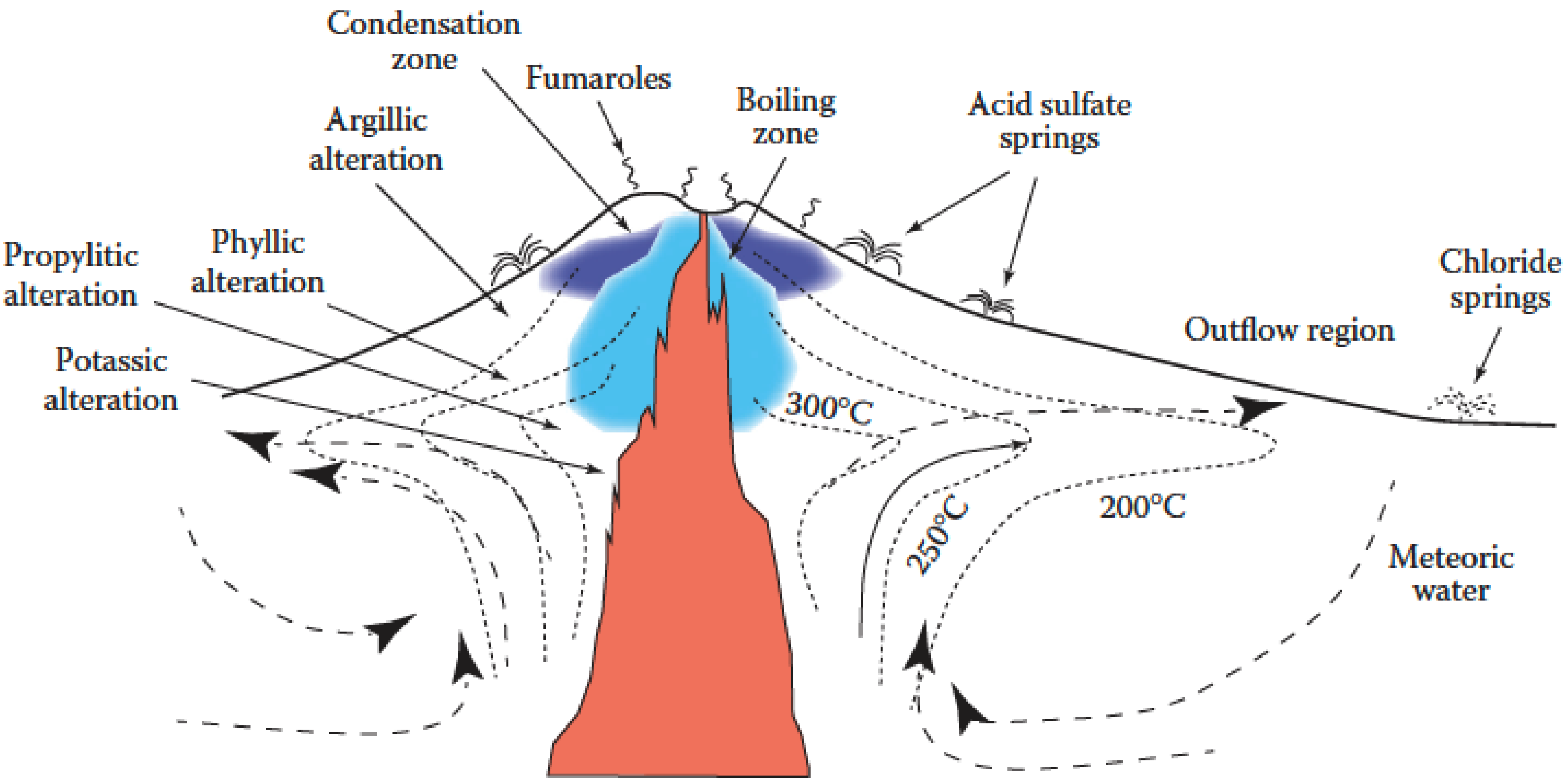
Source: Glassley, W. E., *Geothermal Energy*

Fluid flow and mixing in natural systems

Fluid flow and mixing in natural systems

Up until now, we've talked about stagnant fluid systems.

In geothermal systems, fluids flow.



Source: Glassley, W. E., *Geothermal Energy*

Key points:

Water is a solvent when it interacts with rocks.

Water carries a chemical signature that records the history of its migration through the crust.

This chemical signature can help us evaluate properties and conditions of geothermal reservoirs.

To understand these chemical processes, we need to consider: chemical potentials of the components in a system of phases, what phases are present, the activities and Gibbs energies of the components and phases.

Equilibrium constants and affinities and ion exchange processes can give us information on reservoir temperature, mineralogy, gas composition and reaction path.