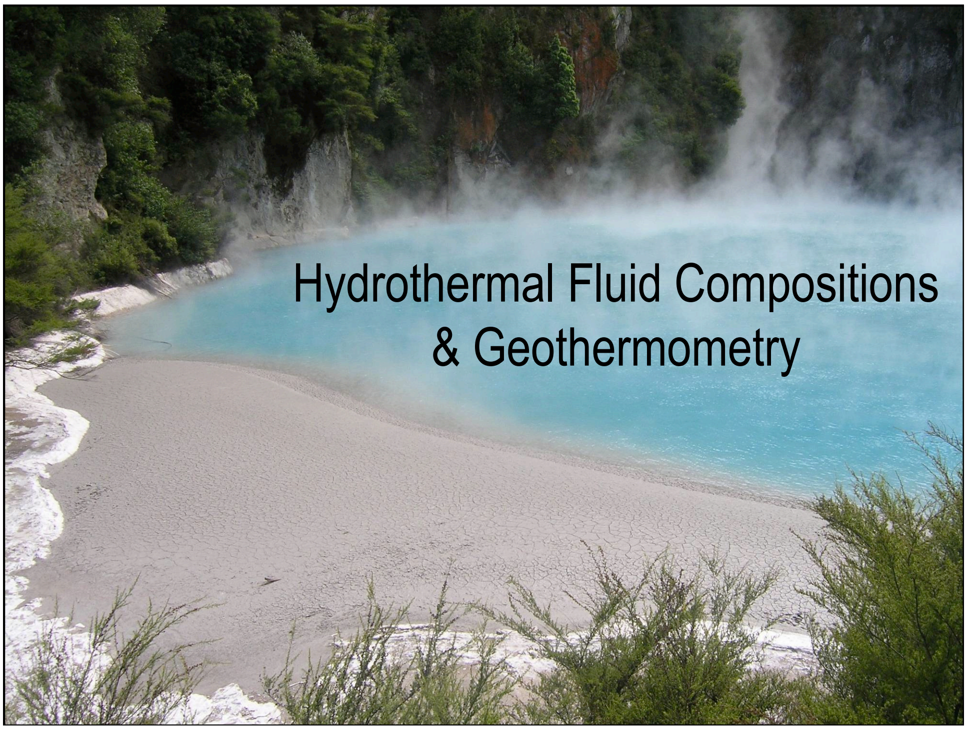


Analyses

Waters

anions: Cl^-, HCO_3^-, SO_4^{-2}
cations: Na^+, K^+, Ca^{+2}, Mg^{+2}, Rb^+, Cs^+, Li^+
neutral: SiO_2, B, CO_2, H_2S, NH_3, As

Gases

geothermal: CO_2, H_2S, NH_3, He, H_2, Ar, N_2, CH_4, O_2
volcanic: SO_2, HCl, HF, CO (plus geothermal gases)

Stable Isotopes	Oxygen ($^{18}O/^{16}O$)	H_2O, SO_4^{-2}
	Hydrogen (D/H)	H_2O, H_2
	Sulfur ($^{34}S/^{32}S$)	H_2S, SO_4^{-2}
	Carbon ($^{13}C/^{12}C$)	CO_2
Radiogenic Isotopes	Tritium	H_2O
	Helium ($^3He/^4He$)	He

Concentration units

Water analyses	mg/kg (parts per million, ppm)
Gas analyses	wt % (weight percent) mol/kg (molal) mmol/100 mol steam µmol/mol mole fraction vol % (volume percent)

Purpose

Tracers:	Cl^-, B, HCO_3^-, SO_4^{-2} N_2, Ar, He, CO_2, H_2S, H_2 $^{18}O/^{16}O$, D/H, $^3He/^4He$
Indicators:	Na^+, K^+, Ca^{+2}, Mg^{+2}, SiO_2, CO_2, H_2
Engineering (scaling-corrosion)	SiO_2, Ca^{+2} , CO_2, HCO_3^- , H_2S, H_2
Environmental	B, NH_3, As, Hg, H_2S

Factors influencing fluid chemistry

Origins of water (e.g. seawater, meteoric water)

Input of magmatic volatiles

- Cl as HCl, C as CO_2, S as SO_2
- evidence from helium isotopes ($^3He/^4He$)

Fluid-mineral equilibria

-minerals (rock type)

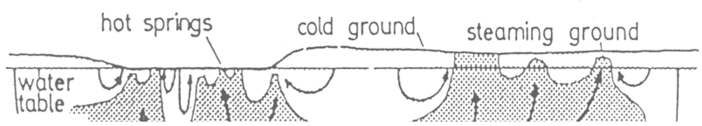
-temperature

-rock dominated (permeability - rock>water)

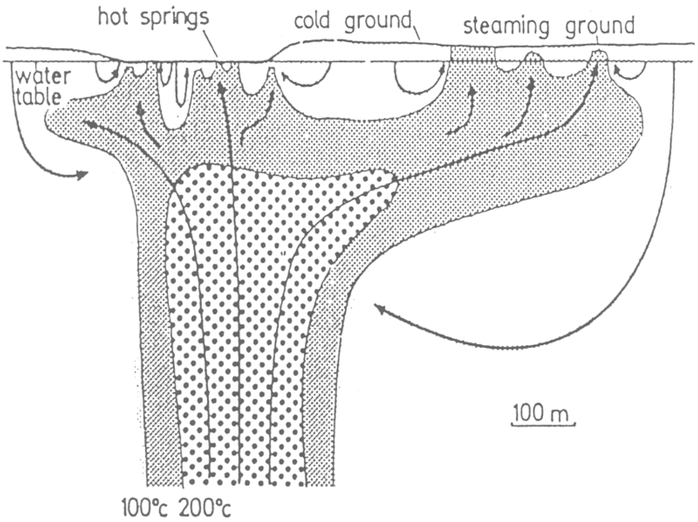
Boiling-dilution

-boiling

-dilution or mixing (permeability - rock<water)



Use fluid chemistry to interpret hydrology



Crustal Fluid Compositions

Analyses of crustal waters (mg/kg, ppm)

	Groundwater Limestone aquifer	Wairakei	White Island	Sea Water	E. Pacific Rise	Salton Sea	Oil Field Brine, Mississippi
T ° C	10	99	79	2	355	340	
pH	7.5	8	1.4	7.8	3.6	5.2	
Na	1.5	1070	5910	10760	10,100	50400	59500
K	0.8	102	635	390	906	17500	538
Mg	4.2	0.4	3800	1290	0	54	1730
Ca	46	26	3150	410	665	28000	36400
SiO_2	8.4	294	360	9.6	1038	400	
Cl	3.5	1770	38700	19340	17600	155000	158200
SO_4	4	26	4870	2710	58	5.4	310
HCO_3	146	76	0	140	251	150	

Giggenbach, 1988

TABLE 1

Chemical composition of thermal water discharges, seawater and solutions of 100g of crustal rocks in 1kg of chloride water in mg/kg.

	Symb.	t(°C)	pH	Na	K	Mg	Ca	Cl	SO_4	HCO_3	ref.
Acid Springs											
White Island, NZ	WI	98°	0.6	5910	635	3800	3150	38700	4870	-	a
Kawa Idjen, Indon.	KI	60°	0.6	1030	1020	680	770	21800	62400	-	a
Mt Ruapehu, NZ	RU	38°	1.2	1120	170	1750	1380	13240	14700	-	a
Tamagawa, Japan	TA	98°	1.3	38	30	35	95	2970	2300	-	a
Guayabal, C. Rica	MV	64°	1.9	56	2	48	99	684	2830	-	a
B.Georginas, Guatem.	ZU	74°	2.0	134	32	26	72	16	1520	-	a
Soda Springs											
Waitangi, NZ	WA	49°	7.3	285	24	9	17	364	49	202	a
Omapere, NZ	NG	30°	6.9	62	9	10	37	25	<1	295	a
Golden Spr., NZ	GS	45°	7.0	224	20	7	11	51	8	670	a
Lake Nyos, Cameroon	LN	23°	5.7	19	7	58	45	1	<1	724	a
Acque Albule, Italy	AA	22°	6.1	138	22	238	1042	163	1470	1403	a
Radkersburg, Austria	RA	72°	8.9	2215	182	47	3	264	398	4130	a
Te Aroha, NZ	TE	79°	8.1	2920	67	4	7	540	1260	6830	a
Geothermal Wells, Springs											
Ngawha NG-9, NZ	NG	230°	7.7	893	79	0.110	3	1260	18	185	a
Jubilee Pool, NZ	NG	56°	7.2	842	72	1.600	9	1180	174	393	a
Wairakei, WK-66, NZ	WK	240°	8.5	995	142	0.040	17	1675	30	<5	a
Champagne Pool, NZ	WK	99°	8.0	1070	102	0.400	26	1770	26	76	b
Broadlands BR-11, NZ	BR	260°	7.4	675	130	0.011	1	964	41	376	a
Ohaki Pool, NZ	BR	98°	7.1	860	82	0.100	3	1060	100	680	b
Miravalles 10,C. Rica	MV	250°	7.8	1750	216	0.110	59	2910	40	27	a
Sal. Bagaces, C. Rica	MV	74°	8.6	2063	85	6.600	33	2700	102	739	a
Zunil ZQ-3, Guatem.	ZU	295°	8.1	933	231	0.012	15	1810	31	51	a
Zunil Spring	ZU	95°	7.0	384	32	39	17	172	234	635	a
Cerro Prieto, Mexico	CP	280°	7.3	5600	1260	0.270	333	10500	14	40	b
Spring N29, Mexico	CP	80°	7.6	5120	664	4.600	357	8790	31	65	b
Tongonan, Philipp.	TO	330°	7.0	3580	1090	0.200	128	6780	16	12	b
Banati Spring, Phil.	TO	98°	8.3	1990	210	0.400	86	3400	74	7	b
Morere Spring, NZ	MO	47°	7.0	6690	84	79	2750	15670	<3	28	a
Salton Sea, Well, USA	SS	330°	5.2	38400	13400	10	22010	118400	4	140	b
Seawater	SW	4°	7.8	10760	390	1290	410	19340	2710	140	
Rock solutions											
basalt	BA	-	-	1900	800	4500	6700	28650	-	-	c
granite	GR	-	-	2800	3300	200	1900	11240	-	-	c
average crustal rock	AC	-	-	2400	2100	2300	4200	19740	-	-	c

refs. a - this work, b - Henley et al. (1984), c - Taylor (1964)

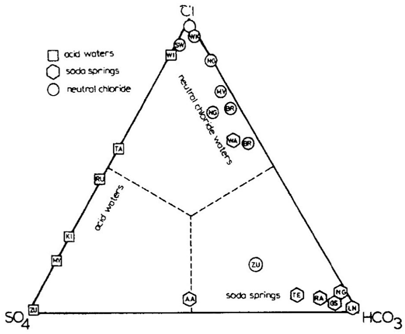


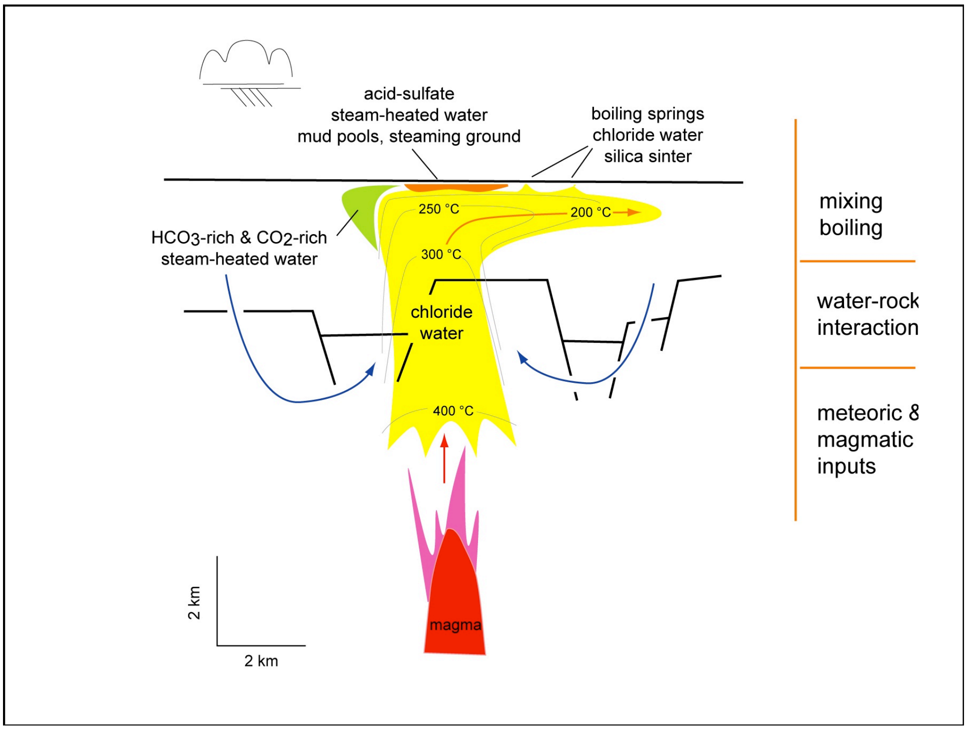
FIG. 2. Relative Cl, SO_4 and HCO_3 contents (mg/kg) of waters listed in Table 1.

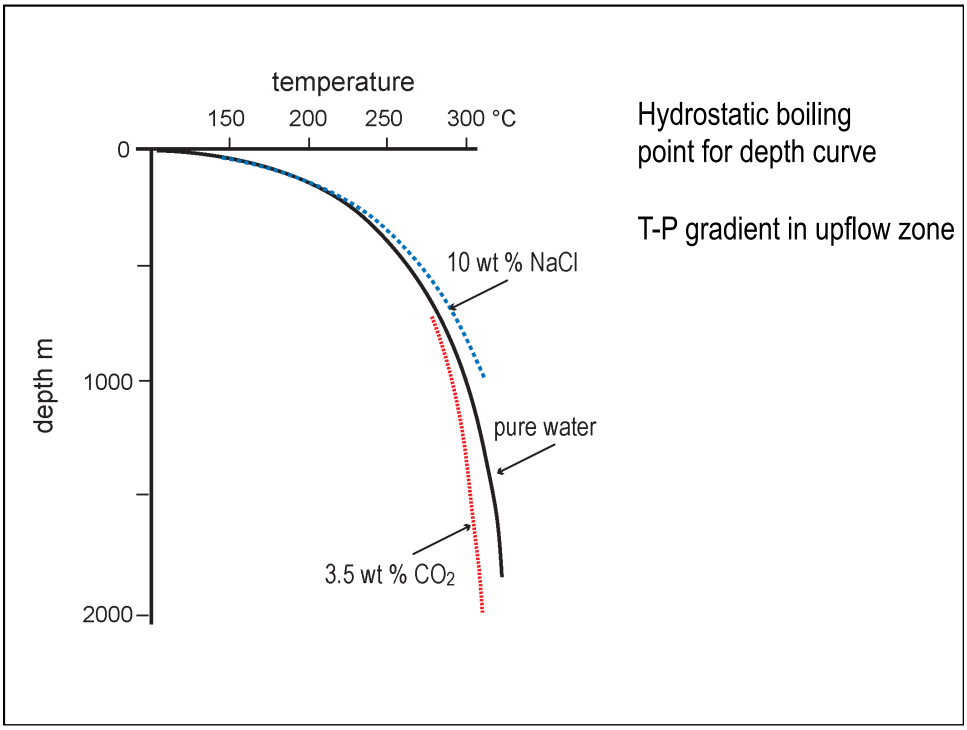
3 main water types

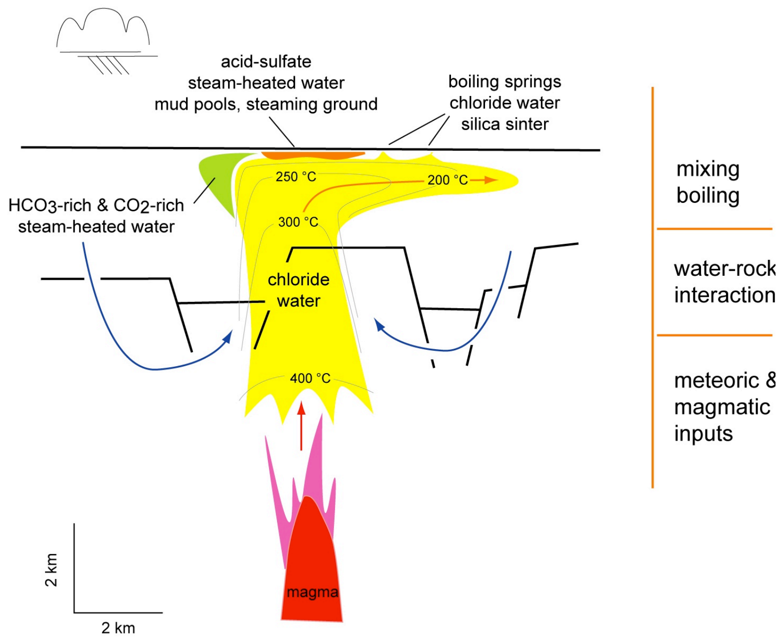
Ternary/Triangular graphs

Geothermal Waters (mg/kg)

	Chloride	Acid Sulfate	Bicarbonate
pH20°C	8.0	1.8	7.0
Na	1070	4	398
K	102	6.2	31
Cl	1770	<2	30
SO4	26	1047	96
HCO3	76	-	8492
SiO2	338	151	190


acid-sulfate
steam-heated water
mud pools, steaming ground
boiling springs
chloride water
silica sinter
250 °C
200 °C
300 °C
HCO3-rich & CO2-rich
steam-heated water
chloride
water
400 °C
magma
2 km
2 km
mixing
boiling
water-rock
interaction
meteoric &
magmatic
inputs


temperature
150
200
250
300 °C
0
1000
2000
depth m
10 wt % NaCl
pure water
3.5 wt % CO2
Hydrostatic boiling
point for depth curve
T-P gradient in upflow zone



Geothermal Waters (mg/kg)

	Chloride	Acid Sulfate	Bicarbonate
pH20°C	8.0	1.8	7.0
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SiO_2	338	151	190


boiling overflowing
chloride spring
Waiotapu


geyser
chloride water
silica sinter
El Tatio, Northern Chile

Discharge of a production well-chloride water

photo J. Hedenquist

Geothermal Waters (mg/kg)

	Chloride	Acid Sulfate	Bicarbonate
$pH_{20°C}$	8.0	1.8	7.0
Na	1070	4	398
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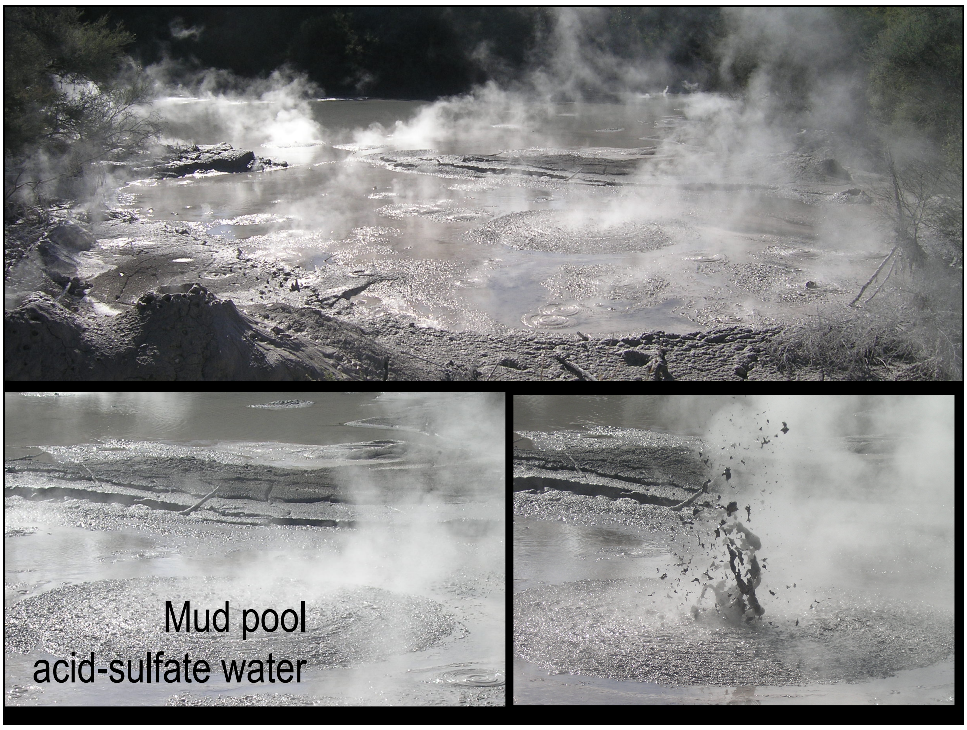
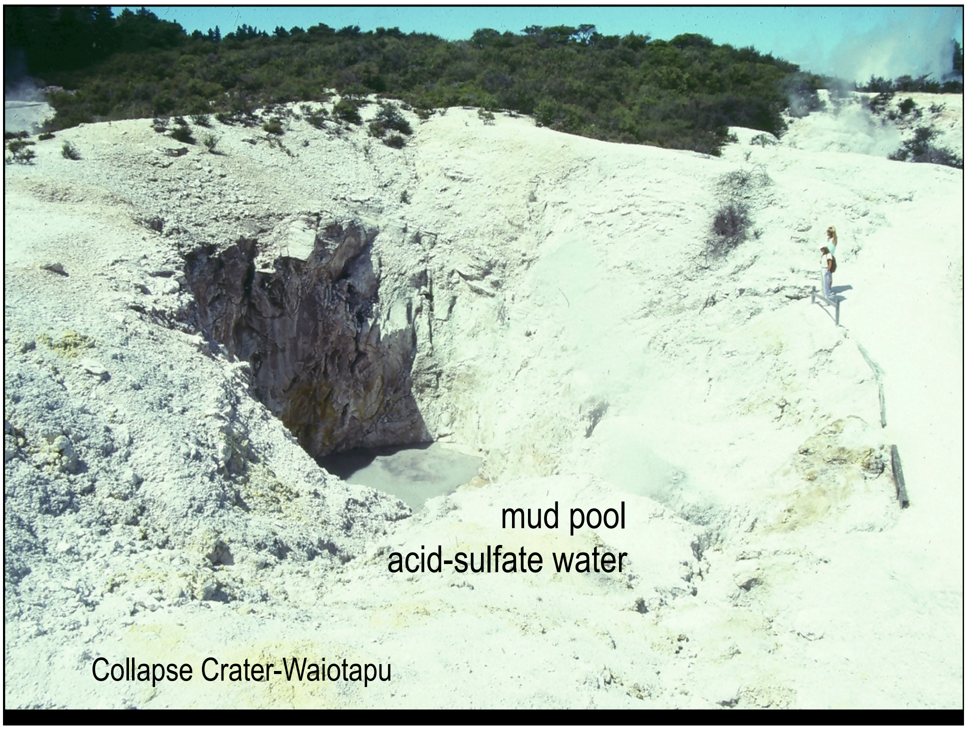
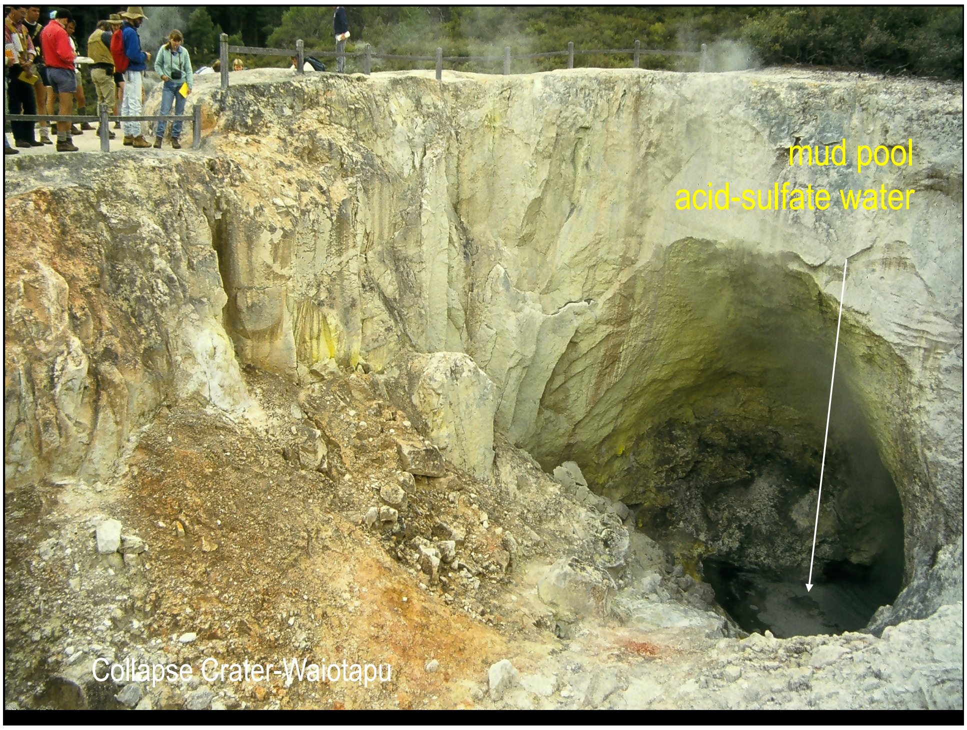
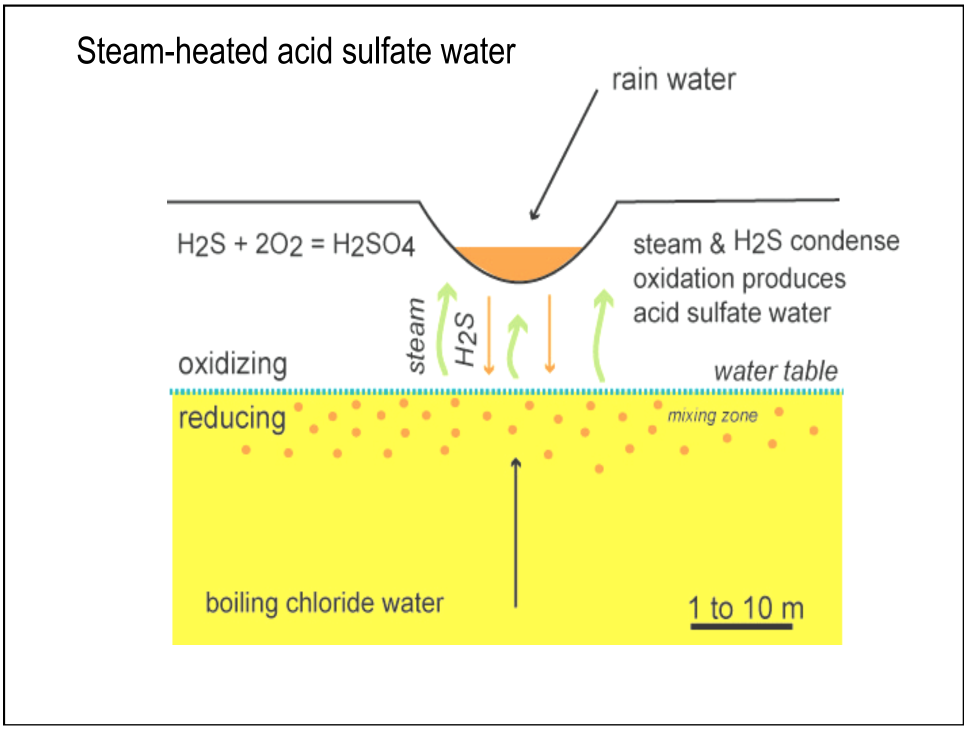
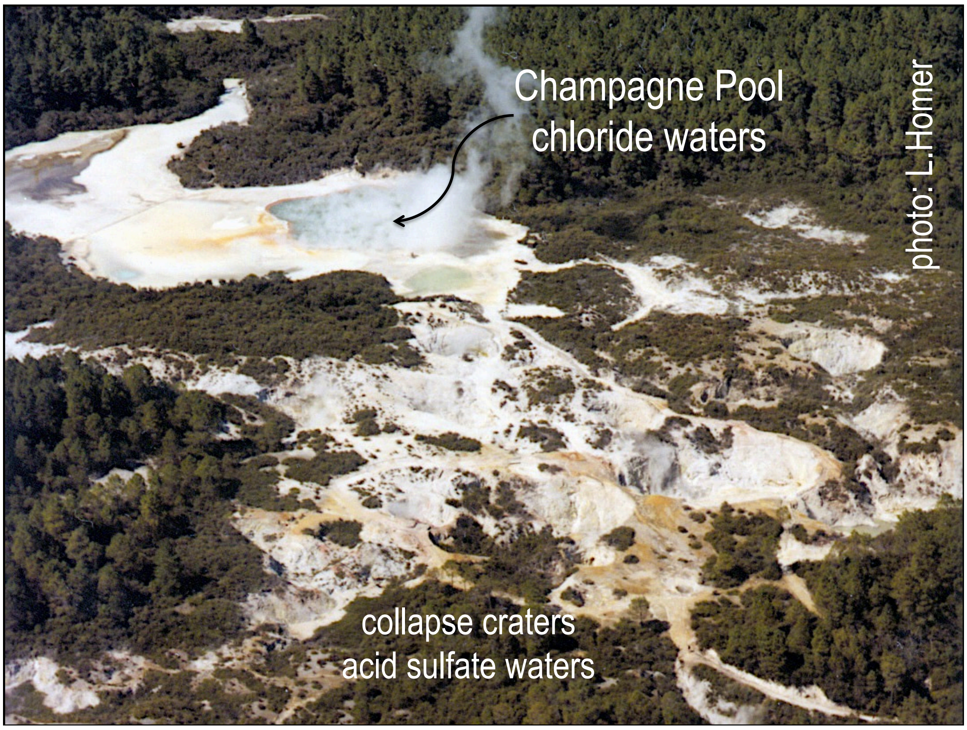

Mud pool
acid-sulfate water


mud pool
acid-sulfate water
Collapse Crater-Waiotapu

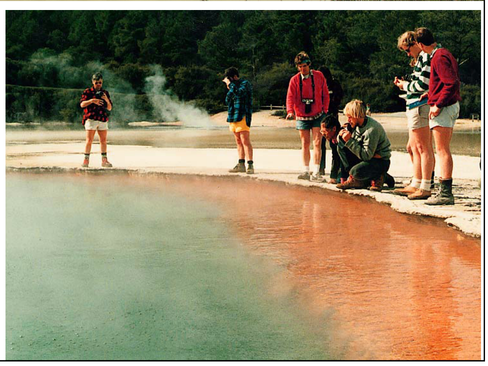

mud pool
acid-sulfate water
Collapse Crater-Waiotapu

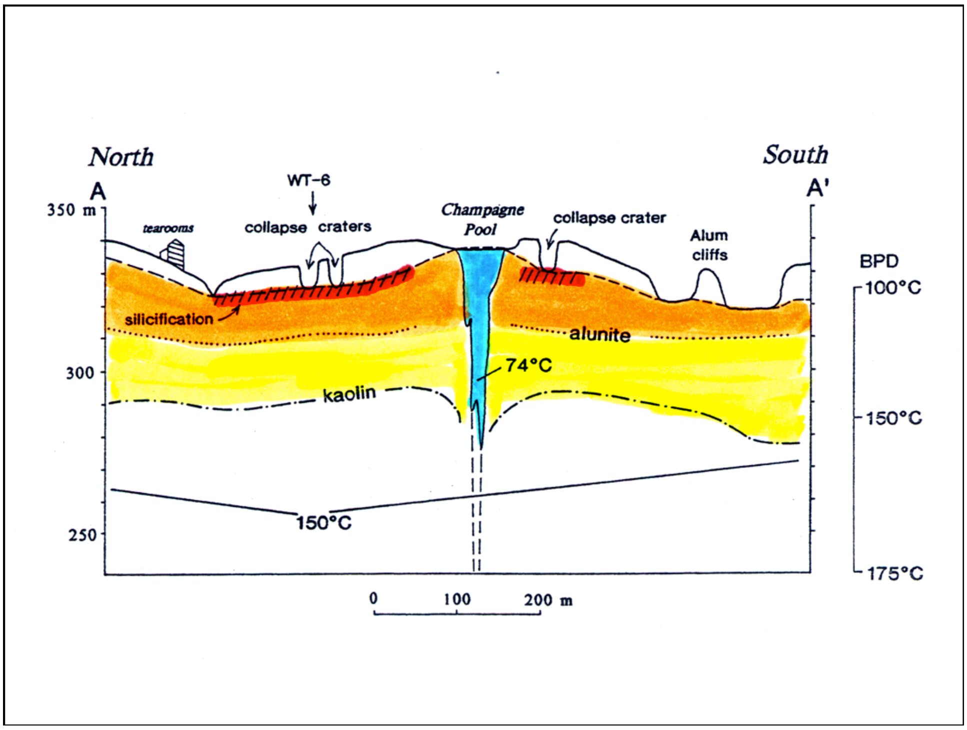

Steam-heated acid sulfate water
rain water
$H_2S + 2O_2 = H_2SO_4$
steam & H_2S condense
oxidation produces
acid sulfate water
steam
H_2S
oxidizing
water table
reducing
mixing zone
boiling chloride water
1 to 10 m

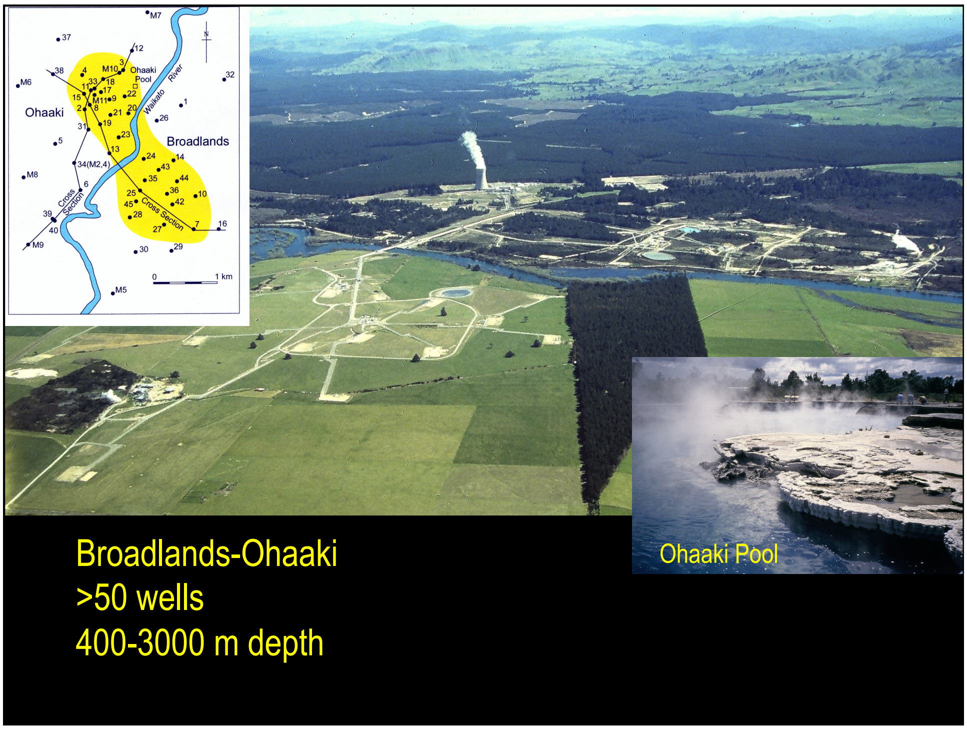


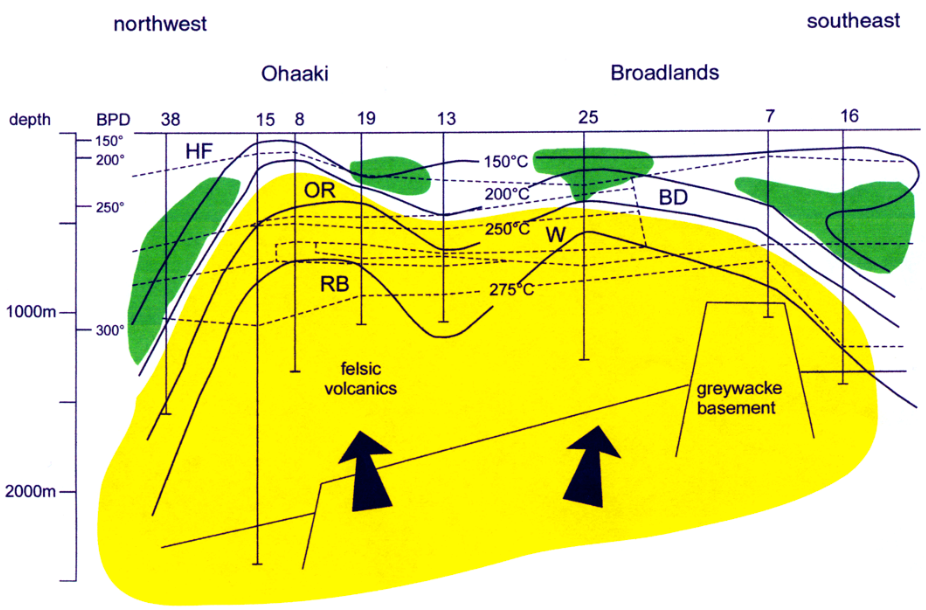
Champagne Pool
chloride waters

As-Sb-Tl-Hg sulfides
540 ppm Au, 750 ppm Ag




North
South
A
A'
350 m
300
250
tearooms
WT-6
collapse craters
Champagne Pool
collapse crater
Alum cliffs
silicification
alunite
74°C
kaolin
150°C
BPD
100°C
150°C
175°C
0
100
200 m

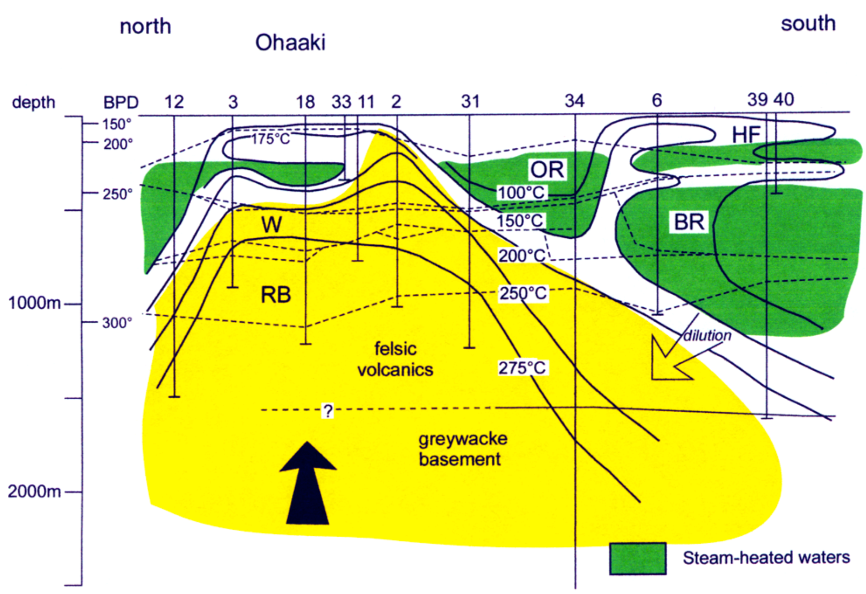

Ohaaki
Broadlands
Ohaaki Pool
Waikato River
Cross Section
0
1 km
Broadlands-Ohaaki
>50 wells
400-3000 m depth
Ohaaki Pool

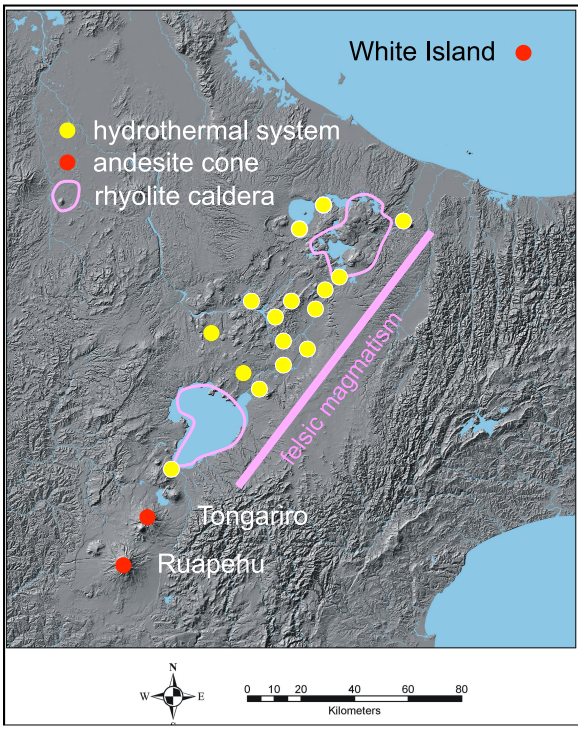


Geothermal Waters (mg/kg)

	Chloride	Acid Sulfate	Bicarbonate
pH20°C	8.0	1.8	7.0
Na	1070	4	398
K	102	6.2	31
Cl	1770	<2	30
SO4	26	1047	96
HCO3	76	-	8492
SiO2	338	151	190

CO2-rich waters





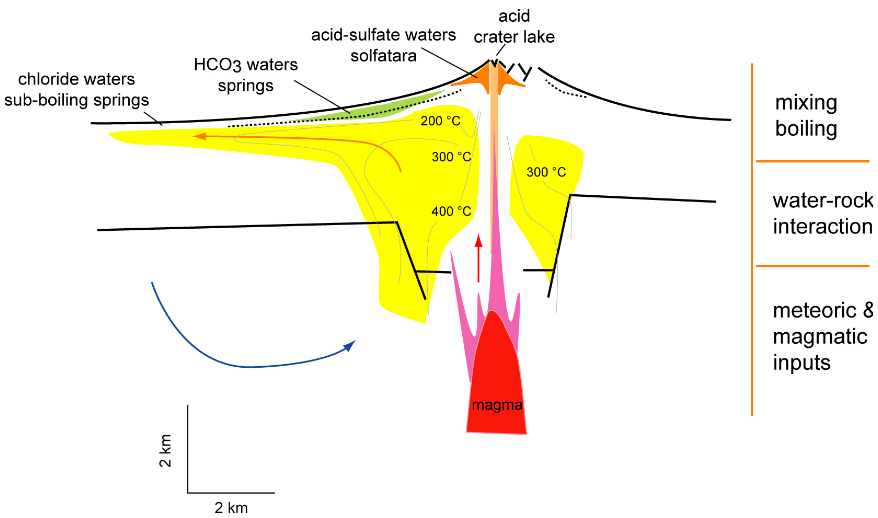
Central TVZ

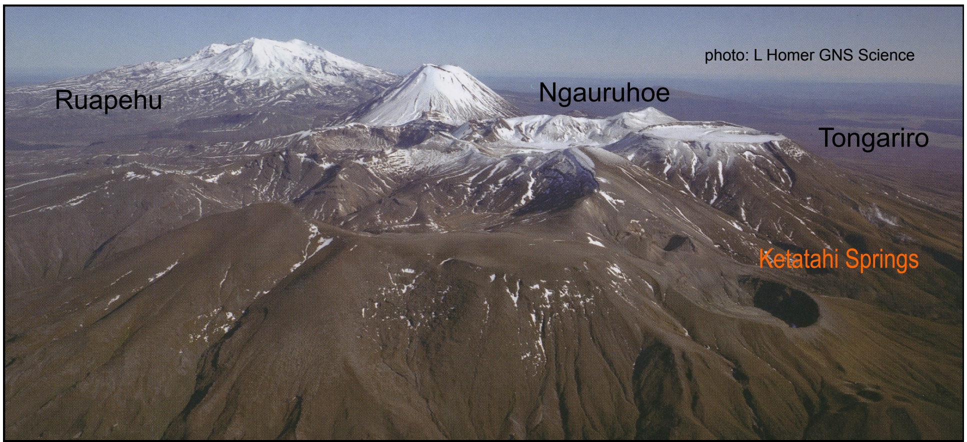
Flat terrain

predominantly rhyolite magmatism

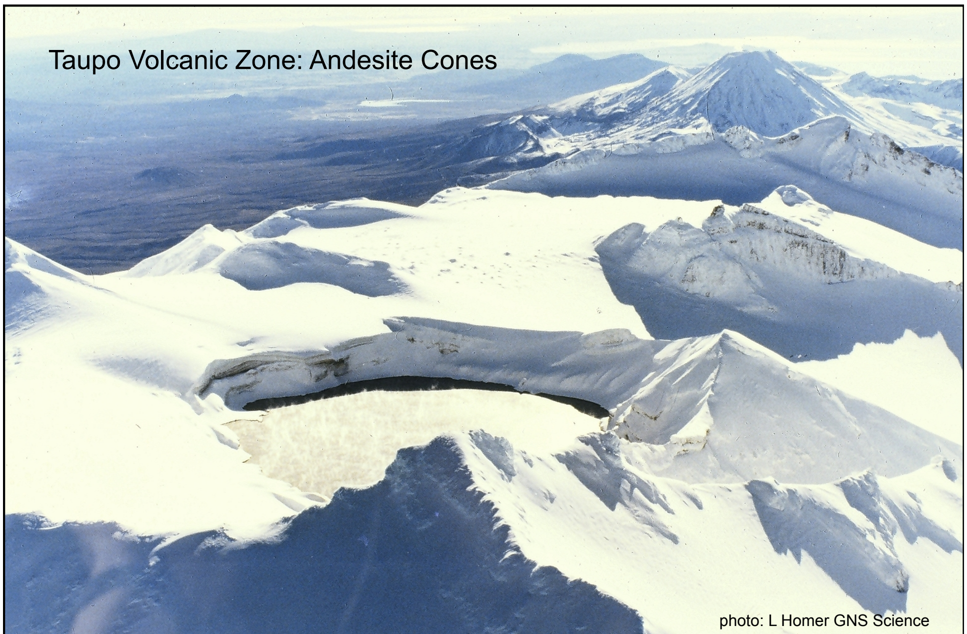
concentrated geothermal activity

High temperature system in steep terrain

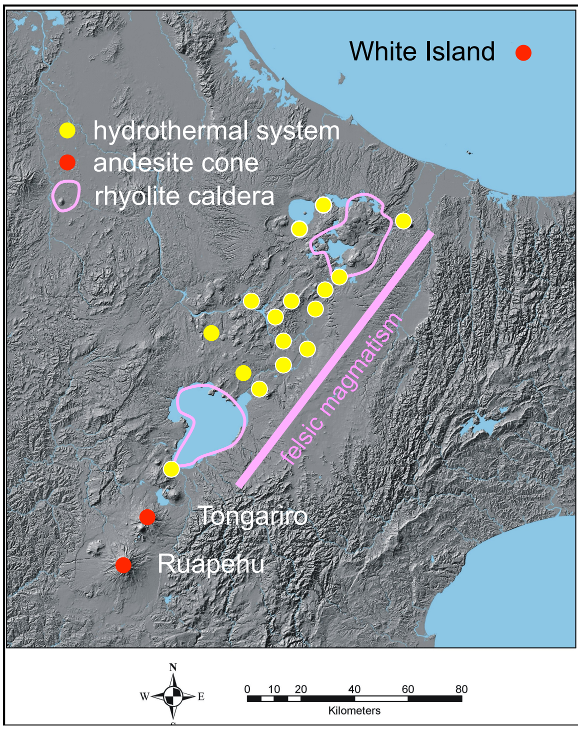




Tongariro and Ngauruhoe andesitic cones, with fumaroles and hot springs (Ketatahi -- 95 to 135° C) on upper flank.



Ruapehu volcano and summit crater lake filled wth acid water, 2700 m elevation.



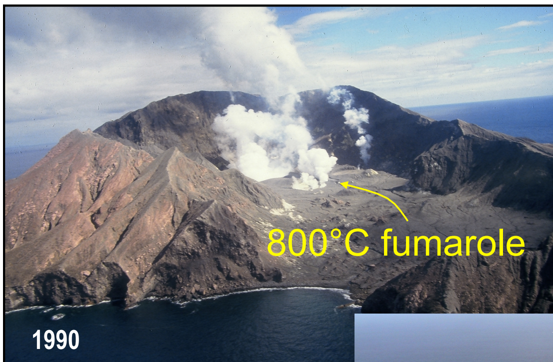
<u>Southern & Northern TVZ</u>

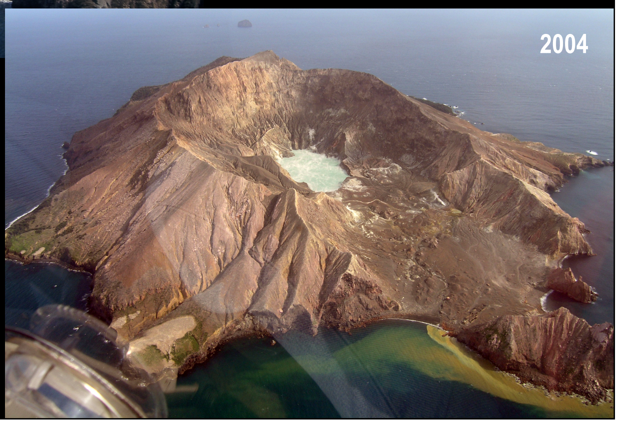
Steep terrain-volcanic cones

predominantly andesitic magmatism

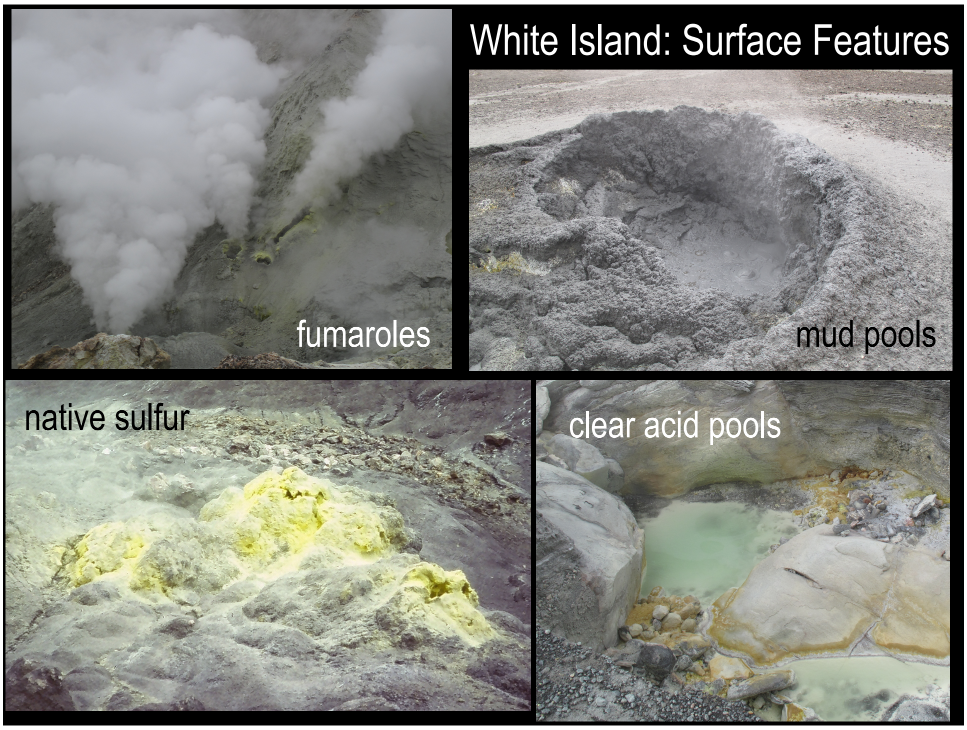
White Island-unique setting

White Island



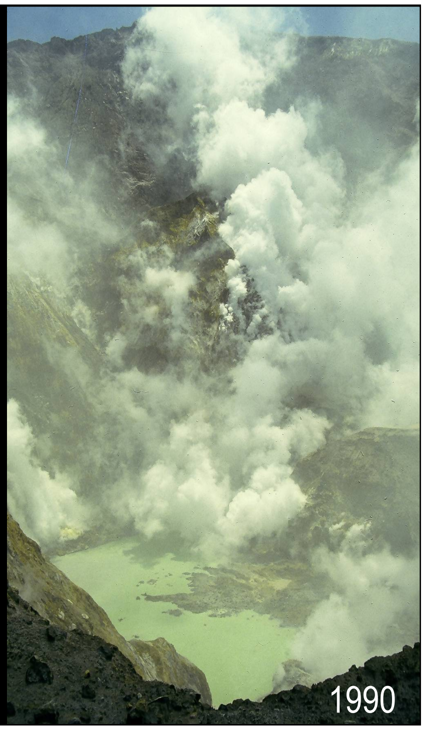


Rapid changes in volcanic activity: days, weeks, years



Acid sulphate chloride water

T°C	79
pH	1.4
Na	5910 ppm
K	635 ppm
Cl	38700 ppm
SO4	4870 ppm
HCO3	0 ppm



Summary--Origins of thermal waters: Chloride waters

Chloride waters are the predominant fluid type in many geothermal systems. They are deeply circulated and evolve through interaction of descending meteoric waters and magmatic volatiles at the base of the convection cell, followed by water-rock interaction as the water ascends the thermal plume. As is typical of deep waters, they are very clear (no suspended particles) and have a blue color in natural springs. They are commonly near neutral pH, being either slightly acidic (lower than neutral pH) or alkaline (higher than neutral pH) generally as a function of the amount of dissolved CO_2. The occurrence of silica sinter deposits is characteristic of boiling chloride springs.

Summary--Origins of thermal waters: Acid-sulfate waters

Acid sulfate waters are low in chloride content and occur in volcanic geothermal areas where steam condenses into surface waters. The sulfate content is highly variable and in geothermal areas it derives from oxidation of hydrogen sulfide (H_2S) in the vadose zone (the subsurface region above the water table). The oxidation of H_2S creates sulfuric acid (H_2SO_4). Geothermal acid sulfate waters form in the shallowest parts of the system above the regional water table, therefore they give little indication as to the nature of the deeper parts of the system. The composition of these waters reflects the dissolution of country rock due to their acid nature, hence they typically contain high concentrations of suspended materials such as a mud pot. Acid-sulfate waters also exist on the flanks and at the summits of active volcanoes and contain appreciable concentrations of chloride (>1000 ppm Cl). In fact the presence of high Cl is the main means of distinguishing acid-sulfate waters of volcanic origin from acid-sulfate waters of steam-heated origin. The source of chloride like sulfate is due to absorption of HCl-SO_2 bearing volcanic gas into meteoric water filled depressions (e.g. a summit crater lake).

Summary--Origins of thermal waters: Bicarbonate waters

Bicarbonate waters, also referred to as CO_2-rich waters, contain low chloride with bicarbonate as the major anion plus variable sulfate. In systems dominated by volcanic country rocks, bicarbonate waters typically form in the marginal and shallow subsurface region where CO_2 gas is absorbed and steam is condensed into cool ground waters; the condensation of steam heats the ground waters hence the term steam-heated is often used. Sodium is generally the main cation, since calcium carbonate (e.g. calcite) is not very soluble and potassium and magnesium are fixed in clays. In contrast to acid sulfate waters, bicarbonate waters form beneath the water table where they are weakly acidic (causing casing damage at Broadlands-Ohaaki), but loss of dissolved CO_2 during ascent to the surface increases the pH of the natural discharge to neutral or slightly alkaline.
In some geothermal systems (e.g Yellowstone and Valles, USA), the formation of bicarbonate waters is influenced by the presences of limestone rock units in the subsurface, and springs discharging at the surface deposit travertine ($CaCO_3$) sinters.

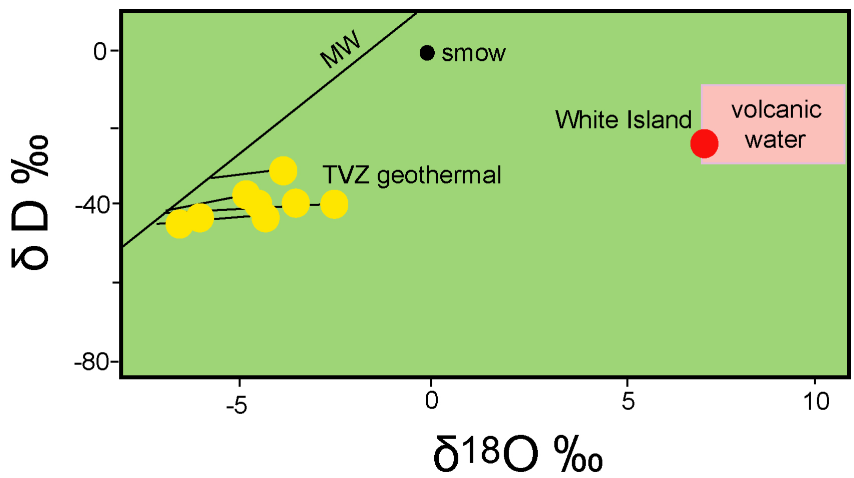
Summary--Origins of thermal waters: Brines

Brines are waters containing high concentrations of solutes; sea water is a common example. Chloride is the principal component, constituting 10,000 to >100,000 ppm, with high concentrations of Na, K, and Ca for charge balance. The pH is weakly acid due to the strong solute concentration. Brines in geothermal systems form in different ways; e.g. connate brines trapped in sedimentary basins, dissolution of evaporite sequences by meteoric waters. In some cases, the density of concentrated brines is sufficiently high so that they do not rise (e.g. Salton Sea, California).

Stable Isotopes: D/H vs $^{18}O/^{16}O$ ratios

meteoric water (MW)
volcanic water

sea water (smow)
geothermal waters (NZ)



K-Na (t>180° C)

Fournier $t°C = \frac{1217}{\log(Na/K) + 1.483} - 273$

Giggenbach $t°C = \frac{1390}{\log(Na/K) + 1.75} - 273$

- Fluid-mineral equilibria at >180 ° C

  $NaAlSi_3O_8 + K^+ = KAlSi_3O_8 + Na^+$

- Temperature dependent equilibrium; experiments and theory.
- Na-spar (albite) & K-spar (adularia) are common in hydrothermally altered volcanic rocks in the reservoir
- Nil to minor re-equilibration in rapidly rising waters
- Effects of mixing & dilution are commonly small
- Effect of boiling also small

K-Mg (t>100° C)

Giggenbach $t°C = \frac{4410}{14 - \log(K^2/Mg)} - 273$

- Fluid-mineral equilibria at >100 ° C

  0.8 K-mica + 0.2 Mg-chlorite + 5.4 Chalcedony (SiO_2) + 2 K^+ =
  2.8 K-feldspar + 1.6 H_2O + Mg^{+2}

- Temperature dependent equilibrium; theory-only.
- K-mica, Mg-chlorite, K-spar & quartz (chalcedony) are common in hydrothermally altered volcanic rocks in the reservoir, extending sometimes to shallower depth
- K-Mg tends to re-equilibrate faster than K-Na, hence it tends to give cooler temperatures; i.e. $T_{KNa} \geq T_{KMg}$
- Very sensitive to mixing with ground water (cold, steam-heated)

deep chloride waters contain	0.01 to 0.1 ppm Mg
ground waters contain	> 1 ppm Mg

Geothermometers (aqueous)

$$t°C = \frac{1390}{\log(\text{Na/K}) + 1.75} - 273$$

Reformulations of fluid-mineral equilibria into numeric expressions that allow calculation of an "equilibration" temperature

The numeric expressions are simple, requiring input of concentrations from water analyses.

They are very easy to apply, but much more difficult to interpret.

Getting the right interpretation is more important than computing temperature.

There are several things to consider.

Aqueous Geothermometers: Basic Assumptions

Fournier (1992)

1. Based on fluid-mineral reactions that reach equilibrium
2. The equilibrium condition is controlled by temperature
3. Adequate amounts of mineral(s) exist to control the equilibrium concentrations of aqueous components (e.g. SiO_2, Na^+, K^+, Mg^+)
4. There is no re-equilibration of the fluid as it rises to the surface via a geothermal well or fault-fracture conduit; i.e. requires rapidly rising waters
5. The concentrations or ratios of aqueous components are unaffected by steam loss, mixing or dilution

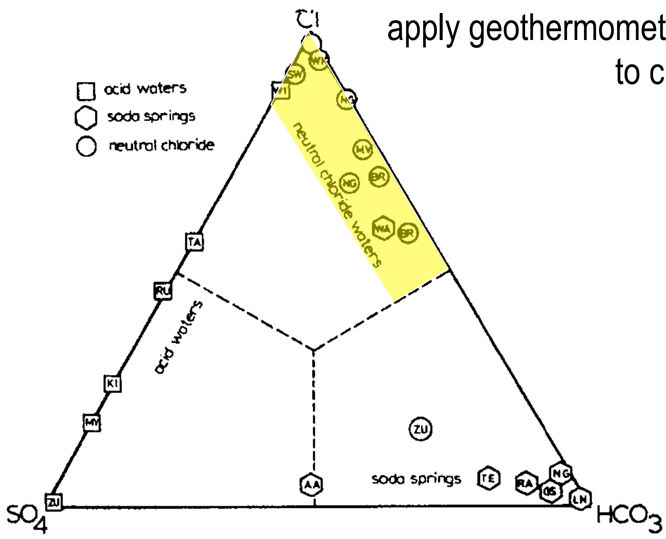
Aqueous Geothermometers: Basic Assumptions

The first three assumptions are probably good for a few reactions that occur in many places. These reactions occur in rock dominated environments where water is trapped in pores spaces making the rock mass greater than the liquid mass.

The last two assumptions are probably not valid for many geothermal fluids so that information is obtained only about the upper part of those systems, or a limiting minimum temperature is indicated.

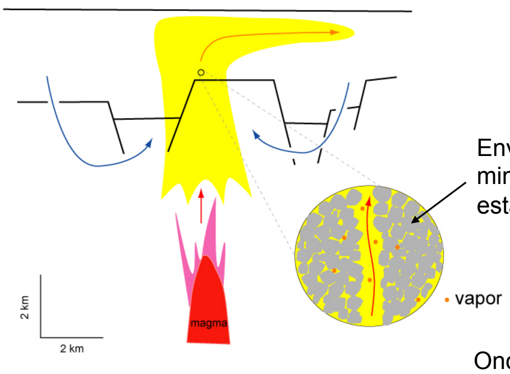
Near neutral pH alkali chloride waters are the most informative for geothemometry. Acid sulfate waters in which constituents are leached from surface rocks are not suitable as geothermometers. Bicarbonate waters can give mixed results.

Fluids from geothermal systems in which sea water circulates may give misleading temperatures because the high salinities prevent establishment of fluid-mineral equilibrium but this is rare.



apply geothermometers (aqueous) to chloride waters

Aqueous Geothermometers: Fluid-Mineral Equilibria



Environment in which fluid-mineral equilibria is established

Once the fluid enters the vertical conduit, the influence of fluid-mineral equilibria is reduced unless flow velocity is very slow

Quartz-SiO_2 (t>100° C): no steam loss

$$t°C = \frac{1309}{5.19 - \log c_{SiO_2}} - 273$$

Limitations? Assumptions?

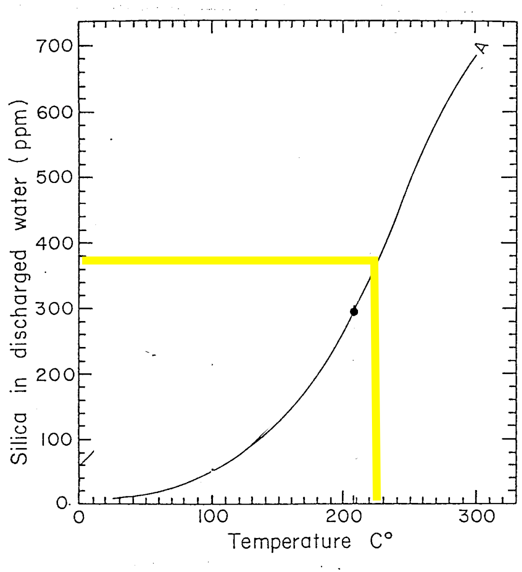
c_{SiO_2} is concentration in mg/kg (ppm) units

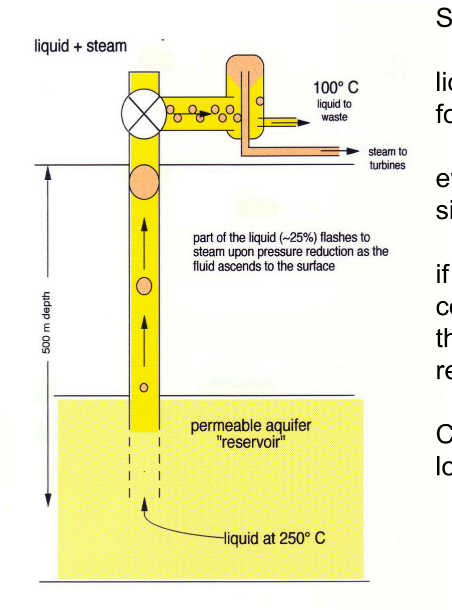
- Fluid-mineral equilibria $SiO_2 + 2H_2O = H_4SiO_4$
- Temperature dependent equilibrium; experiments and theory.
- Quartz (SiO_2) is common in hydrothermally altered volcanic rocks & also many sedimentary, igneous & metamorphic rocks
- Re-equilibration in rapidly rising waters tends to be slow
- Effects of boiling (steam loss) & mixing/dilution are significant
- Only used in low enthalpy (sub-boiling) geothermal systems

Quartz-SiO_2

A hot spring water contains 370 mg/kg SiO_2.

At what temperature is this concentration in equilibrium with quartz?





Steam loss effect on silica

liquid enters well and steam forms in well due to decompression

evaporation of steam concentrates silica in the aqueous phase

if no quartz deposits, then the silica concentration of the liquid reaching the surface is greater than the reservoir water.

Can we calculate the effect of steam loss on the silica concentration?

Quartz-SiO_2 (t>150° C): maximum steam loss

$$t°C = \frac{1522}{5.75 - \log c_{SiO_2}} - 273$$

Limitations? Assumptions?

c_{SiO_2} is concentration in mg/kg (ppm) units

- Fluid-mineral equilibria $SiO_2 + 2H_2O = H_4SiO_4$
- Temperature dependent equilibrium; experiments and theory.
- Quartz (SiO_2) is common in hydrothermally altered volcanic rocks & also many sedimentary, igneous & metamorphic rocks
- No re-equilibration in rapidly rising waters especially production wells; in boiling chloride springs surrounded by silica sinter, amorphous silica saturation limits T_{qtz} to ≤ 220 °C
- Effects of boiling (steam loss) & mixing/dilution are significant; only used in high enthalpy (boiling) geothermal systems

Considerations of the Quartz-Silica Geothermometer

- works best for waters having subsurface t>100°C in low enthalpy systems & t>150°C in high enthalpy systems ; i.e. applicable to a wide range of geothermal waters
- strong effects of steam separation associated with subsurface boiling
- strong effects of mixing associated with subsurface flow
- aqueous SiO_2 controlled by solids other than quartz (e.g. amorphous silica in sinter surrounding chloride pools)
- SiO_2 precipitation after sampling (requires treatment, usually acidification or dilution)
- effect of pH on quartz solubility (small at pH<9 which is typical of most chloride waters)
- used for determining feed temperatures in production wells
- always calibrate against temperature, enthalpy and other equilibration temperatures