

Workshop Module

# GEOCHEMISTRY FOR GEOTHERMAL DEVELOPMENT

Yogyakarta, 21-25 August 2017

**BPSDM, Ministry of Energy and Mineral Resources**  
in collaboration with  
**Universitas Gadjah Mada - Utrecht University -**  
**Geocap Capacity Building Programme**



Universiteit Utrecht

Workshop Module

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# Geochemistry for Geothermal Development

Yogyakarta, 21-25 August 2017

By:  
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**BPSDM, Ministry of Energy and Mineral Resources**  
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# 01 Geothermal System

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**GEOCHEMISTRY FOR GEOTHERMAL DEVELOPMENT**  
**UGM – UU – Geocap Capacity Building Program**  
**21 – 25 August, 2017**



Bird's eye view of the Darajat geothermal field, West Java  
(Courtesy of INAGA)

## **01. GEOTHERMAL SYSTEM**

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Adapted from geothermal lecture handouts by Pri Utami at the Postgraduate Study Program, Geological Engineering UGM and Geothermal Institute, The University of Auckland.



### **Geothermal Systems | Pri Utami**

#### **1.1. Definition**

##### **Geothermal Energy**

Geothermal is a source of heat energy contained in hot water, steam, and rock along with other associated minerals and gases that are genetically inseparable in a geothermal system.

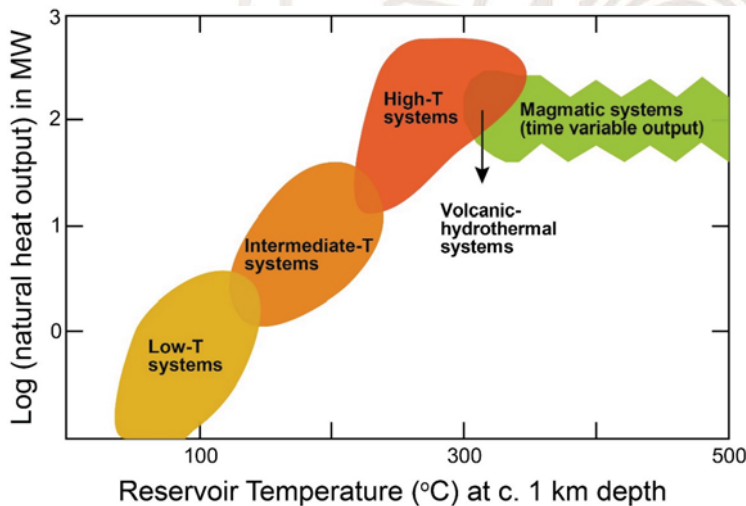




## Geothermal System

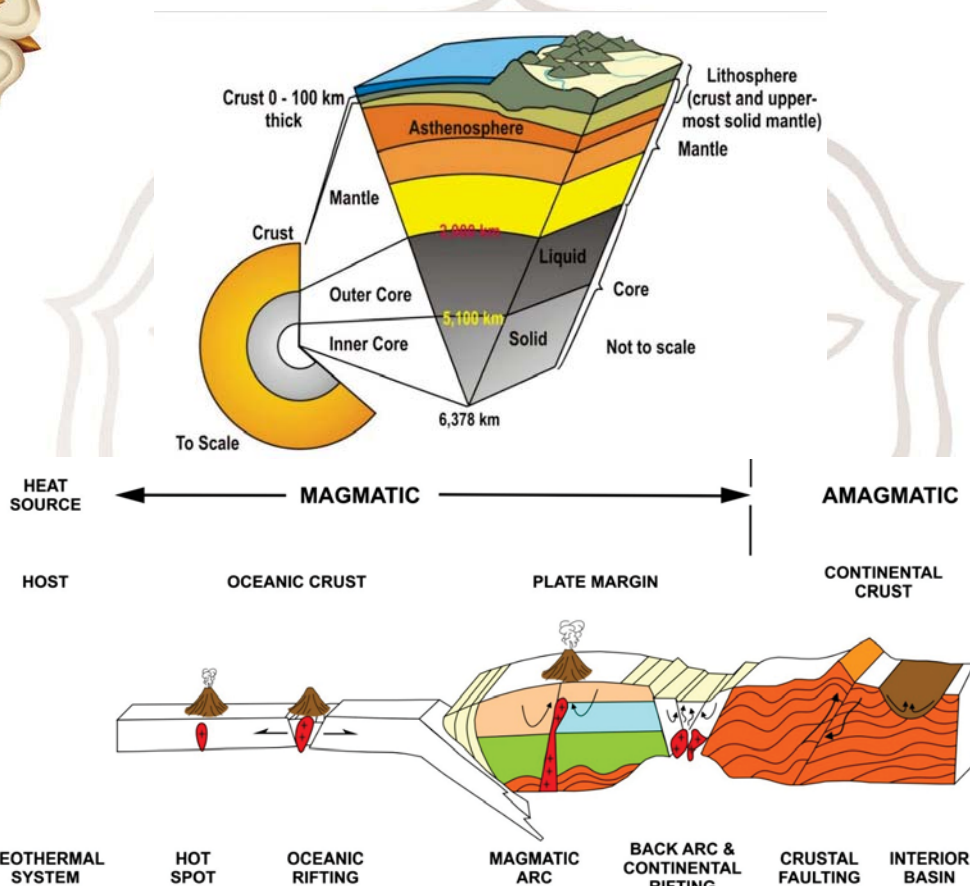
A general term that describes natural heat transfer within a confined volume of the Earth's crust where heat is transported from a "heat source" to a "heat sink," usually the free surface (Hochstein and Browne, 2000).

## Classification



(adapted from Hochstein & Browne 2000)

There are several bases of classification of geothermal systems, e.g. the degree of convection, reservoir temperature, fluid phase, geologic setting (tectonic, affiliation with magmatism, volcanism, landform).



Adapted from Corbett and Leach (1998)





Resource	(a)	(b)	(c)	(d)	(e)
Low temperature resources	< 90	<125	<100	≤150	≤190
Intermediate temperature resources	90-150	125-225	100-200	-	-
High temperature resources	>150	>225	>200	>150	>190

Temperature in °C

Source:

(a) Muffler and Cataldi (1978).

(b) Hochstein (2000).

(c) Benderitter and Cormy (1990).

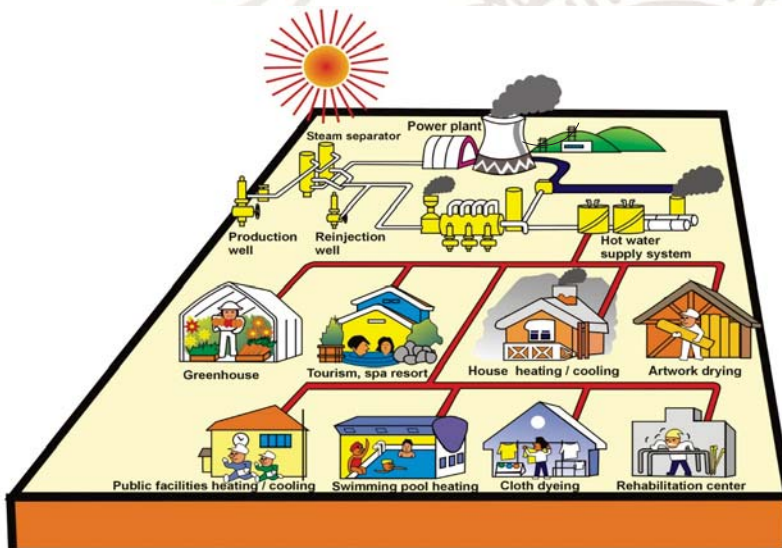
(d) Nicholson (1993).

(e) Axelsson and Gunnlaugsson (2000)

([www.geothermal-energy.org](http://www.geothermal-energy.org))



The type of geothermal system that is now economically most feasible is where **magmatic intrusions** are emplaced high enough in the crust that they induce **convective circulation of groundwater**.



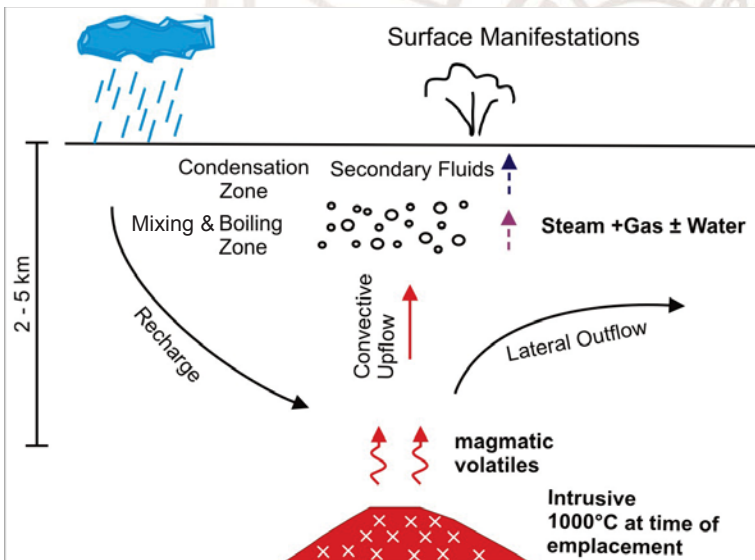
There are other types of geothermal systems (a-magmatic) such as those occurring due to heat sweep through deep-reaching fractures, or deep basin brines, but these are too cool, too deep, or too saline to allow economic generation of electricity.



## 1.2. Types of geothermal systems

### Hydrothermal system

A type of geothermal system where heat is transferred from a heat source (often a cooling pluton) to the surface by “free convection,” involving “meteoric” fluids with or without traces of magmatic fluids.



Liquids discharged at or near the surface are replenished by “meteoric” water derived from the outside (“recharge”) that is drawn in by the rising fluids.



### Volcanic system

A type of geothermal system where heat and mass is transferred from an igneous body (usually a magma chamber) to the surface involving convection of magmatic fluids and sporadic discharge of magma (subsurface melts); meteoric fluids are not involved in the heat transfer process, or are minor.

### Volcanic-hydrothermal systems (also called magmatic hydrothermal system)

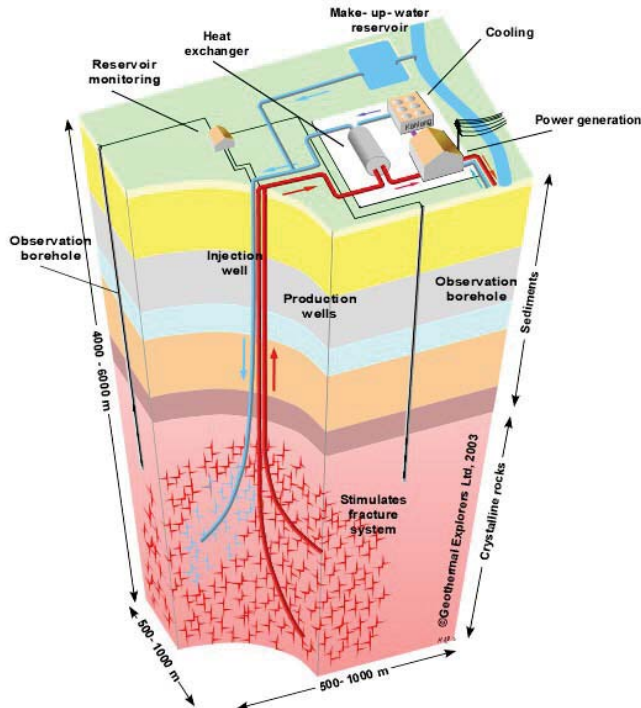
A combination of a “hydrothermal” and a “volcanic” system, where ascending magmatic (primary) fluids commonly mix with meteoric (secondary) fluids (rarely sea water).





## Other types of geothermal system

### Hot Dry Rock Geothermal System



High-pressure water is pumped through a specially drilled well into a deep body of hot, compact rock, causing its *hydraulic fracturing*.

The water permeates these artificial fractures, extracting heat from the surrounding rock, which acts as an "enhanced" reservoir.

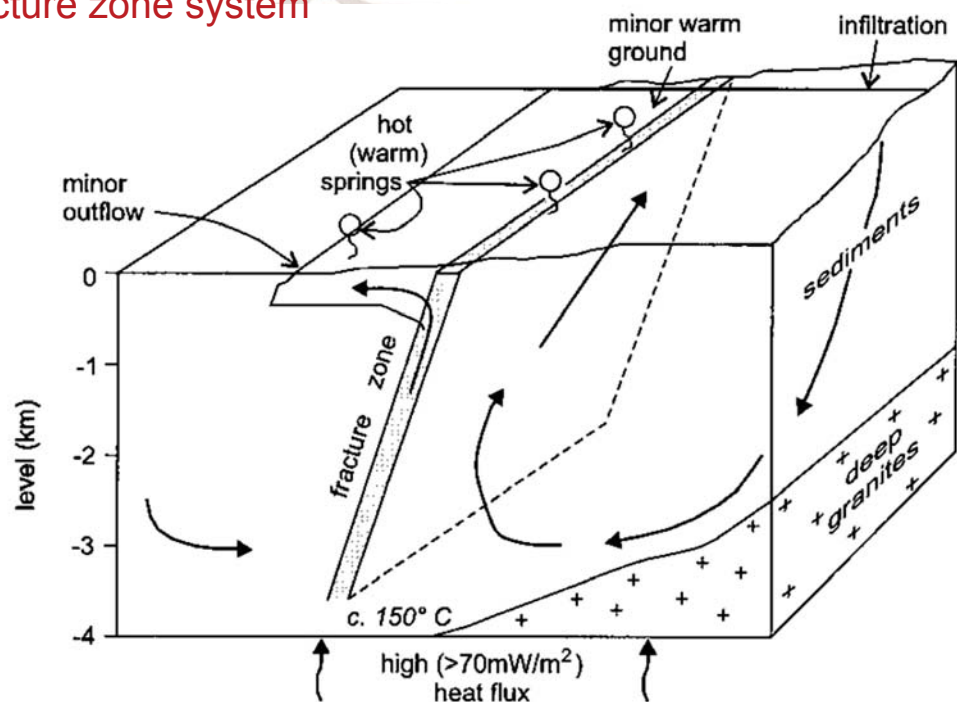
This 'reservoir' is later penetrated by a second well, which is used to extract the heated water.

First HDR experiment: Los Alamos, New Mexico (in 1970)

Other projects: Soultz-sous-Forêt (France), Habanero (Australia), Landau (Germany), Desert Peak (USA)



## Fracture zone system



Conceptual model of a heat sweep system (free convection) discharging hot fluids through a deep reaching fracture zone (fracture zone system). The heat source gives a higher than normal terrestrial heat flow; this setting can occur far away from active margins and volcanism. The model is based on the Fuzhou system in South China (Hochstein and Browne, 2000).





### 1.3. Geothermal Systems in Global Tectonic Settings

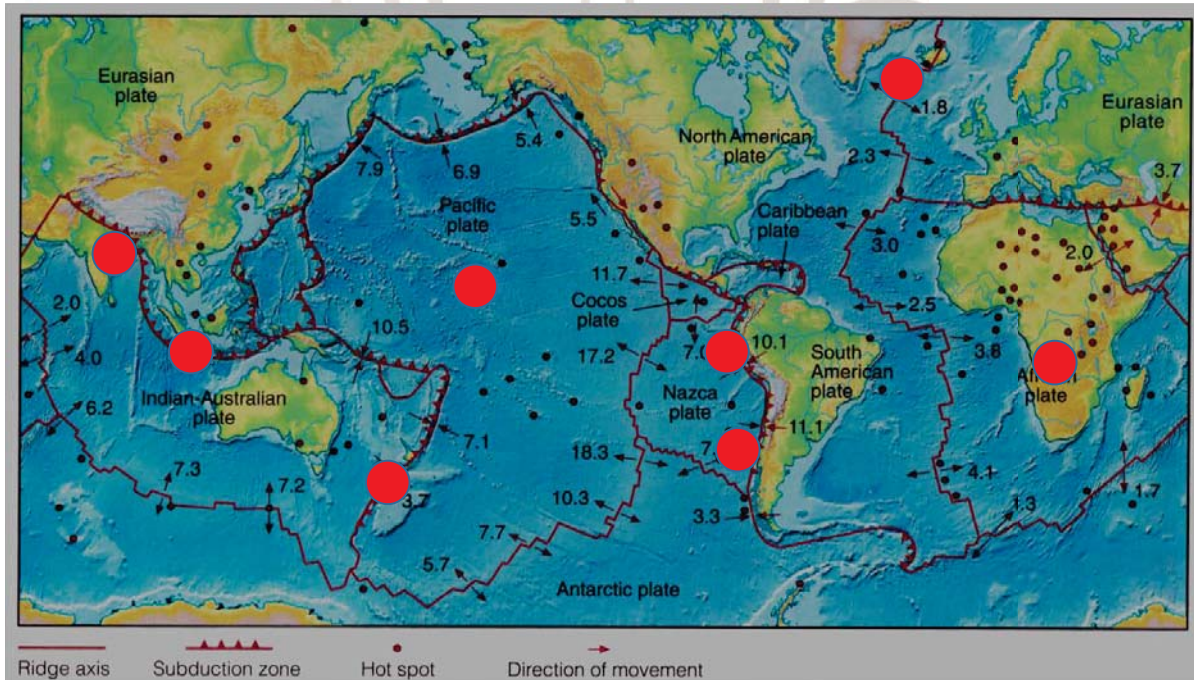


Plate tectonic map (Wicander and Monroe, 2001)

Large red dots: sites of high-temperature geothermal systems representing typical tectonic settings. Numbers: velocity of plate movement in cm/yr.



### Geothermal fields in Indonesia



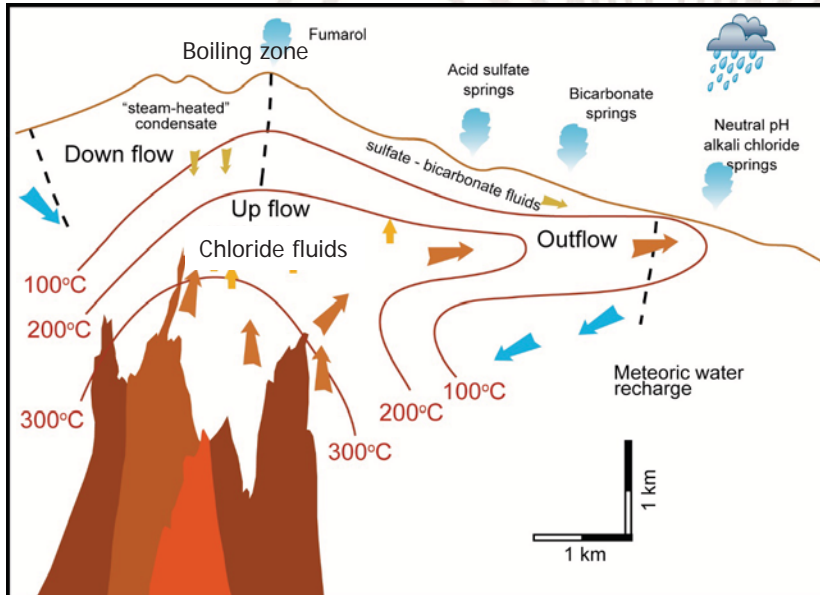
GEOTHERMAL PROJECTS IN BIDDING STAGE (785 MW)	PROPOSAL/STUDY (345 MW)	PPA SIGNED/PREPARATION FOR EXPLORATION (1425 MW)	CONSTRUCTION STAGE (620 MW)
<ol style="list-style-type: none"><li>1. Seulawah (2x55 MW)</li><li>2. Pusuk Bukit (2x55 MW)</li><li>3. Sipoholon (1x20 MW)</li><li>4. Bontol (60 MW)</li><li>5. Way Ratai (1x55 MW)</li><li>6. Danau Ranau (2x55 MW)</li><li>7. G. Endut (1x40 MW)</li><li>8. G. Ceremai (2x55 MW)</li><li>9. Umbul Telomoyo (1x55 MW)</li><li>10. Sembalun (1x20 MW)</li><li>11. Mataloko (20 MW)</li><li>12. Merana/Masaingi (2x10 MW)</li><li>13. Songa Wayau (1x5 MW)</li><li>14. Bora Pulu (40 MW)</li><li>15. Oka Ile Ange (10 MW)</li></ol>	<ol style="list-style-type: none"><li>1. Karaha 2 &amp; 3 (110 MW) COD 2020</li><li>2. T. Perahu (60 MW) COD 2020</li><li>3. Iyang Angopuro (1x55 MW) COD 2021</li><li>4. Sarula III (110 MW) COD 2024</li><li>5. Bedugul (1x10 MW)</li></ol>	<ol style="list-style-type: none"><li>1. Rajabasa (220 MW) COD 2023 &amp; 2024</li><li>2. Ungaran (1x55 MW) COD 2021</li><li>3. Ijen (2x55 MW) COD 2020</li><li>4. Alitadi (1x5 MW) COD 2019</li><li>5. Jaboi (2x5 MW) COD 2019 &amp; 2020</li><li>6. Sorik Merapi (3x60 MW) COD 2021 &amp; 2022</li><li>7. C. Cisukrame (1x50 MW) COD 2020</li><li>8. Rawa Dano (1x110 MW) COD 2020</li><li>9. T. Perahu I (110 MW) COD 2020</li><li>10. Tampomas (1x45 MW) COD 2020</li><li>11. Guci (1x55) COD 2021</li><li>12. Batu Raden (2x110 MW) COD 2021 &amp; 2023</li><li>13. Telaga Ngebel (3x55 MW) COD 2020 &amp; 2021</li><li>14. Sokoria (6x5 MW) COD 2020, 2021, 2022, 2023</li></ol>	<ol style="list-style-type: none"><li>1. Sarulla I (330 MW) COD 2017 &amp; 2018</li><li>2. Ulubelu 3 &amp; 4 (110 MW) COD 2016 &amp; 2017</li><li>3. Lumut Balai 1 &amp; 2 (110 MW) COD 2017 &amp; 2019</li><li>4. Karaha Bodas (30 MW) COD 2016</li><li>5. Lahendong 5 &amp; 6 (40 MW) COD 2017 &amp; 2018</li></ol>
PPA DISCUSSION/ RENEGOTIATION (438 MW)	EXPLORATION (745 MW)	READY FOR EXPLOITATION/ Fin. CLOSED (365 MW)	PRODUCTION STAGE (1430,5 MW)
<ol style="list-style-type: none"><li>1. S. Sekincau (158 MW) COD 2024</li><li>2. W. Windu (2x110 MW) COD 2020</li><li>3. Hu'u (2x10 MW) COD 2024</li><li>4. Jailolo (40 MW) COD 2021/22/23</li></ol>	<ol style="list-style-type: none"><li>1. Muara Laboh (220 MW) COD 2017 &amp; 2024</li><li>2. Rantau Dadap (220 MW) COD 2019 &amp; 2020</li><li>3. Sungai Penuh (110 MW) COD 2024</li><li>4. Hululais (110 MW) COD 2019 &amp; 2020</li><li>5. Ulumbu (5 MW) COD 2019 &amp; 2021</li><li>6. Kota Moberu (80 MW)</li></ol>	<ol style="list-style-type: none"><li>1. Patuha (110 MW) COD 2019</li><li>2. Cibuni (10 MW) COD 2020</li><li>3. Lumut Balai 3 &amp; 4 (110 MW) COD 2024</li><li>4. Tulehu (20 MW) COD 2018 &amp; 2019</li><li>5. Dieng 2 &amp; 3 (115 MW) COD 2019</li></ol>	<ol style="list-style-type: none"><li>1. Sibayak (12 MW)</li><li>2. Kamojang (240 MW)</li><li>3. Wayang Windu (220 MW)</li><li>4. Gn. Salak (360 MW)</li><li>5. Darajat (255 MW)</li><li>6. Dieng (60 MW)</li><li>7. Ulumbu (10 MW)</li><li>8. Mataloko (1,5 MW)</li><li>9. Lahendong (80 MW)</li><li>10. Ulubelu 1 &amp; 2 (110 MW)</li><li>11. Patuha (55 MW)</li></ol>







## Geothermal system in high-relief volcanic terrain



- Volcanic island arc setting
- Andesitic volcanism
- Shallow igneous intrusion heat source
- Vapor zones are common
- Upflow is characterised by fumarolic and steam-heated type manifestations
- Primary chloride-type reservoir fluid may not reach the surface
- Long outflow structure
- Difficult to explore

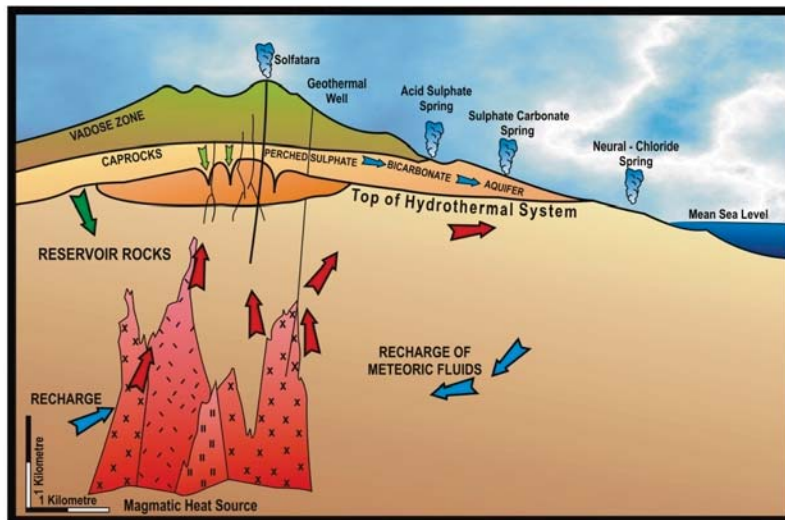
(diagram adapted from Corbett and Leach, 1994).



Lunch break



## 1.4. Components of geothermal systems

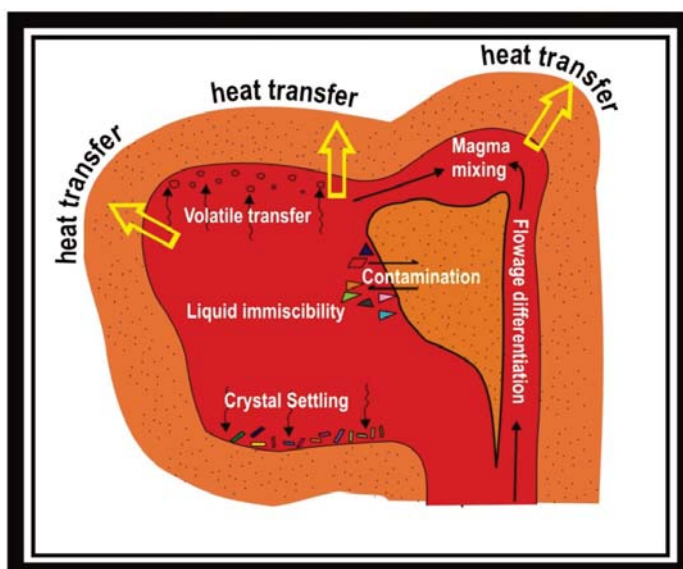


Let's have a closer look to the components of a convective, volcano-hosted geothermal system.

- Heat source
- Reservoir
- Recharge fluids
- Discharge at the surface (thermal manifestations)



### Magmatic heat source



Magmatic heat source that is required to generate a potential geothermal system is an igneous intrusive rock:

Emplaced at a relatively shallow depth (~2 to 7 km ?).

Still transferring heat to its surroundings.

Multiple intrusions are generally long lived e.g., Palinpinon (Rae et al, 2004), Ngatamariki (Arehart et al, 2002).

The cooling igneous intrusions transfer heat and magmatic volatiles ( $H_2O$ ,  $CO_2$ ,  $SO_2$ ,  $HCl$ ,  $HF$ ...) to the surrounding rocks and fluids.

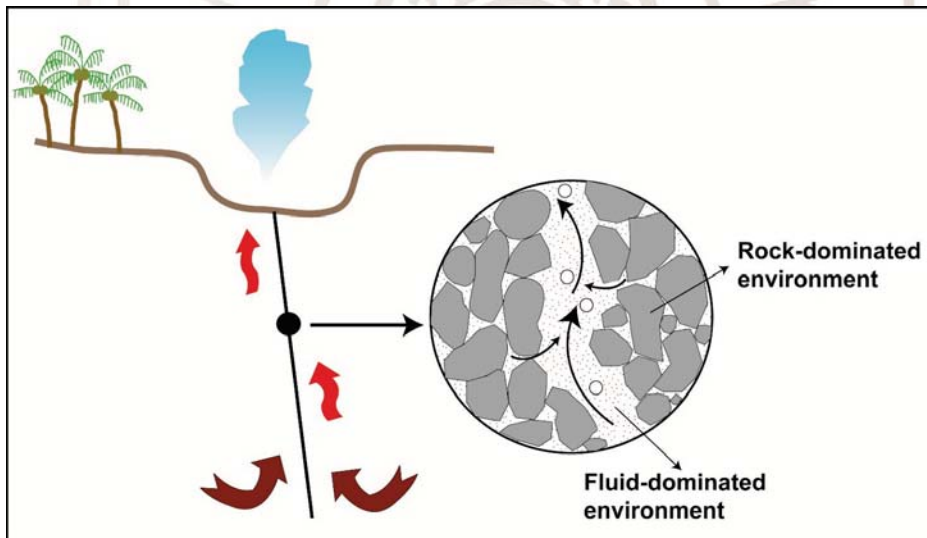




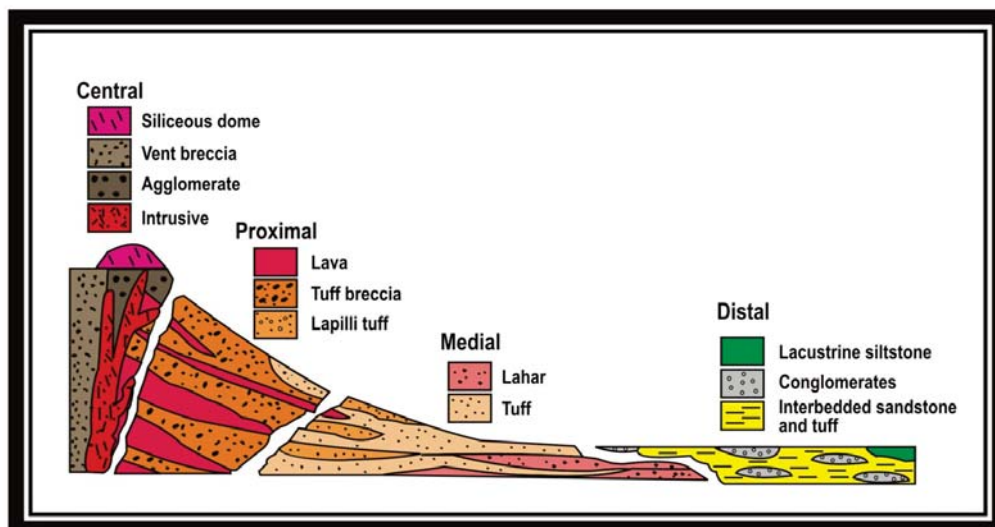
## Reservoir rocks

Any type of rock (igneous, volcanoclastics, sedimentary, metamorphic) that has **permeability** can be a geothermal reservoir.

Permeability is the capability of rock to pass fluids.



## Reservoir rocks

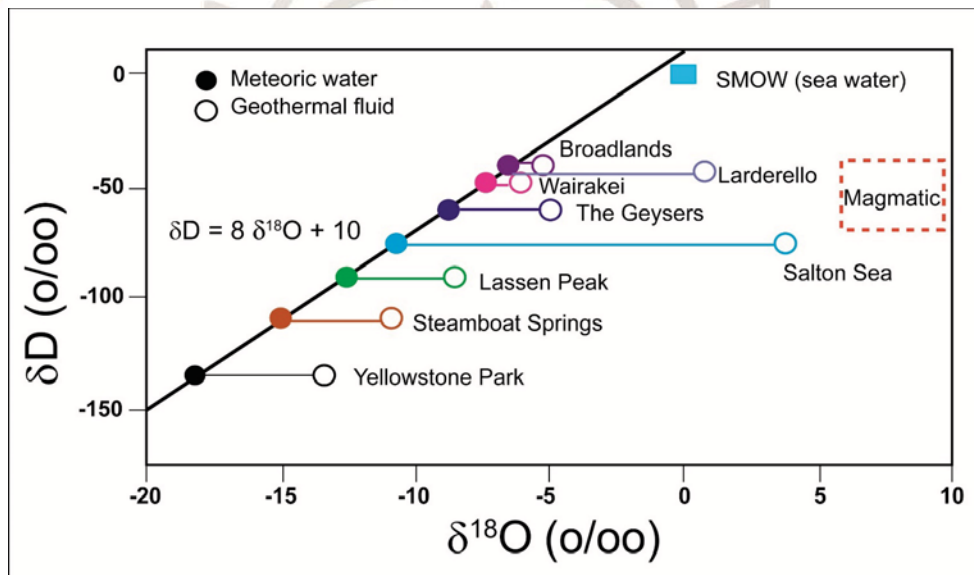


In volcanic terrain fluids move through: (Bogie and Mackenzie, 1998)

- Inter granular porosity
- Contact between two different lithologies
- Fractures, joints and faults



## Recharge fluids



(From Nicholson, 1993)

### Origin of hydrothermal fluid – isotopic study

- Similar  $\delta D$  content of hydrothermal fluids and meteoric water.
- Positive shift of  $\delta^{18}O$  due to fluid-rock interactions and minor magmatic contributions.
- Bulk of hydrothermal fluids is of meteoric origin.



## 1.5. Thermal Manifestations in Volcano-hosted Geothermal System

### Topography and hydrologic structures

Hydrology of convective geothermal systems is determined by topography.

Surface manifestations can be used as guides to understand hydrological structure of the systems.

- Systems in low-relief terrain
- Systems in high-relief terrain



Wairakei geothermal field, NZ



Darajat geothermal field, Indonesia





Most of convective geothermal systems manifest themselves at the surface. The types and occurrences of the manifestation, and the total heat discharged at the surface are controlled by:

- Heat input at the bottom of the reservoir.
- Reservoir parameters (e.g., permeability).
- Fluid parameters (e.g., density, viscosity, temperature).
- Hydrological framework of the system.
- Other factors controlling the outflow path of the hot fluids.

Thermal manifestations can be classified based on their mode of heat discharge.



### **Classification of surface discharge features**

Based on the mode of discharge of heat, active thermal manifestations can be classified into:

- a. Diffuse discharge (i.e. warm ground, steaming ground, evaporation at the free water surface).
- b. Direct/concentrated discharge (i.e. warm and hot springs, steam vents, fumaroles, etc).
- c. Intermittent discharge (i.e. geyser).
- d. Catastrophic discharge (i.e. hydrothermal eruption).
- e. Concealed discharge (i.e. seepage, concealed outflows).





## 1. Diffuse discharge

### Warm ground, steaming ground, evaporation on a free water surface

#### Warm ground

Warm ground can be found over parts of the reservoir of systems which come to surface, usually around features with intense heat discharge such as steaming ground and hot pools.

Its existence is recognized by measurement of thermal gradient (usually down to 1 m depth).

Vegetation is hardly affected by warm ground, unless the temperature gradient exceeds 25 to 30°/m

#### Steaming ground

Steam can originate either from:

- Shallow evaporating subsurface hot water, or
- Flashing at greater depth

Vegetation growth stops or stunts when the temperature at 10 – 15 cm depth is near boiling point; free steam can be detected in the surface.



The term 'steaming ground' has been used to describe thermal manifestations where vapor from the upper part of a liquid- or vapor-dominated geothermal reservoir reaches the surface (Hochstein & Bromley, 2005).

A steep temperature gradient develops close to the surface, which enhances heat transfer by conduction within a thin near-surface soil layer. Some minor steam can be diffusively discharged through the surface but significant steam is often discharged directly to the air through cracks, vents and fumaroles.



Steaming ground, El Tatio geothermal system, Chile (photograph by P.A. Letelier)





Evaporation from hot Champagne pool, Waioatapu thermal area, NZ.



Warm ground, Rotorua lakeshore, NZ.



## 2. Direct (concentrated) discharge:

Warm & hot spring, gas/ steam vent, fumarole, mud pots/pools

### Warm and hot springs

Warm and hot springs are associated with all types of geothermal systems.

“Warm” springs,  $T < 50^{\circ}\text{C}$ ; “Hot” springs,  $T > 50^{\circ}\text{C}$ .

Hot, acidic or slightly acidic springs are typical discharge features for steam-dominated and two-phase systems.

Hot, neutral pH chloride springs over a hot-water dominated system are often associated with silica sinter.







Near-neutral chloride hot spring, Tempang Village, Lahendong



Acid sulfate hot springs, Kasuratan Village, Lahendong



## Hot pools

Hot pools over hot water-dominated system often occupy the centre of ancient eruption features.

Over the steam-dominated system hot pools can occur over quenched fumaroles.

Division of hot pools:

- Calm pool (surface temperature < boiling point, small or no outflow).
- Boiling pool (surface temperature is at boiling point, usually accompanied by hot springs; example: Ohaaki pool).
- Ebullient pool (strong upwelling of water is the result of steam flashing at some depth beneath the pool).

*Only the outflow of pools should be sampled for an assessment of geochemistry.*

*Chemistry of stagnant pools can be very significantly different from that of nearby pools with outflow, due to concentration of constituents.*





## Mud pools & mud volcano



*Acid sulfate hot springs with mud pool and mud volcanoes, Linau thermal area, Lahendong.*

Minor steam and non condensable gases ( $\text{CO}_2$ ) discharge from numerous small vents.

Mud stays in a liquid state by condensation of steam, the upwelling of the liquid is caused by the discharge of  $\text{CO}_2$ .

Mud volcano is a special case of a mud pool where the gas discharge is confined to a single vent.



## Steam vents, solfatara, and fumaroles

**Steam vents** are features which discharge almost dry steam or a two-phase mixture of wet steam and some hot water.

A steam vent with significant sulfur deposition is called **solfatara**.

High content of  $\text{H}_2\text{S}$  in the steam discharge over a volcanic geothermal system can lead to the build up of sulfur mounds (e.g., Vanua Lava, New Hebrides; Tatun, Taiwan, Kawah Ijen, East Java)

Larger steam vents are called **fumaroles**.



Steam vent, Linau thermal area, Lahendong.



Fumarole, Linau Village, Lahendong, North Sulawesi.





The solfatara field of Kawah Ijen, East Java with sulfur deposit being mined.



### 3. Intermittent discharge

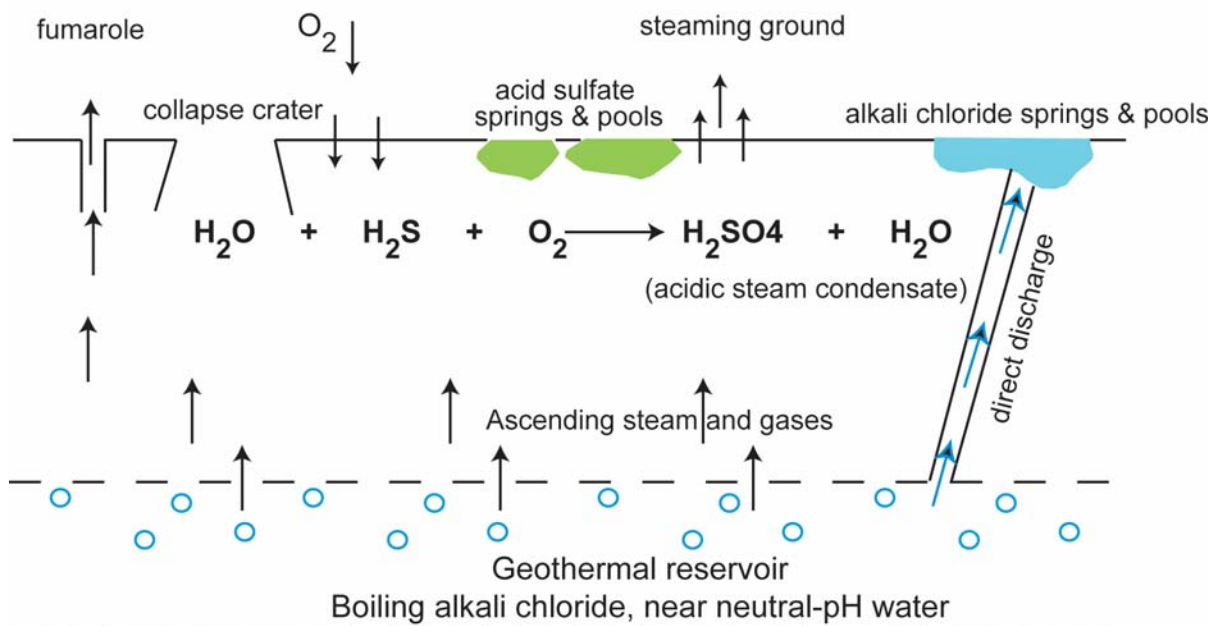
#### Geyser

A geyser is an eruption of hot water, steam and non-aqueous gas from a hydrothermal system, usually but not always with a cyclic frequency which ejects mostly only trivial amounts of solid material (Browne & Lawless, 2001).



Pohutu Geyser, New Zealand.





Schematic diagram showing the occurrence of thermal features and the near surface interactions (not to scale).



#### 4. Catastrophic discharge

##### Hydrothermal eruption

- An eruption ejecting at least some solid material, whose energy derived solely from heat loss and phase changes in a convective geothermal system (Browne and Lawless, 2001).
- Hydrothermal eruptions have occurred in many hot water-dominated geothermal fields and are potentially damaging to life and property.
- Not easy to predict but it is worthwhile to identify danger signs: evidence of previous hydrothermal eruptions, superheated steam emission or shallow gas accumulation, unstable steaming slopes that could lead to sudden removal of overburden, etc.



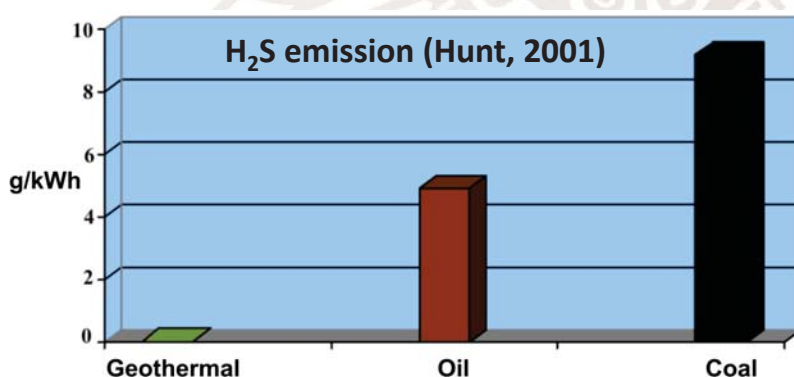
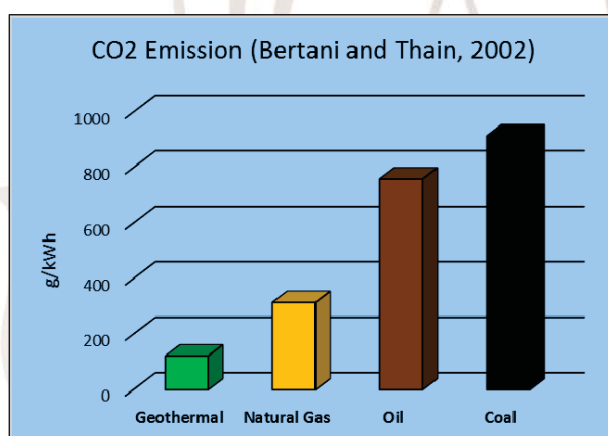


## 1.6. The Advantage of Geothermal Energy

- Environmentally friendly
- Renewable and can be used sustainably
- Indigenous and can be utilized in place
- Dissolved substances produced in the geothermal fluid is injected back into the reservoir to replenish the water that has been extracted
- Some solids are "by product" with economic value, such as  $\text{SiO}_2$ , S, Zn, etc.
- Sustainable: a long-lived magmatic heat source can ensure the sustainability of natural heat supply and is not expected to run out in human history
- Modest land use



## Advantages of geothermal energy (cyclic, high-temperature, magma-related systems)



### ENVIRONMENTAL-FRIENDLY

- Geothermal power production discharges very significantly much less pollutants than that of fossil fuels.





## RENEWABLE

Heat source and recharge fluids are both naturally renewed.

## SUSTAINABLE

- Geothermal systems are long-lived (Western Pacific: ~300 - 500 ka) and the produced thermal fluids are naturally recharged.
- There is engineering strategy to ensure their sustainability, i.e., re-injection of the extracted fluids for maintaining the heat and mass balance of the geothermal reservoir.



- Geothermal fluid whose heat has been extracted is re-injected into the deep reservoir, such that no thermal fluid is let to contaminate the surface/near surface environment.





### INDIGENOUS

Geothermal is an indigenous energy, meaning that it can only be directly utilized in place, and can not be transported elsewhere before being converted into electricity.

Being an indigenous energy resource, its development must be prioritized in order to elevate the prosperity of surrounding communities.

### RELIABLE

Being renewable, sustainable and indigenous, geothermal energy is reliable, because its supply is **INDEPENDENT** from seasoned or energy market fluctuations outside the country.

### MINOR LAND USE

Land required for surface facilities is relatively small ( $\sim 3.5 \text{ km}^2/100 \text{ MWe}$ ; Bromley et al, 2010)

## **02 Role of Geochemistry in Geothermal Development**

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(Universitas Gadjah Mada)



**GEOCHEMISTRY FOR GEOTHERMAL DEVELOPMENT**  
**UGM – UU – Geocap Capacity Building Program**  
**21 – 25 August, 2017**



**02. ROLE OF GEOCHEMISTRY IN GEOTHERMAL DEVELOPMENT**



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**Role of Geochemistry in Geothermal Development | Agung Harijoko**

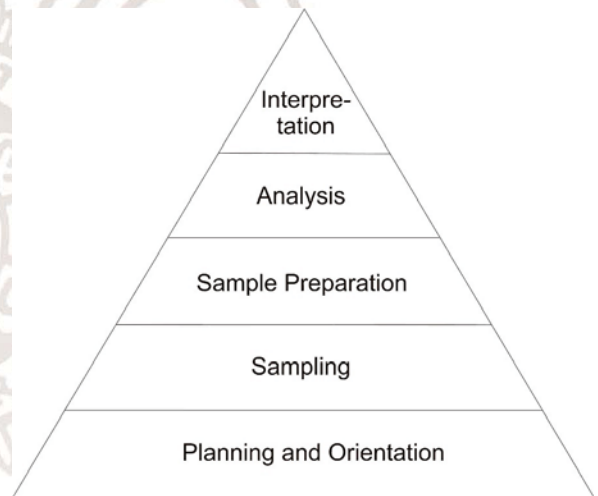


**2.1. Introduction**

- Definition of Geochemistry → branch of Earth Science that applies chemical principles to deepen an understanding of the Earth system and systems of other planets. (<http://earth.yale.edu/geochemistry>)
- Main goals in Geothermal Geochemistry Studies:
  - Identify the origin of geothermal fluids.
  - Quantify the processes governing their compositions and associated chemical and mineralogical transformations during water-rocks interaction.
  - Monitoring during production.
  - Environmental impact assessment.
- Other goals of geochemistry:
  - Monitoring during production.
  - Environmental impact assessment.



- Principles and Stages in Geochemical Studies
  - Planning and orientation
  - Sampling
  - Sample preparation
  - Analysis
  - Interpretation
- Basic philosophy:
  - Geothermal fluids on the surface (aqueous solutions or gas mixtures) reflect physico-chemical and thermal conditions in the geothermal reservoir at depth



## Physical and Chemical Characteristics of Geothermal Fluids

- Physical characteristics
  - Higher temperature than ambient temperature
  - One phase of water or 2- phase mixture of water and steam
- Chemical characteristics
  - Aqueous solutes and gas components
  - Major, minor elements and isotopes
  - Dissolved elements classified as conservative and reactive elements





## Role of Geochemistry in Geothermal Development | Agung Harijoko

Chemical composition of thermal and mineralized waters from New Zealand (WK,NG,MO,MU,WI), Guatemala (ZU), Costa Rica (MV), Colombia (RA,RB), Mexico (AR), India (MA), Thailand (FN), Solomon Islands (PR), Vanuatu (YA) and Cameron (LN) in mg/kg (Giggenbach, 1991)

Area	°C	pH	Li	Na	K	Rb	Cs	Mg	Ca	B	HCO <sub>3</sub>	SiO <sub>2</sub>	SO <sub>4</sub>	Cl
WK Wairakei, well	240	8.5	10.7	1170	167	2.20	2.00	0.01	20	26	5	590	35	1970
WK Wairakei, spring	99	7.7	14.5	1220	140	2.30	2.10	4.50	30	43	30	320	30	2100
NG Ngawha, well	230	7.1	10.9	880	75	0.30	0.75	0.10	3	895	310	385	26	1240
NG Ngawha, spring	80	7.2	10.4	910	64	0.29	0.60	1.40	11	850	330	150	446	1290
ZU Zunil, well	300	8.4	8.1	1030	210	1.90	2.00	0.01	11	45	150	890	61	1700
ZU Zunil, spring	87	8.7	0.6	260	37	0.08	0.02	43.0	43	5	500	200	195	170
MV Miravalles, well	245	7.5	5.7	1970	238	1.05	0.60	0.02	73	54	40	590	36	3300
MV Miravalles, spr.	73	8.5	3.4	1970	79	0.21	0.14	6.50	22	48	910	112	120	2600
RA Ruiz, acid spring	62	1.2	0.3	280	224	0.37	0.04	155	214	8	-	154	10670	1350
RB Ruiz, neutral s.	94	8.0	3.8	610	78	0.56	0.62	5.1	48	19	175	180	41	1000
AR Araro, spring	92	8.1	6.6	705	50	0.43	1.12	0.3	30	75	63	230	135	1010
MA Manikaran, spring	94	7.4	1.2	93	21	0.15	0.14	3.3	51	3	190	75	35	130
FN Fang, spring	99	9.0	0.6	122	8	0.14	0.29	0.1	1	<1	145	195	22	27
PR Paraso, spring	56	5.6	1.8	1210	178	0.74	0.09	26.6	289	16	6	150	205	2340
YA Yasur, spring	99	8.8	0.3	1270	73	0.16	0.01	0.3	17	21	75	270	280	1690
LN Lake Nyos, lake	23	5.4	.01	15	5	.004	.001	35.0	30	<1	400	45	<1	<1
WS Waitangi Soda Spr.	49	7.3	1.7	285	24	0.11	0.07	8.9	17	3	265	176	48	365
MO Morere, spring	47	7.0	4.6	6700	84	0.10	.004	80.0	2360	57	30	27	<3	15800
MU Maui, well	130	7.5	3.6	7880	440	0.71	0.08	48.0	190	15	630	36	18	12600
WI White Isl. spring	98	0.6	2.9	5910	635	5.40	0.36	3800	3150	160	<1	-	4870	38700
SW Seawater	4	7.8	0.2	10560	380	0.13	<.01	1270	400	5	140	-	2710	19000



## Role of Geochemistry in Geothermal Development | Agung Harijoko

### Controlling factors for chemical compositions of geothermal fluids

- Dissolution of primary minerals
  - Increased concentration of conservative elements (Cl, B, Br, etc)
- Precipitation of secondary minerals
  - Decreased concentration of reactive elements (e.g. Al, Mg, Fe)
- Sources of geothermal water
  - Meteoric water, oceanic water, connate water, magmatic water
- Contribution of magmatic volatiles
- Hydrological processes
  - mixing and boiling





## Contribution of Geothermal Method in the Development of Geothermal Energy

- Initial exploration stage
- Drilling stage
- Monitoring/production stage



## 2.2. Geochemistry in Geothermal Exploration



- Geothermal water types
- Identify source(s) of water, generally using stable isotopes and ratios of conservative elements
- Estimate subsurface temperature by using geothermometer
- Provide data to construct a conceptual model of the geothermal system
- Scaling tendencies
- Assessing quality of water and steam with the intended use and potential environmental effects.



## Geothermal water type



- Chloride water
  - The water is clear to blue green in color
  - Fed directly from deep reservoir
  - Dominant anion is Cl
  - pH is near-neutral
  - Discharge usually surrounded by silica sinter
  - The type of water most suitable for geothermometry



- Sulphate water
  - Derived from:
    - Mixing of chloride and sulphate water
    - Near surface discharge and oxidation of H<sub>2</sub>S in chloride water
    - Near surface condensation of volcanic gasses and magmatic vapour into meteoric water
    - Leaching of sulphur bearing rock
  - Acidic (pH 2–5)
  - Surrounded by sulphur deposits
  - Water is white to dark grey in color
  - Temperature is warm to hot
  - Associated with fumarole complex

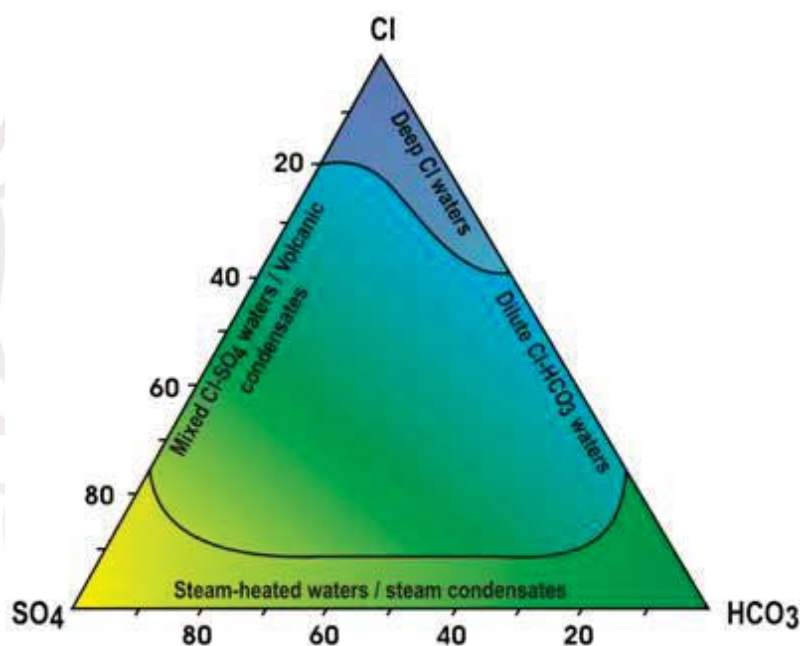




- Bicarbonate water
  - Near neutral pH
  - Warm to cold temperature
  - Sulphate may be present in variable amounts with chloride in low concentrations
  - Surrounded by calcite deposit (travertine)
  - May be derived from deep reservoir, but not very suitable for geothermometry



### Classification of Scale Water





## Identifying source of water

- Possible sources of water
  - Meteoric water
    - High  $\text{HCO}_3^-$  and  $\text{Mg}^+$  (in diagram NaK-Mg), Ca
    - Low  $\text{Cl}^-$
    - Stable isotope follow Global / Local Meteoric Water Line (GMWL / LMWL)
      - $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$  (Craig, 1961)
      - $\delta^2\text{H} = 8\delta^{18}\text{O} + 13$  (Wandowo, dkk, 2001)
  - Oceanic water
    - High Cl, Na, Mg
  - Connate water
    - Enriched in I, B,  $\text{SiO}_2$
    - Combined Na, Ca
    - Soluble organic components and low in  $\text{SO}_4$  and Mg relative to ocean water
    - $\text{D}/\text{H} \leq \text{ocean}$ ,  $^{18}\text{O}/^{16}\text{O} > \text{ocean}$



- Magmatic water
  - $\delta^{18}\text{O} = +6 - +9 \text{‰}$  (White, 1957)
  - $\delta^2\text{H} = -40 - (-60) \text{‰}$  (White, 1957)
  - $\delta^{18}\text{O} = +10 - \pm 2 \text{‰}$  (Giggenbach, 1991)
  - $\delta^2\text{H} = -20 - \pm 10 \text{‰}$  (Giggenbach, 1991)
  - Relatively high in Li, F,  $\text{SiO}_2$ , B, S,  $\text{CO}_2$
  - Low in Ca, Mg, combined N(?)





Method to identify source(s) of water :

- Cl /B ratio
- Stable isotopes ( $^2\text{H}$ ,  $^{18}\text{O}$ )



### Identifying the source(s) of water using Cl /B ratios

- Cl/B ratio is often used to indicate a common reservoir source for waters
- Some caution is required, since waters from the same reservoir can show differences in this ratio
- Differences can be induced by a change in lithology at depth over a field or by the adsorption of B onto clays during lateral flow

**Approximate Ranges In Chemical Components of Ocean Water, Oil-Field Brines Dominated by Chloride, and Volcanic Sodium-Chloride Springs**

Ratios, by weight	Ocean*	Oil-field brines+	Volcanic hot springs**
$\text{HCO}_3/\text{Cl}^{++}$	0.0074	0.0001-1	0.01-3
$\text{SO}_4/\text{Cl}$	0.14	0.00000-1	0.01-0.5
F/Cl	0.00007	0.00001-0.001	0.0005-0.1
Br/Cl	0.0034	0.0001-0.01	0.0001-0.001
I/Cl	0.000003	0.00003-0.02	0.00001-0.0005
B/Cl	0.00024	0.00001-0.02	0.01-0.1
K/Na	0.036	0.001-0.03	0.03-0.3
Li/Na	0.00001	0.0001-0.003	0.003-0.03
Ca + Mg/Na + K	0.153	0.01-5	0.001-0.2

(White, 1957)

tion source of water using stable i



**Left Plot:  $\delta^{18}\text{O}$  (‰) vs SMOW vs  $\delta^2\text{H}$  (‰) vs SMOW**

Location	$\delta^{18}\text{O}$ (‰) (SMOW)	$\delta^2\text{H}$ (‰) (SMOW)
Lazarote - Canaries	~13.5	~-15
Dalloi - Ethiopia	~13.5	~-18
Wairakei - N Zealand	~0.5	~-25
Larderello - Italy	~2.5	~-28
The Geysers - Calif	~2.5	~-30
M. Arniata - Italy	~3.5	~-32
Hekle - Iceland	~4.5	~-35
La - Calif	~4.5	~-40
Hot Springs Mt. Lassen - Calif	~0.5	~-45
Prieto - Mexico	~0.5	~-48
Hot Springs - Nevada	~0.5	~-50
Yellowstone Park	~0.5	~-55
Juvenile water	~4.5	~-55

**Right Plot:  $\delta^2\text{H}$  (‰) vs SMOW vs  $\delta^{18}\text{O}$  (‰) vs SMOW**

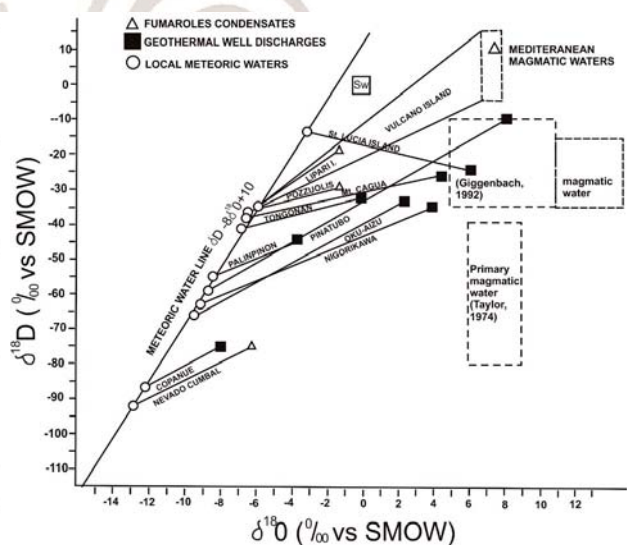
Location	$\delta^{18}\text{O}$ (‰) (SMOW)	$\delta^2\text{H}$ (‰) (SMOW)
Lazarote - Canaries	~13.5	~-15
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M. Arniata - Italy	~3.5	~-32
Hekle - Iceland	~4.5	~-35
La - Calif	~4.5	~-40
Hot Springs Mt. Lassen - Calif	~0.5	~-45
Prieto - Mexico	~0.5	~-48
Hot Springs - Nevada	~0.5	~-50
Yellowstone Park	~0.5	~-55
Juvenile water	~4.5	~-55

**Legend:**

- $\Delta$  FUMAROLAS CONDENSED
- $\blacksquare$  GEOTHERMAL WELLS
- $\circ$  LOCAL METEORIC

**Lines:**

- METEORIC WATER LINE  $\delta\text{D} = 8\delta^{18}\text{O} + 10$
- GEOTHERMAL LINE  $\delta\text{D} = 5\delta^{18}\text{O} + 10$
- GEOTHERMAL LINE  $\delta\text{D} = 3\delta^{18}\text{O} + 10$







## Estimate subsurface temperature by using geothermometer techniques

### Different Geothermometers

- Solute geothermometers
  - Silica (Bodvarsson 1960, Bodvarsson and Palmason 1961, Fournier and Rowe 1966, Arnorsson 1975, Fournier 1977 and Fournier and Potter 1982)
  - Na/K (Ellis and Wilson 1961)
  - Na-K-Ca
  - Na/Li, Li/Mg and K-Mg



- Gas geothermometers
  - High temperature:
    - Main gas  $\text{CO}_2$  and  $\text{H}_2\text{S}$  (~ 90%)
    - $\text{NH}_3$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2$ , (minor)
    - $\text{O}_2$ , noble gases, HC, B, As, Hg (trace)
  - Low temperature:
    - Same but  $\text{N}_2$  and  $\text{CH}_4$  may be dominant
  - Magmatic: HCl, HF,  $\text{SO}_2$ ,  $\text{CO}_2$



- Oxygen isotope geothermometers
- Hydrogen isotope geothermometers
- Carbon isotope geothermometers
- Sulphur isotope geothermometer



### Provide data to construct conceptual model of geothermal system

An important goal in geothermal exploration is to construct a conceptual model, including:

- Upflow and outflow zones
- Hydrological pattern
- Mixing models
  - Chloride enthalpy plot





## Mixing Models

We may use of graphics for mixing calculations.

Example, mixing between 100 ton of 10°C water (enthalpy: 42 J/gm) with 200 ton of 265 °C water (enthalpi: 1159 J/gm).

$$(100/300) (42) + (200/300)(1159) = 787 \text{ J/gm}$$

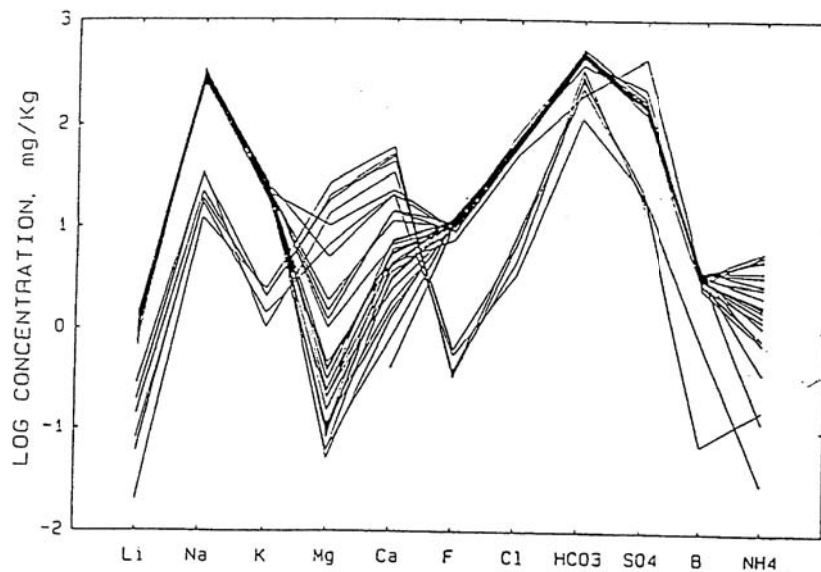


## Mixing Water

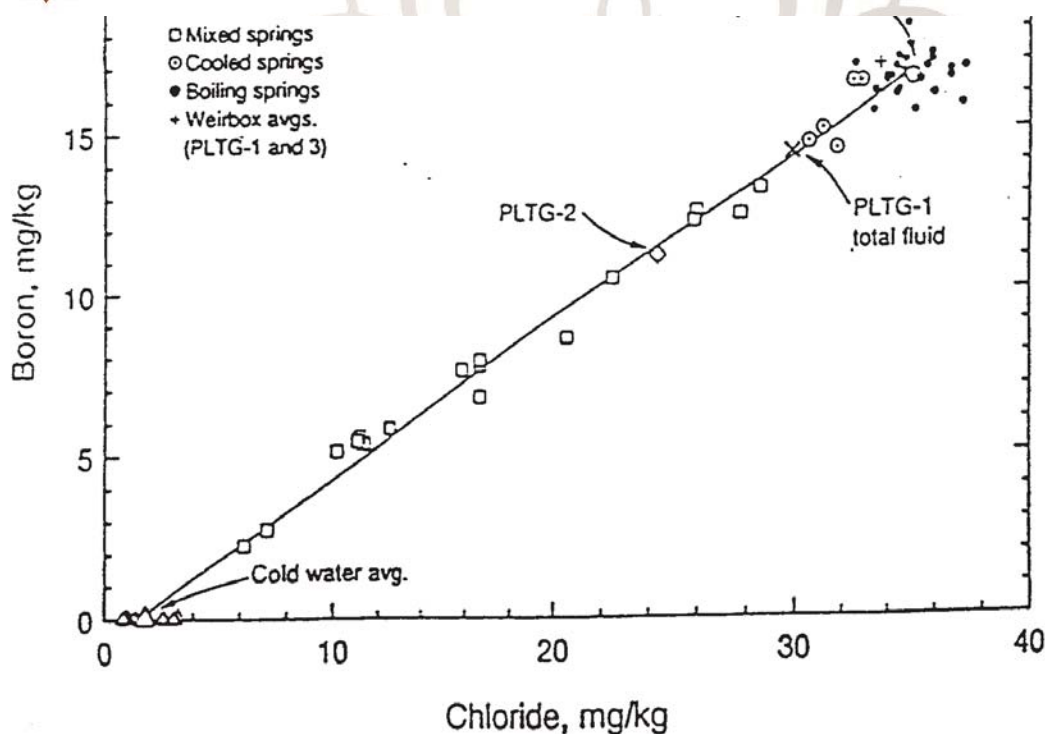
Mixing of two waters can be indicated in a plot of one conservative species against another.



### Spider diagram/Schoeller diagram



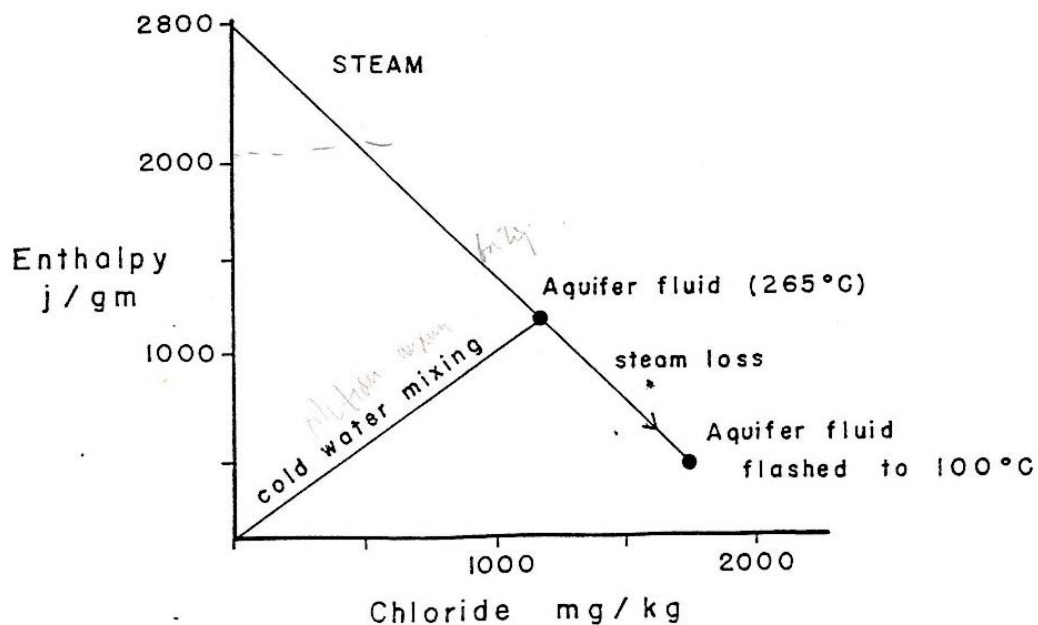
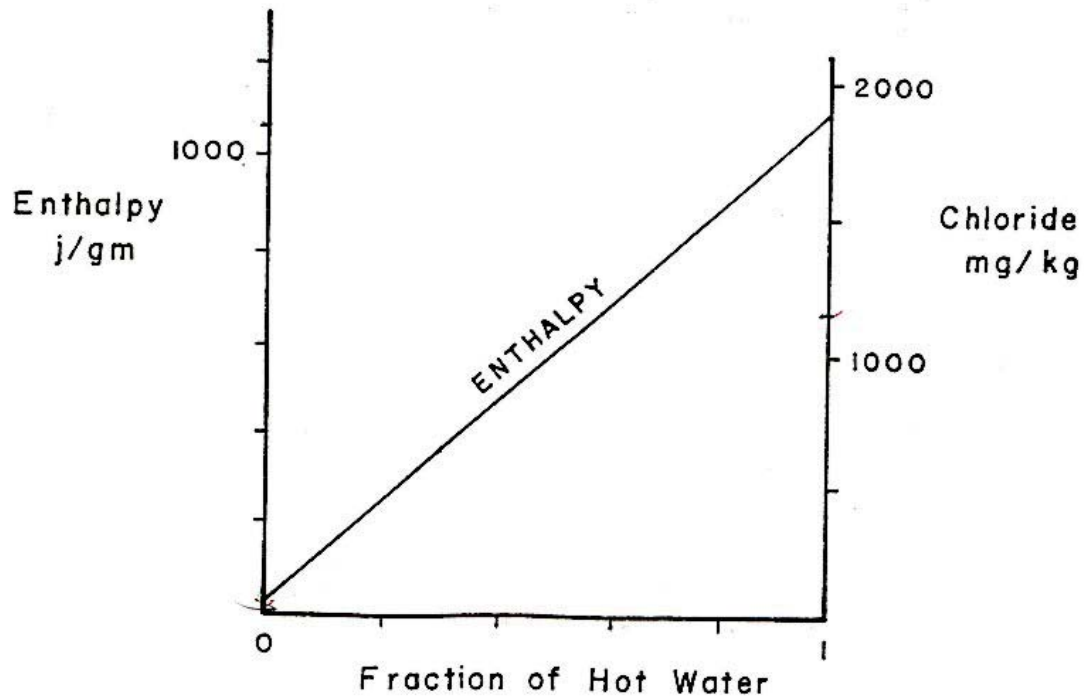
- Effect of mixing with dilute water is indicated by vertical shift without changing the pattern.
- Thermal waters have higher Li, Na, K, F, Cl, SO<sub>4</sub> and B.
- Cold waters have higher Mg and Ca with HCO<sub>3</sub> almost the same as thermal water







### Mixing model of deep and shallow water

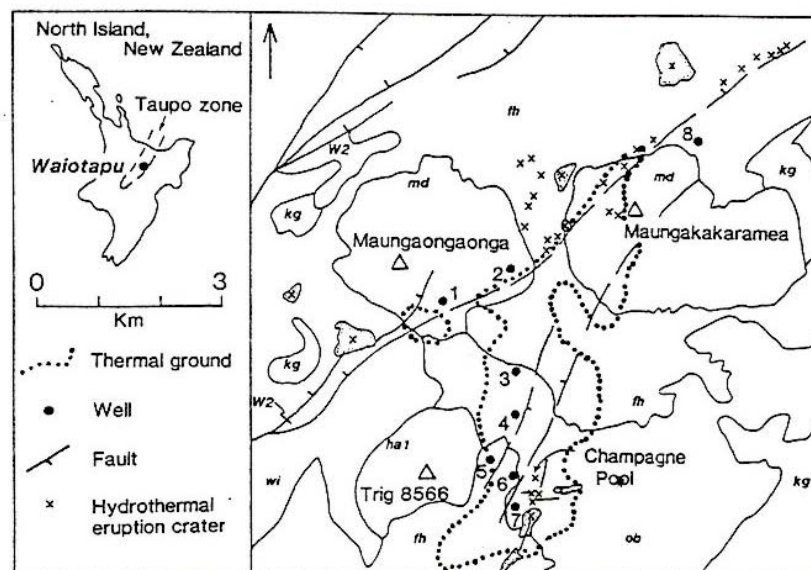




The following data Table 2.2 from Waiotapu will be used to further demonstrate the use of chloride-enthalpy plots to delineate mixing trends.

**Table 2.2. Enthalpy, Cl and T data from Waiotapu wells and spring**

	$T_{Qtz}$ °C	$H_{Qtz}$ (J/gm)	$Cl_{discharge}$ (mg/kg)	$Cl_{reservoir}$ (mg/kg)
Champagne Pool	218 (75 surface)	934	1898	1405
Wt-3	183	770	673	568
Wt-4	218	934	1600	1235
Wt-5	161 (TNa-K)	680	949	839
Wt-6	208	889	1063	840
	198	843	950	771
	221	948	1450	1110
Wt-7	203	866	1260	1010
	203	866	1285	1028
	214	916	1310	1021



**Figure 2.4** Geologic map of the Waiotapu area, modified from GRINDLEY (1959) and NAIRN (1973). The trace of faults, loci of hydrothermal eruption craters, and extent of thermal ground are shown, as are the locations of the eight wells. Stratigraphic nomenclature: fh, lacustrine sediments and volcanic breccias; md, Maungakakamea Dacite; kg, Kaingaroa Ignimbrite; ob, Onuku Breccia Formation; qb, Crystal-rich tuff; W2, Waiora Formation; ha1, Haparangi Rhyolite; wi, Waiotapu Ignimbrite; nk, Ngakoro Andesite; po, Paeroa Ignimbrite sheets A, B and C (separated by volcanic breccias and reworked tuffs).



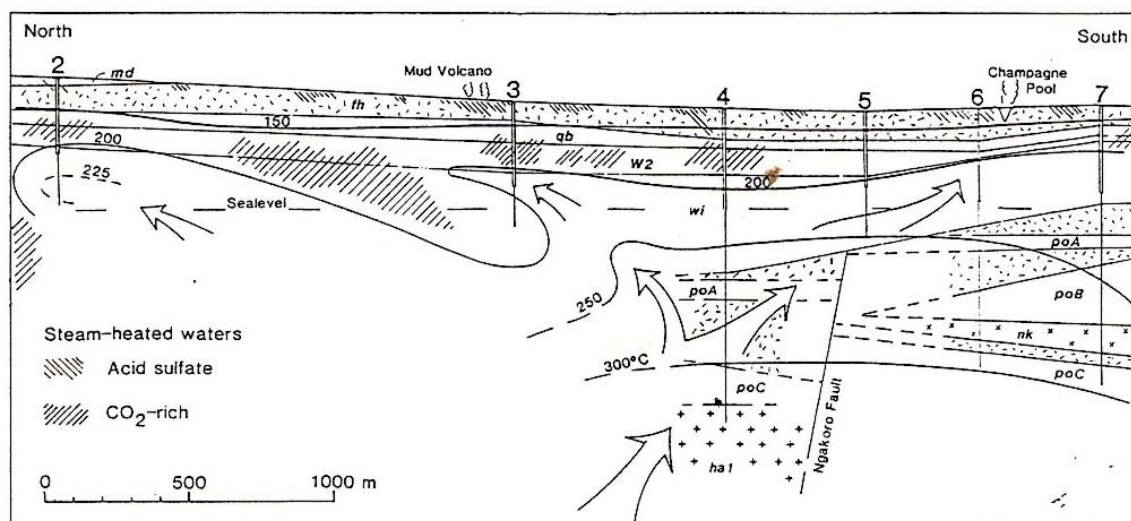
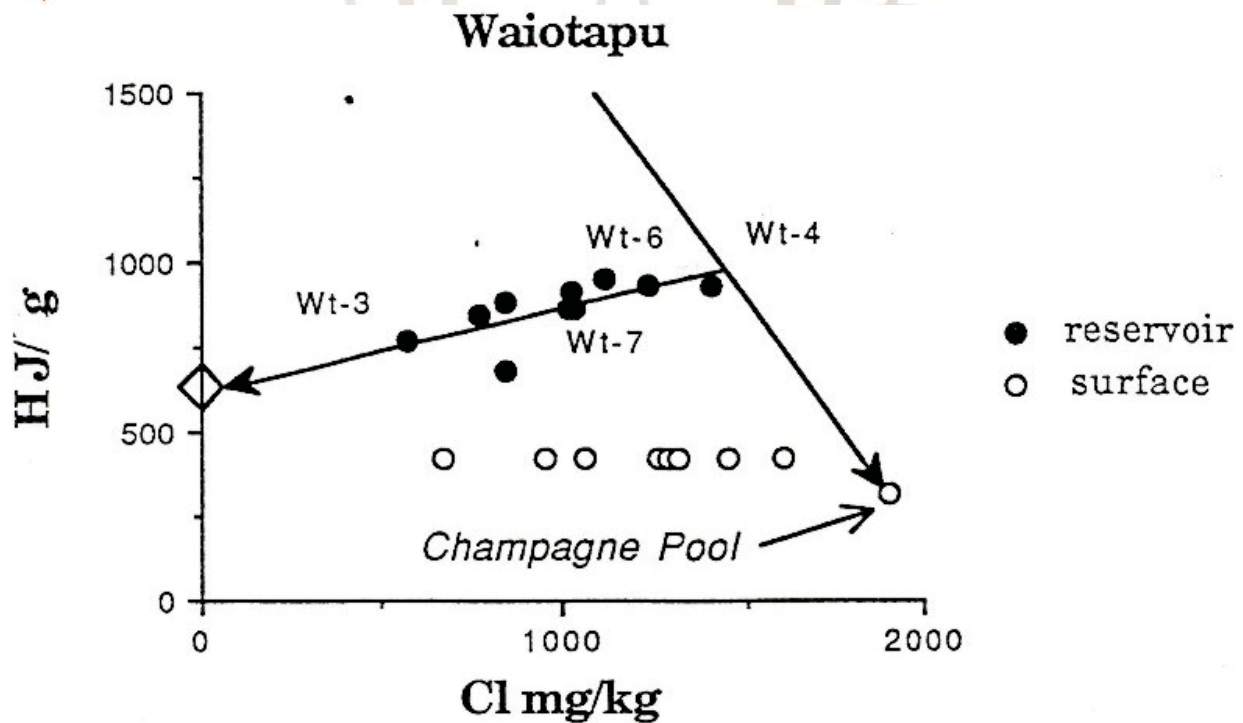


Figure 2.6 Geologic north-south cross section through the Waiotapu system, showing measured temperatures down wells and deduced isotherms. The distribution of surficial acid-sulfate and shallow CO<sub>2</sub>-rich steam-heated waters have been inferred from hot spring compositions, mixing relations between wells, and position of thermal inversions. From Hedenquist and Browne (1989).



## Scaling tendencies

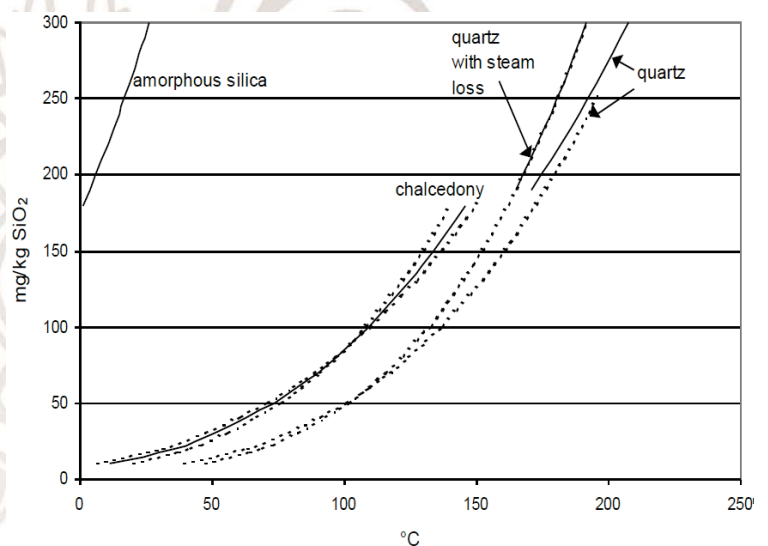
Types of scaling:

- Silica scaling
- Carbonate scaling



## Silica scaling

The silica concentration in geothermal systems is controlled by the solubility of quartz and chalcedony (Fournier and Rowe, 1966; Mahon, 1966) and increases with increasing temperature. During cooling the silica is in solution until solubility of amorphous silica is reached. At still lower temperature the water becomes supersaturated and silica depositions can be expected (Gunnlaugsson, 2012).







The silica saturation index (SSI) is often used to indicate the potential for silica scale deposition. It is defined as the ratio of silica concentration in the solution to the equilibrium solubility of amorphous silica. Silica scaling will only occur when that SSI value is greater than 1 and is generally not problematic for SSI values <1.4, depending on temperature (Brown, 2011).

$$\text{Log } C = -\frac{1309}{T} + 5.19$$

C: Silica concentration

T: Temperature (in °K)



### Carbonate scaling

- Calcite scaling is on the other hand associated with boiling and mixing of inflow from two or more aquifers, each with different chemistry and temperature.
- Calcite scaling associated with boiling is always by far the strongest at the first level of boiling.
- The magnitude of calcite supersaturation caused by boiling depends on the salinity of the water and its temperature.



## Assessment of the quality of water and steam for intended use and environmental effects

Sulphur compounds:  
 $H_2S$  gas is toxic at low concentrations; when oxidized to sulphuric acid, it also can cause corrosion



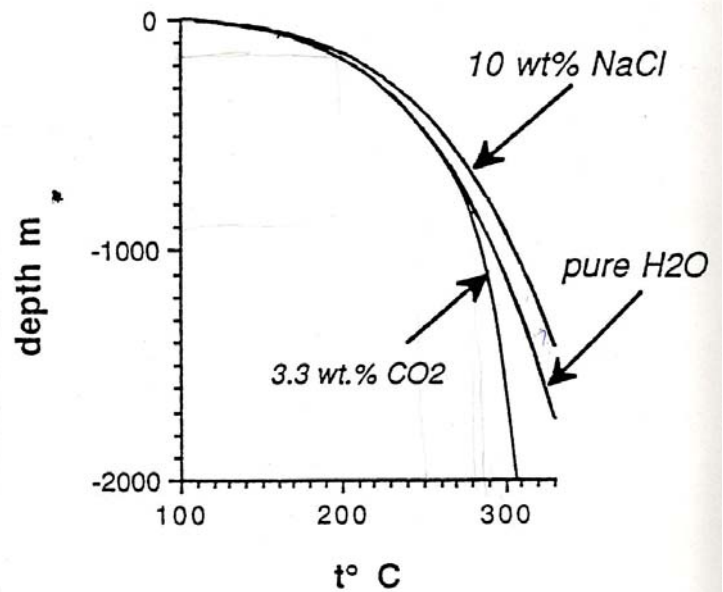
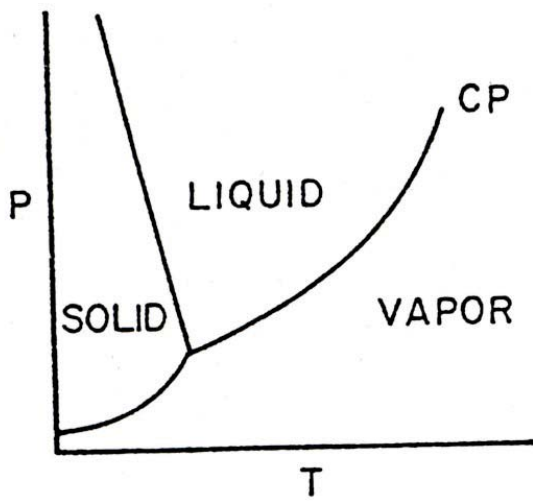
Both are present in discharging from sulphur compounds geothermal fluids.



## 2.3. Geochemistry in Geothermal Production

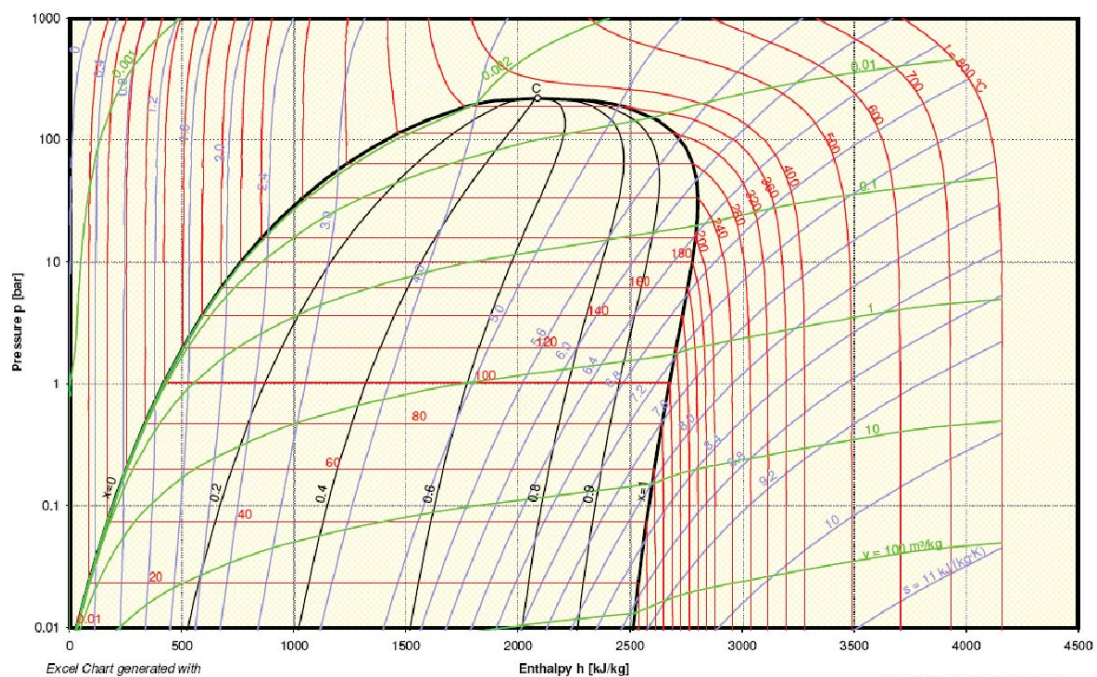
- Boiling is separation of steam (vapor) from water (liquid), usually occurring adiabatically.
- Boiling occurs at certain pressure and temperature following phase equilibrium.





## Pressure enthalpy diagram

logP-H diagram

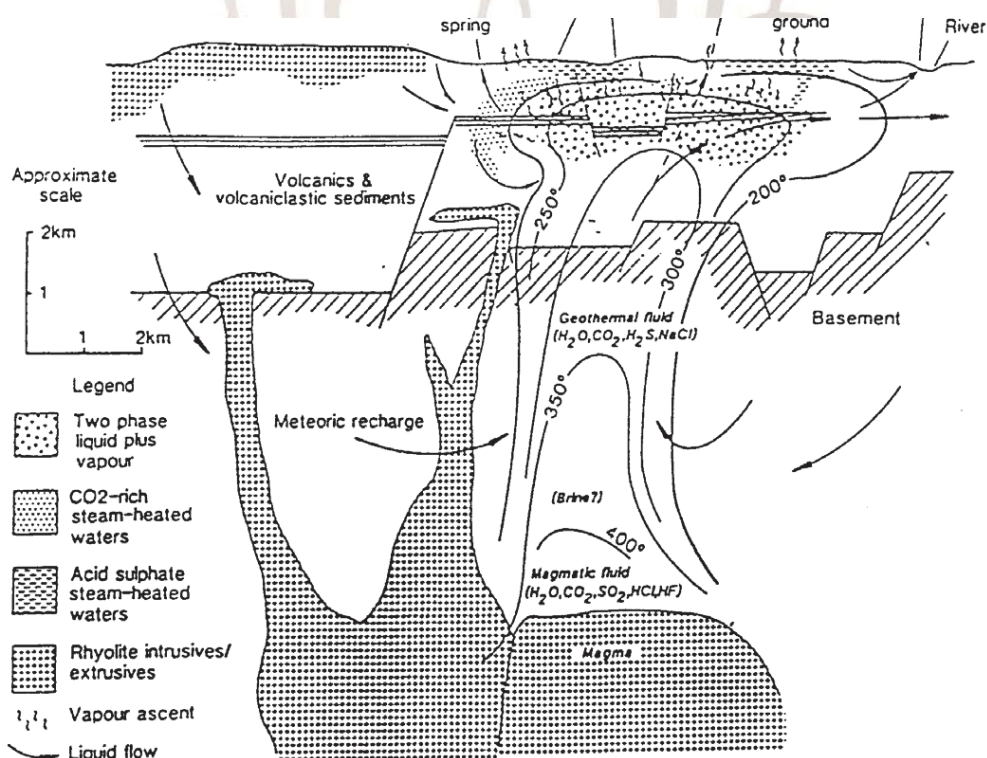


Excel Chart generated with  
Steam97 Excel Add-In

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- Adiabatic processes may occur when hot geothermal water ascend quickly through a fracture zone (natural condition) or wellbore (exploitation).
- Boiling results in steam and liquid fractions. As the process is adiabatic, it will be isoenthalpic.
- Non volatile components such as silica and chloride will remain in the liquid phase, while volatile components such as CO<sub>2</sub>, H<sub>2</sub>S will degas and become incorporated in the steam phase.







## Steam fraction calculation

- Example: reservoir temperature is 265°C according to the surface and undergo boiling at temperature of 100°C.
- How much steam can be produced?

$$H_{T0}^l = xH_{Tb}^l + yH_{Tb}^v$$

$$x + y = 1$$

H: enthalpy

l, v: liquid and vapor

x : liquid fraction

y: steam, (vapor) fraction

T<sub>0</sub> initial temperature

T<sub>b</sub> boiling temperature



$$y = \frac{H_{T0}^l - H_{Tb}^l}{H_{Tb}^v - H_{Tb}^l}$$

$$y = 0.328$$

$$H_{265}^l = 1159 \text{ J / gm}$$

$$H_{100}^l = 419 \text{ J / gm}$$

$$H_{100}^v = 2676 \text{ J / gm}$$

$$H_{res} = H_l + y(H_v - H_l)$$

What is the effect to the composition??

To calculate the dissolved solid we use the equation

$$C_{Cl}^l = (1 - y)C_{Cl,Tb}^l + yC_{Cl,Tb}^v$$

Suppose the Cl concentration in the reservoir fluid is 1145 mg/kg

After boiling the concentration increases to: 1704 mg/kg

Similar for gas. But in this case of gas more complicated because not all of the gas goes to the steam, some of it still remains dissolved in the liquid phase.

So, partition coefficients are needed to calculate this.





$$C_o = yC_v + (1-y) C_L,$$

$$C_o/C_L = 1 + y(B-1).$$

Gas distribution coefficients,  $B = C_v/C_L$ , for common geothermal gases (from Giggenbach, 1980). [t in °C]

$\log B_{NH_3}$	=	1.4113 - 0.00292 t
$\log B_{H_2S}$	=	4.0547 - 0.00982 t
$\log B_{CO_2}$	=	4.7593 - 0.01092 t
$\log B_{CH_4}$	=	6.0783 - 0.01383 t
$\log B_{H_2}$	=	6.2283 - 0.01403 t
$\log B_{N_2}$	=	6.4426 - 0.01416 t



- The well bore sampling may be conducted at “weir box”
- $C_{\text{weirbox}} = C_{\text{sample}} / (1-y)$
- $C_{\text{reservoir}} = C_{\text{sample}} (1-y)$

H (J/gm)	Separation pressure (b.g)	Cl	SiO <sub>2</sub>
1203	6.5	13800	808

b.g= bar gauge = bar absolute - 1



- First step is calculating the steam fraction between separation point and weir box.
  - $H_{l, 7.5 \text{ b.a } 168} = 710.5 \text{ J/gm}$
  - $H_{l, 100} = 419 \text{ J/gm}$
  - $(H_v - H_l)_{100} = 2257 \text{ J/gm}$
- $y = 0.129$
- $C_{Cl, \text{ weir}} = 15844 \text{ mg/kg}$
- $C_{SiO_2 \text{ weir}} = 928 \text{ mg/kg}$



- $H_{l, \text{ res}} = 1203$
- $H_{l, 7.5 \text{ b.a.}, 168} = 710.5 \text{ J/gm}$
- $(H_v - H_l)_{100} = 2056 \text{ J/gm}$
- $y = 0.24$
- $C_{Cl \text{ res}} = 10488 \text{ mg/kg}$
- $C_{SiO_2 \text{ res}} = 614 \text{ mg/kg}$



## 2.4. Geochemistry in Geothermal Monitoring

- Response of geothermal reservoirs to production load
- Injection
- Frequency of sampling for monitoring studies and the selection of chemical and isotopic components for analysis
- Presentation of monitoring data
- Conservative components
- Reactive aqueous components
- Reactive gaseous components
- Deuterium and  $^{18}\text{O}$



## Response of geothermal reservoirs to production load

- Increased recharge of water into the reservoir, from above, below or laterally
- Enhanced boiling in the case of reservoirs with temperatures in excess of  $100^{\circ}\text{C}$
- Wells become unproductive but cold water recharge may also do so by considering steam and, thus, reducing boiling





## Injection

- The reason for injection is twofold. It is environmentally friendly and helps maintain reservoir pressures, at least, if the waste fluid is injected through special wells back into the reservoir.
- For injection, either special wells must be drilled or non-productive wells must be used.
- On the long run, injection of waste brine into a producing reservoir may have some negative effects. If the same water is recycled, successive steam loss will increase its salinity, which may in turn lead to scaling problems.



## Frequency of sampling for monitoring studies and the selection of chemical and isotopic components for analysis

- More frequent sampling is required for dry and wet steam wells than for hot water wells
- Sample frequency is highest during the early stages of discharge of a well
- Samples should be taken for analysis of all major components in both water and steam samples but otherwise partial analysis is considered sufficient
- Decrease in the concentration of the incompatible components Cl and B in the liquid water phase of well discharges, at a particular separation pressure, are indicative of cold water recharge
- Changes in deuterium and  $^{18}\text{O}$  may reflect recharge from a different source into producing aquifers
- recharge of injected waste brine can be expected to be reflected in increasing Cl concentrations
- Increasing dho values for deuterium and  $^{18}\text{O}$  in the fluid discharged from producing wells.



## Presentation of monitoring data

- The principal variable for monitoring studies is time
- There are two possibilities for representating time variations in the concentrations of chemical and isotopic components in well discharge fluids:
  - One is to select the total discharge compotition
  - The other is to show concentration variations in the discharged water (aqueous components) and steam (gaseous components) phases, respectiely



## Conservative components

- The most widely used natural chemical and isotopic components to trace recharge into geothermal reservoirs are chloride and deuterium.





## Reactive aqueous components

- Many aqueous component reactions can, on the other hand, be regarded as instantaneous, such as those involving  $\text{CO}_2$ , bicarbonate or cation hydrolysis.
- Quartz and Na/K geothermometry results should always be compared in order to infer the boiling mechanism responsible for excess enthalpy wells.
- Sulphate is controlled by anhydrite solubility in many geothermal fluids.
- Sulphate could be incompatible or controlled through a redox equilibrium with  $\text{H}_2\text{S}$ .
- Deep and hot wells ( $>250^\circ\text{C}$ ) have aqueous sulphate concentrations running in few tens of ppm.
- Shallower and less hot wells ( $<250^\circ\text{C}$ ) have aqueous sulphate concentration of a few hundreds of ppm.



## Reactive gaseous components

- Reactive gaseous components:  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{H}_2$ .
- $\text{CO}_2$  appears to be controlled by mineral solution equilibria, at least in some reservoirs.
- Concentrations of  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and  $\text{H}_2$  can be used as geothermometers.
- $\text{H}_2\text{S}$  is much more soluble in water than  $\text{H}_2$ .
- Increases in  $\text{H}_2$  temperatures in the steam of well discharges, in excess of  $\text{H}_2\text{S}$  temperatures are indicative of an increasing initial, or equilibrium, steam fraction in the aquifer, and visa versa.





## Deuterium and $^{18}\text{O}$

- Deuterium and  $^{18}\text{O}$  contents in fluids discharged from wells may change with time during exploitation
  - The exploitation may lead to rapid recharge of local groundwater
  - The recharging water may not develop a similar  $^{18}\text{O}$  shift as in the initial water
  - The original geothermal fluid may contain a significant magmatic component
  - Injected water can be responsible, which, as a result of steam loss, has deuterium and  $^{18}\text{O}$  contents different from those in the initial reservoir fluids
  - Exploitation may alter the boiling mechanism in producing aquifers

## 03 Fluid-Rock Interactions

Pri Utami  
(Universitas Gadjah Mada)





Altered ground, Kawah Sikidang (Dieng)

### 3. FLUID-ROCK INTERACTIONS



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Adapted from geothermal lecture handouts by Pri Utami at the Postgraduate Study Program, Geological Engineering UGM and Geothermal Institute, The University of Auckland.



#### Fluid-rock interaction | Pri Utami

### 3.1. Introduction

Hydrothermal alteration is a mineralogical, textural, and chemical response of rocks to a changing thermal and chemical environment in the presence of hot water, steam or gas.

Hydrothermal alteration takes place as the rocks are exposed to hydrothermal environment, whose conditions differ from those at their original environment.

Hydrothermal environment: T 50 – 300°C, the presence hydrothermal fluids (that is not pure H<sub>2</sub>O).

Hydrothermal system is a natural laboratory that gives unlimited chance for us to study heat and mass transfer from the deeper parts of the Earth, interactions between rocks and fluids, mineral deposition.

Hydrothermal system is also a source of energy, therefore hydrothermal alteration study that helps us understanding the system is important in geothermal field development.



### 3.2. Methods of study

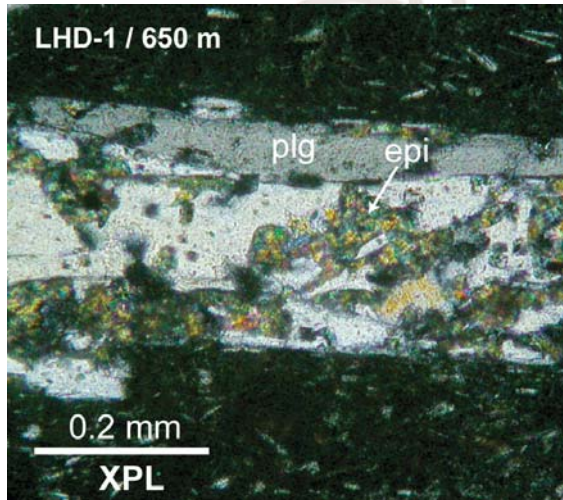
- Petrography – to determine their lithology, the primary and hydrothermal mineralogy, styles of alteration, textures of replacement, as well as the sequence of deposition of hydrothermal minerals in veins.
- X-ray diffractometry (XRD) – to analyse bulk rock mineralogy, but best to identify clay minerals.
- X-ray fluorescence (XRF) – to quantitatively determine the concentrations of trace and major elements in rocks.
- Scanning Electron Microscopy (SEM) – to study the textural relationship between minerals in 3D perspective.
- Electron Microprobe (EMP) – to analyse the chemical compositions of the primary and hydrothermal minerals.
- Fluid inclusion analyses - to deduce the temperature and apparent salinity of the fluids circulating in the system during the alteration process.
- .....



### 3.3. Three styles of hydrothermal alteration

1. Replacement of primary constituents by secondary (hydrothermal minerals) through fluid – mineral interactions.
2. Direct deposition of hydrothermal minerals in open spaces (fractures, vugs) due to the processes affecting the circulating fluids such as boiling, mixing, or cooling.
3. Leaching/removal of primary constituents by acidic thermal fluids





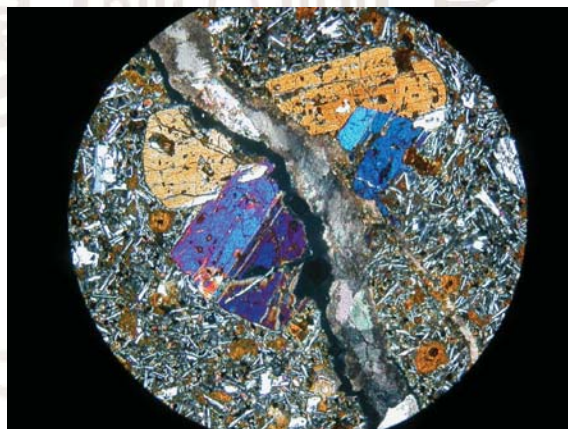
### Replacement

- Records interaction between primary constituents and the altering fluids
- Slow process
- Incomplete alteration is common suggesting that equilibrium between fluid and rock is not always achieved
- Often field-wide

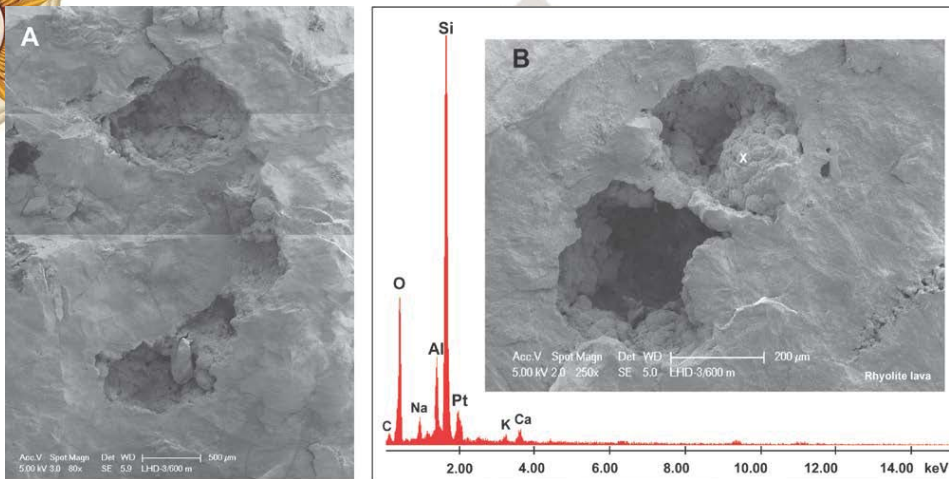


### Direct deposition

- Records processes affecting the fluids (e.g., boiling, cooling, mixing, pH changes)
- Local







SEM image of a leached rhyolite lava from well LHD-3/600 m



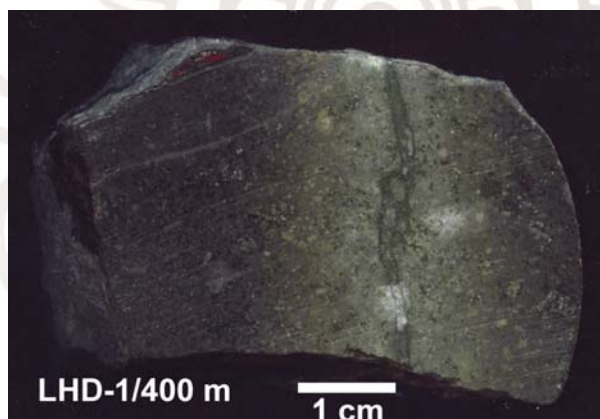
## Leaching

Leaching records removal of constituents by acidic fluids



## 3.4. Intensity of Alteration

- A measure on how much the hydrothermal minerals formed compared to the primary minerals in a rock  
 $I.A = 0$  : rock is unaltered, all the primary minerals are fresh  
 $I.A = 1 = 100\%$ : all primary minerals have been altered to hydrothermal minerals, original texture obliterated.
- Intensity of alteration does not account for the type of hydrothermal minerals formed !



Increased intensity of alteration towards the fluid channel in andesite lava (LHD-1/400 m)





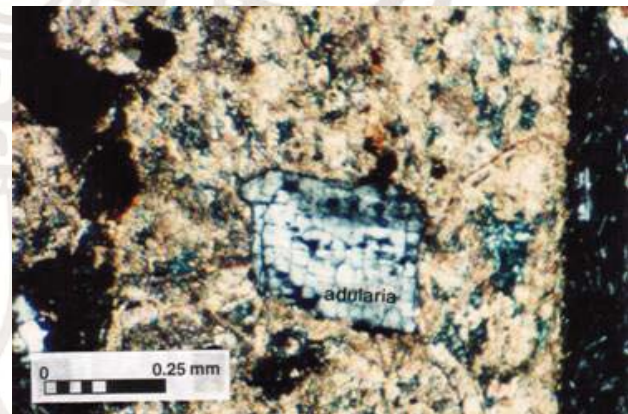
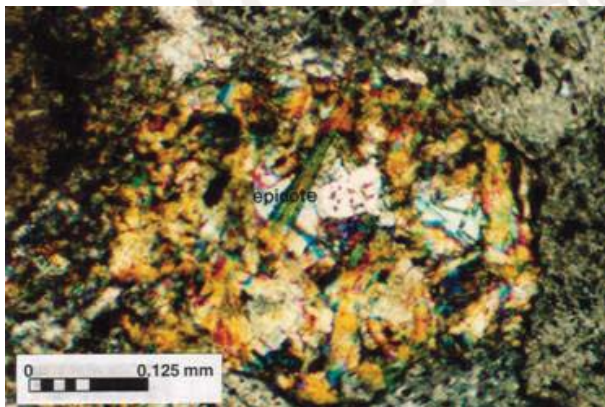
### 3.5. Rank of Alteration

Describes the empirical ranks of temperature or permeability as shown by the occurrence of the temperature or permeability mineral indicators.

Examples:

Epidote, high temperature indicator ( $\geq 250$  °C)

Adularia, high permeability indicator



### 3.6. Factors controlling hydrothermal alteration

The types and abundance of hydrothermal minerals are determined by the prevailing physical and chemical conditions of the system, mainly:

1. Temperature
2. Fluid chemistry
3. Permeability
4. Boiling, cooling, and fluid mixing
5. Duration of hydrothermal activity

Therefore, some hydrothermal minerals can be used as the indicators of temperature, fluid chemistry, relative permeability, and the process in the system.

Studies on hydrothermal mineral paragenesis (sequence of replacement and/or deposition) can be used to reconstruct the natural changes that took place in a hydrothermal system.







### 3.7. Applications of hydrothermal alteration study in geothermal field development

1. To help estimate the subsurface temperature before the well is measured
2. To assess the compositions of the reservoir fluid
3. To help set the casing
4. To estimate the position of the well in the hydrological framework of the system (upflow, outflow, recharge)
5. To predict the characteristic of fluid during production
6. To predict the response of the reservoir to re-injection



### Clues from some hydrothermal minerals

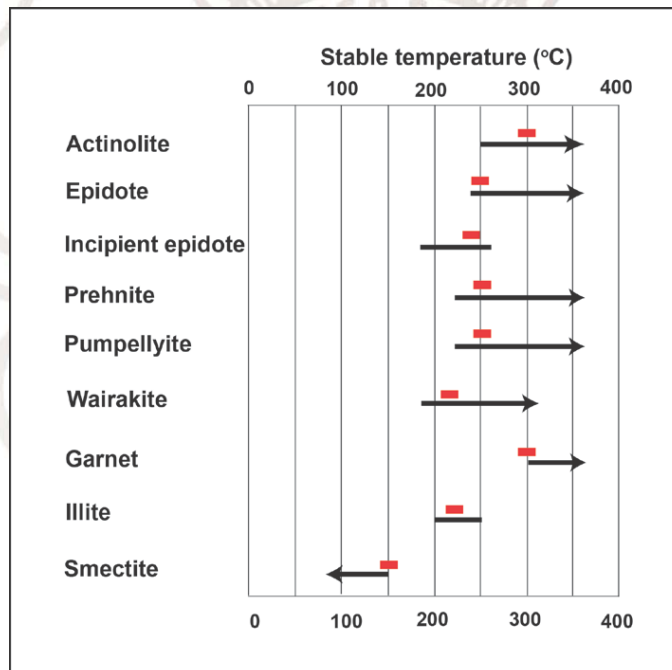
Illite	$T > 220\text{ }^{\circ}\text{C}$
Epidote	$T > 250^{\circ}\text{C}$ , low $\text{CO}_2$ content, neutral pH fluid
Kaolinite	Low pH, oxidation by meteoric water (shallow) or magmatic-related fluid (deep)
Dickite	High-temperature polymorph of kaolinite, magmatic-related fluid (deep)
Calcite	High $\text{CO}_2$ content; space-fill calcite with bladdered/platy/angel's wing morphology: boiling
Adularia	good permeability indicator; vein adularia:boiling
Opal, chalcedony, quartz	Silica scaling, reduced permeability, later stage



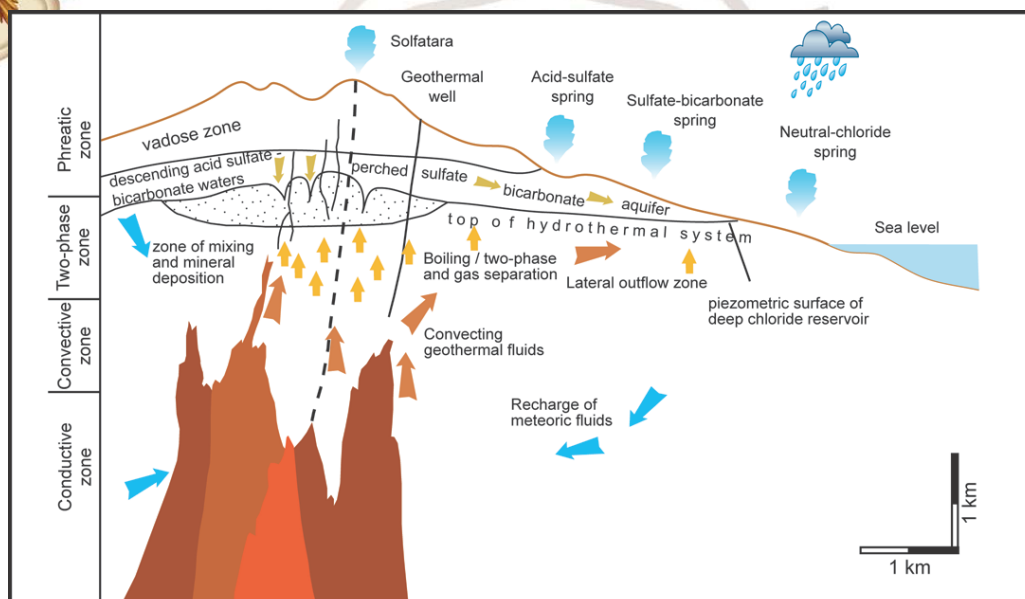


### 3.8. Hydrothermal alteration and temperature

The formation and stability of hydrothermal minerals are thermally controlled therefore, there are hydrothermal minerals that serve as **geothermometers**, i.e., those containing (OH) or  $n\text{H}_2\text{O}$



### Hydrothermal alteration and pressure



Pressure in hydrothermal system rarely exceeds 200 bar. Pressure controls the depth at which boiling occurs. Boiling gives “traumatic” effects on fluid chemistry:

- Loss of steam
- Removal of  $\text{H}_2\text{S}$  and  $\text{CO}_2$
- Precipitation of hydrothermal minerals



### 3.9. Hydrothermal alteration and permeability

The influence of the parent rocks to hydrothermal alteration is through the control of permeability by texture and porosity.

The equilibrium between rock and fluid is seldom achieved in rocks with low permeability.

Deposition of hydrothermal mineral is controlled by permeability

Examples:

- Densely welded tuff at Broadlands and Wairakei have locally remained unchanged despite high temperature as the fluid access is difficult (Browne and Ellis, 1970).
- Marked hydrothermal alteration zoning occur around the fluid channels in Matsukawa, Japan as described by Sumi and Takashima (1976).

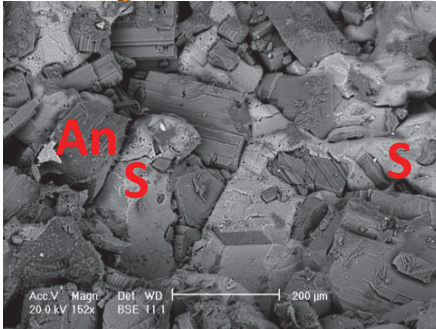


### 3.10. Hydrothermal alteration and fluid compositions

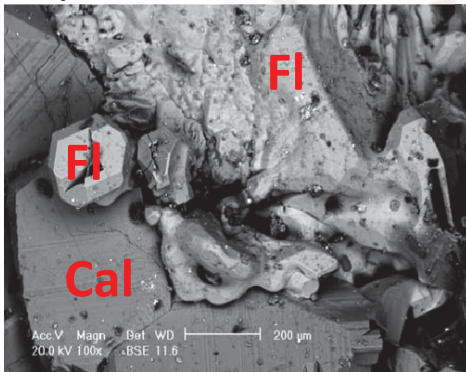
In many geothermal systems the chemical composition of geothermal fluids correlate with the observed zoning of hydrothermal alteration often have not been measured due to the difficulties in obtaining the representative reservoir fluid.

The advanced theoretical geochemistry, however, allow quantitative description and interpretation of geochemical characteristics of the altering fluids based on the detailed studies of spatial and compositional relations among the hydrothermal minerals.

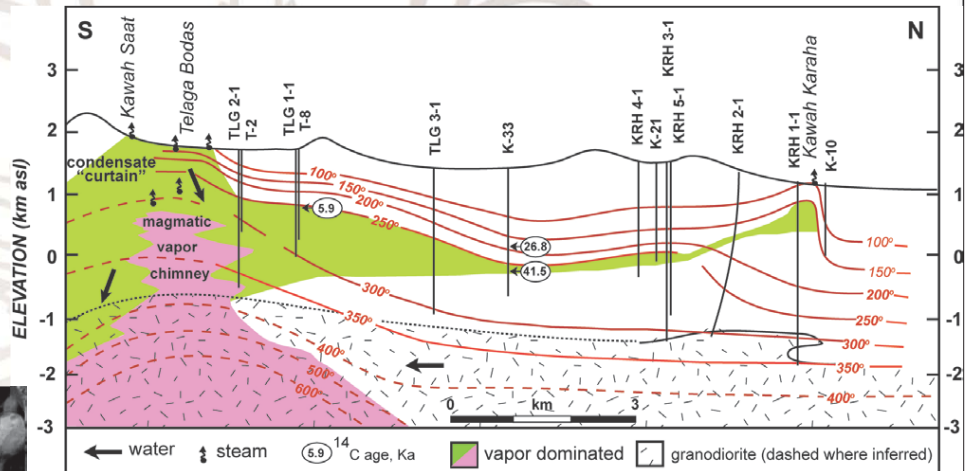




Native sulfur deposited after anhydrite.



Fluorite deposited after calcite

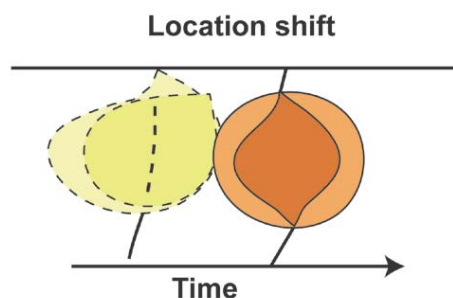
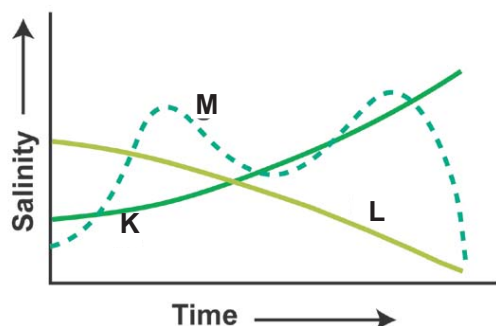
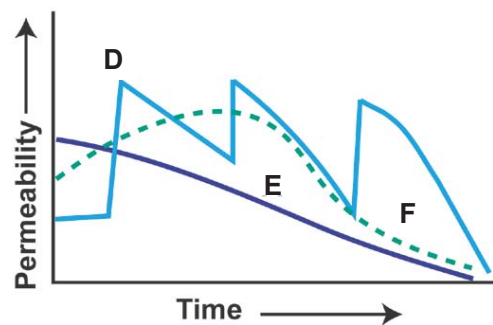
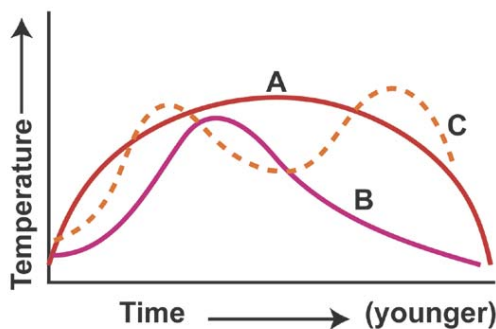


Subsurface model of the Karaha – Telaga Bodas geothermal system West Java (adapted from Moore et al, 2004)

Back-scattered Scanning Electron Microscopy (SEM) image (Moore et al, 2002)



### 3.11. Natural changes during the life of a hydrothermal system

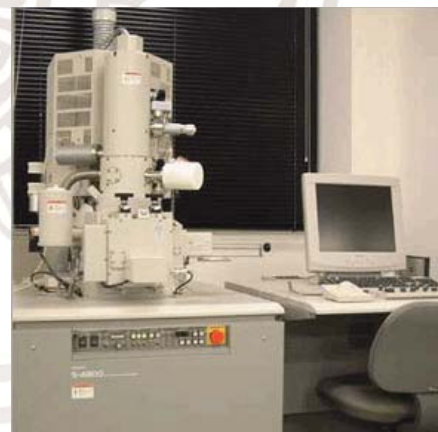


(adapted from Browne, 1995)

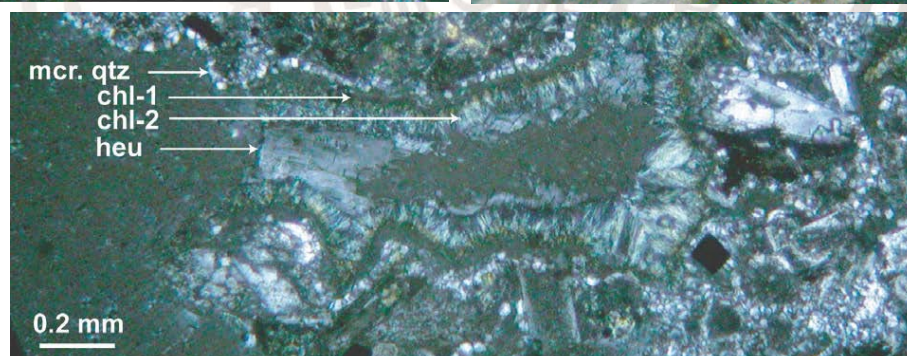
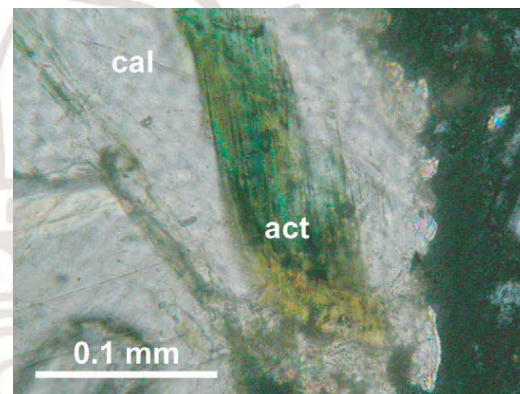
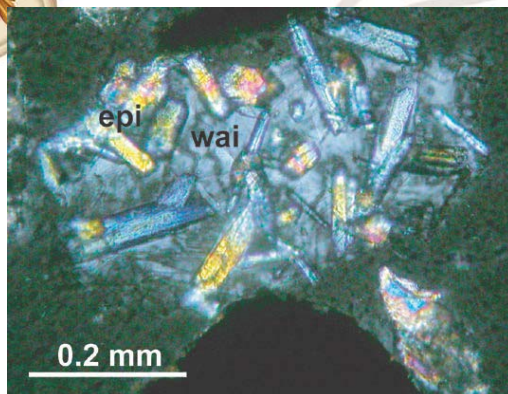
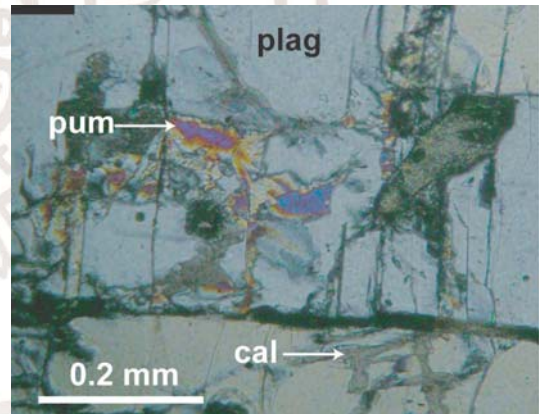
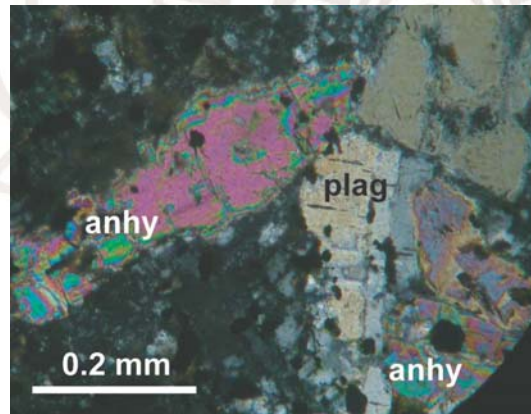
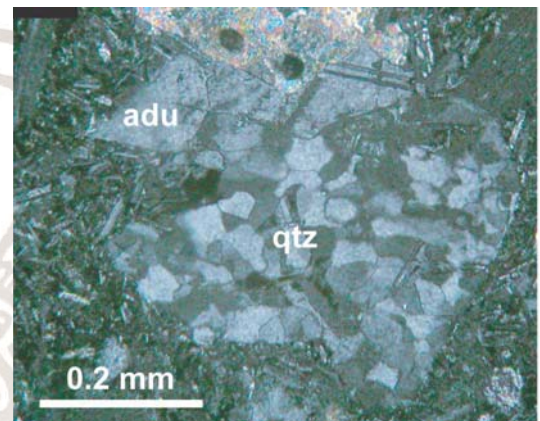
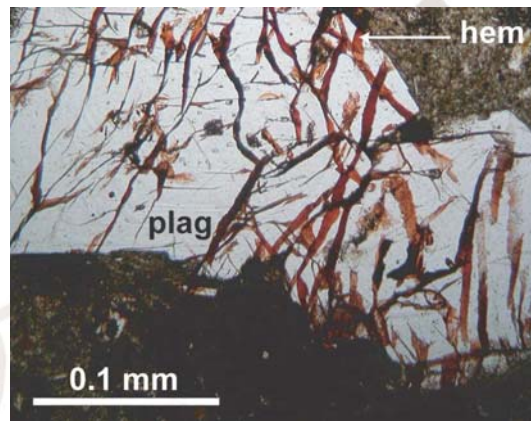


### 3.12. Hydrothermal mineralogy

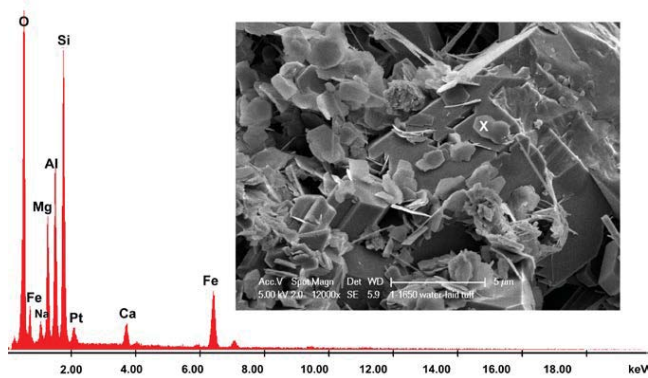
Carbonates	calcite, aragonite, siderite, ankerite
Sulphates	anhydrite, gypsum, barite
Sulphides	pyrite, chalcopyrite, pyrrhotite, marcasite, galena, sphalerite
Oxides	hematite, magnetite, leucoxene, diaspore
Phosphates	apatite
Halides	fluorite
Clays	smectite, illite, chlorite, interlayered clays
Feldspars	albite, adularia
Silicas	quartz, cristobalite, trypidite
Calc-silicates	epidote, actinolite, clinozoisite, pumpellyite, prehnite, tourmaline, titanite, zeolites (wairakite, mordenite, heulandite,...)



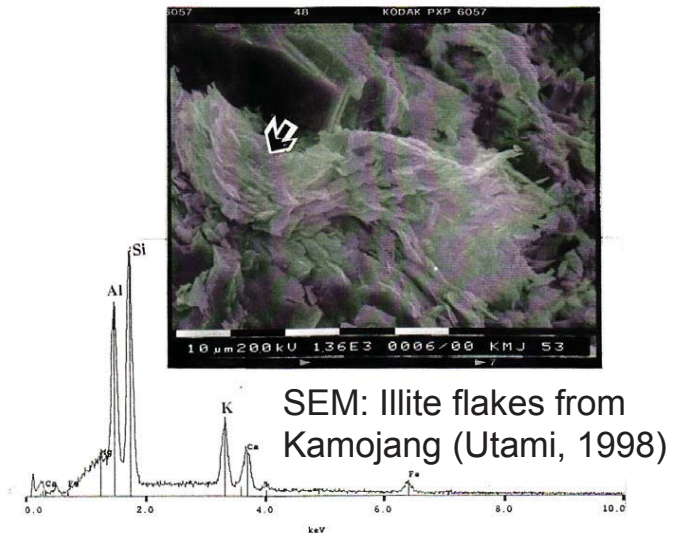




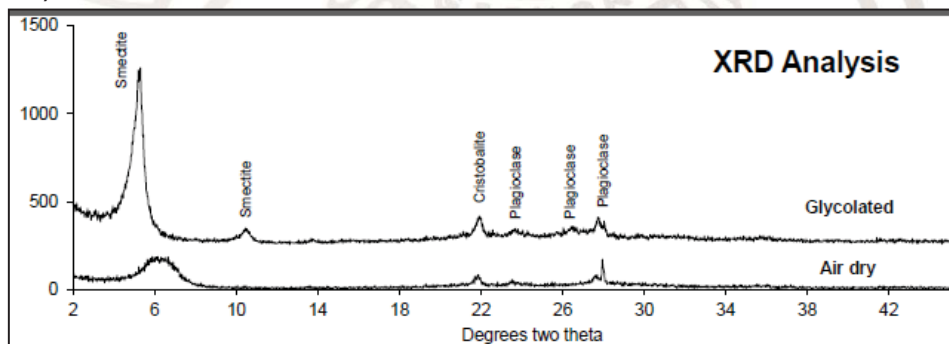




SEM: Chlorite plateles from Lahendong (Utami, 2011)



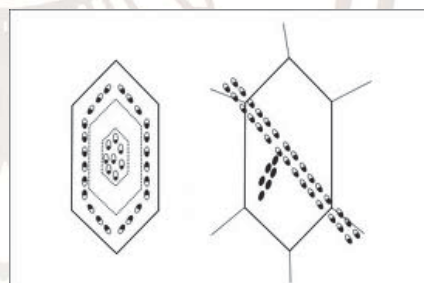
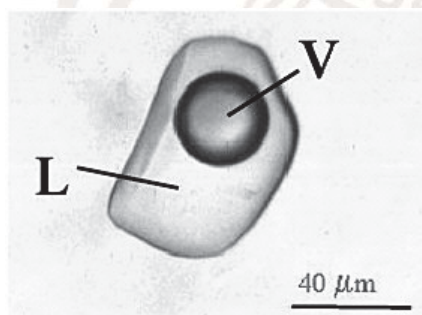
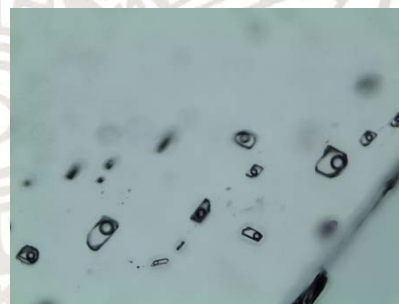
SEM: Illite flakes from Kamojang (Utami, 1998)



### 3.14. Fluid inclusions

Fluid inclusions are small ( $\ll 0.1$  mm) fluid samples trapped during the growth or healing of a crystal.

Fluid inclusions are commonly hosted by vein minerals, e.g., quartz, calcite, anhydrite, others (fluorite, sphalerite).







By means of fluid inclusion micro-thermometry we can assess:

- Temperature
- Fluid salinity
- Trends of temperature and fluid salinity in time and space
- The phase of the fluid
- Physical process: boiling, dilution, mixing, conductive cooling



### 3.15. Concluding Remarks

Hydrothermally altered rocks are the record of interactions between hot fluids and the rocks and the process affecting the circulating fluids in the system.

Hydrothermal minerals serve as indicators of the prevailing condition in the system at the time the minerals formed, including:

- Temperature & pressure
- Permeability
- Fluid composition

Integration between the conditions inferred from hydrothermal alteration studies with the present-day/measured conditions provide good understanding of the trend of the behavior of the system through time, and hence can help build development strategy of the field.



## Relevance for the assessment: case study Lahendong Geothermal Field



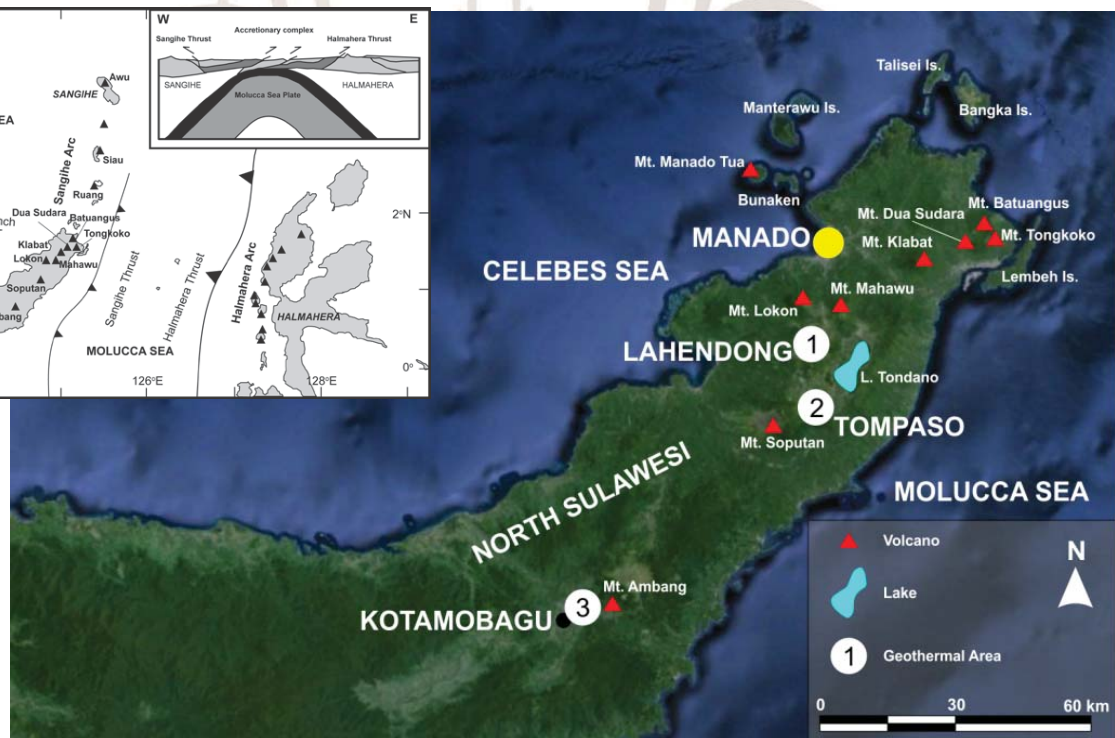
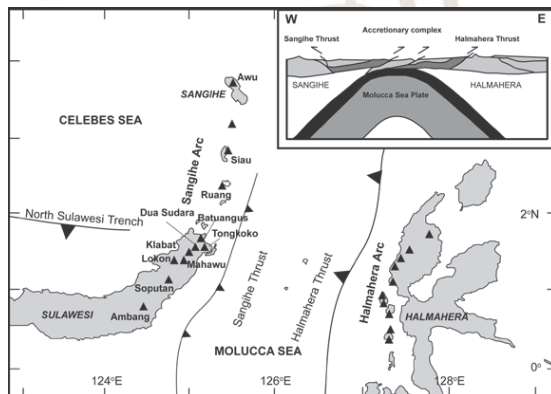
Adapted from oral presentation by Pri Utami and others at the World Geothermal Congress 2015 under the title Hydrothermal Alteration and the Evolution of the Lahendong Geothermal System, North Sulawesi.



## Outline

- Location and field overview
- Geology
- Hydrothermal alteration mineralogy
- Space-fill mineral paragenesis
- Stable isotope analyses
- Evolution of the Lahendong geothermal system
- Conclusions

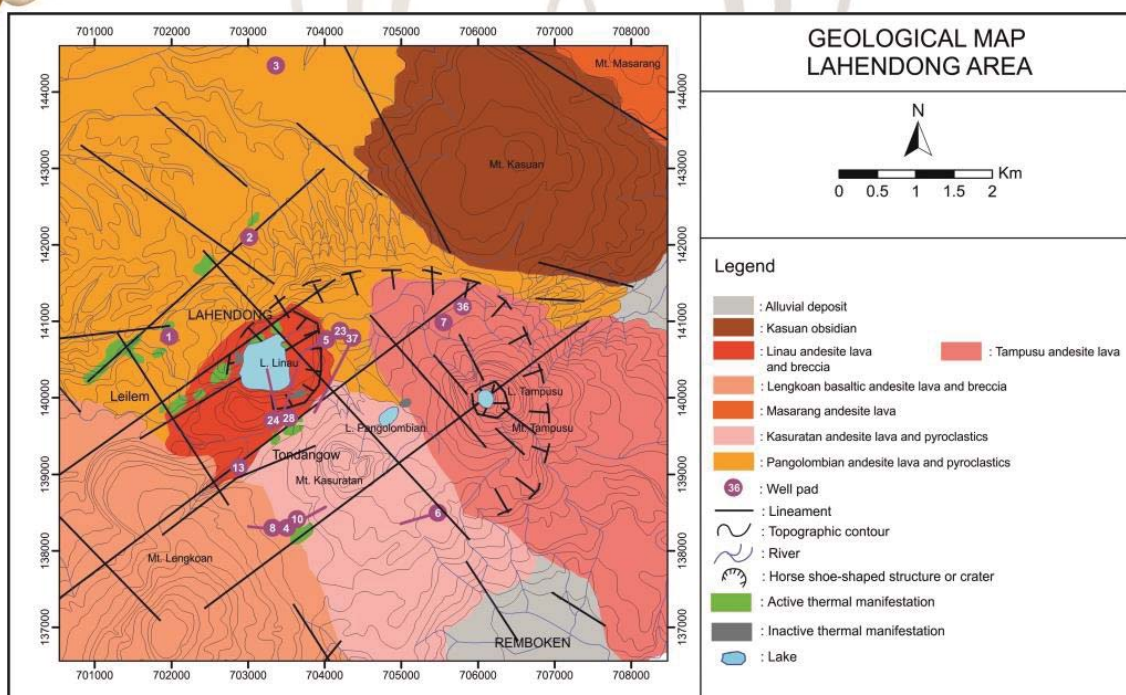
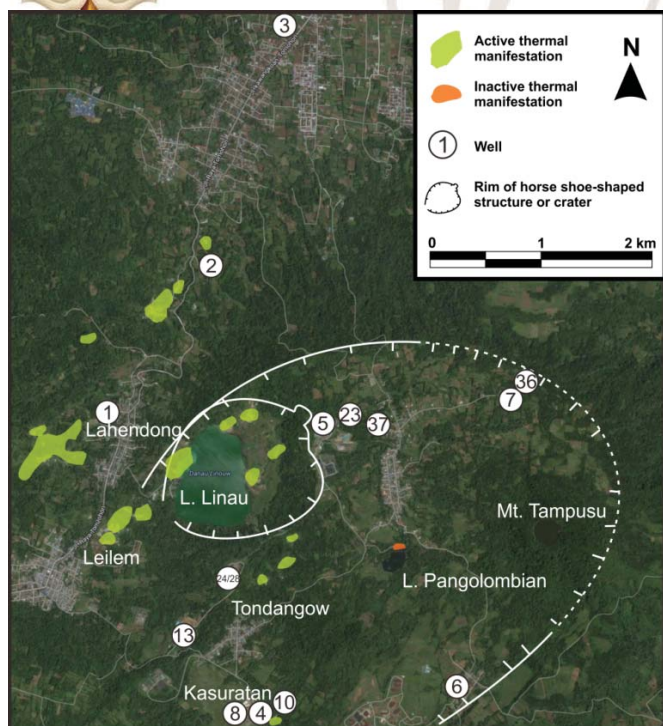




### Field overview

- First geothermal field in Eastern Indonesia to be developed for electricity generation.
- Current power production is 60 MWe.
- 28 wells (1500 – 2500 m depth), with typical temperature of 250 °C at – 250 m RSL.
- High-relief volcanic terrain in arc-arc collision setting.
- Liquid-dominated system with fumarolic and steam-heated manifestations at 750 m asl.





(UTC Pertamina, 2013)



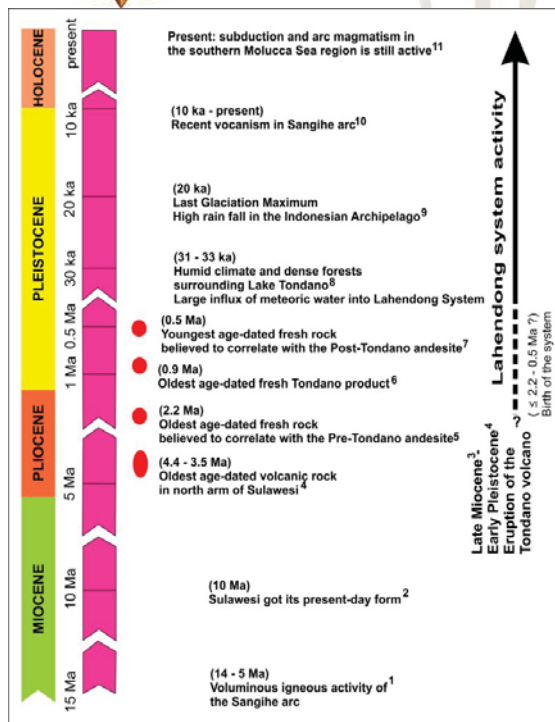


Diagram showing the inferred time of the emergence of the Lahendong geothermal system within the framework of the known geologic history of the north arm of Sulawesi region (Utami, 2011).

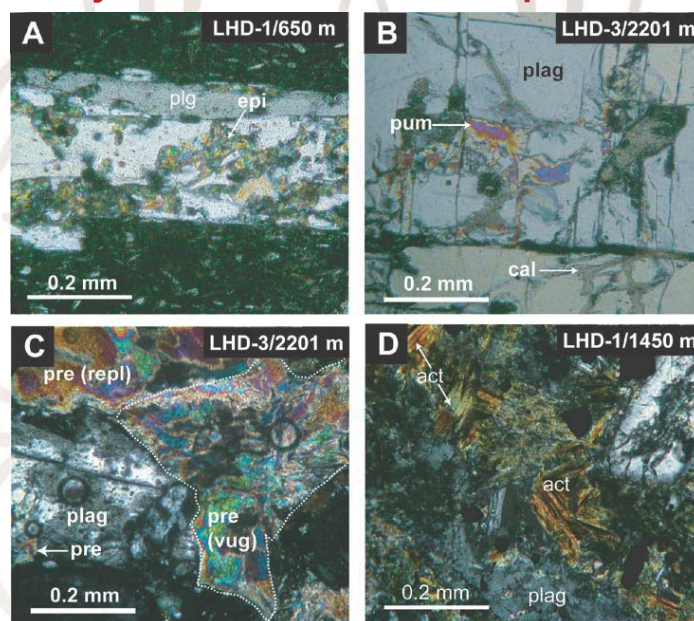
Hydrothermal activity started possibly after the peak of the voluminous volcanism in the Sangihe arc.

Meteoric water recharge became abundant since ~31 ka.

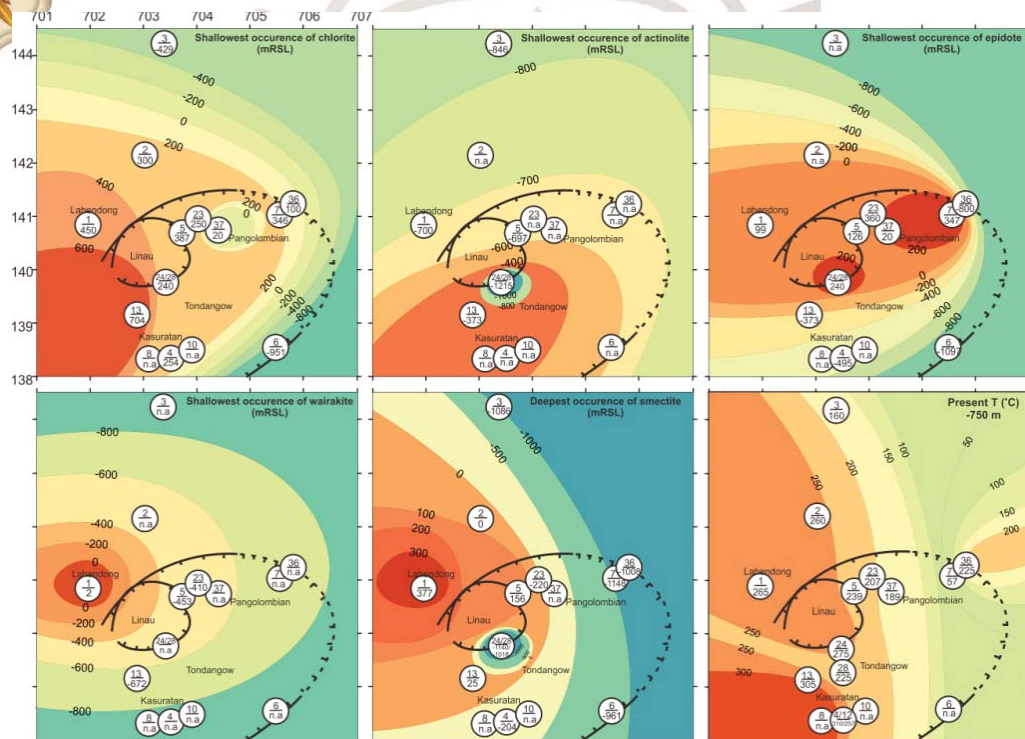
1 = Hamilton (1979), 2 = Hall (1997), 3 = Suari et al. (1987), 4 = Morrice et al., (1983), 5 – 7 = PT. Gondwana (1988), 8 = Dam et al., (2001), 9 = Bush and Philander (1999), 10 = Hamilton (1988), Hall (2000), 11 = Macpherson (2003).



## Subsurface hydrothermal alteration: replacement mineralogy



- Product of fluid – mineral interactions
- Field-wide distribution



Inactive altered ground marking the Old Pangolombian thermal activity.

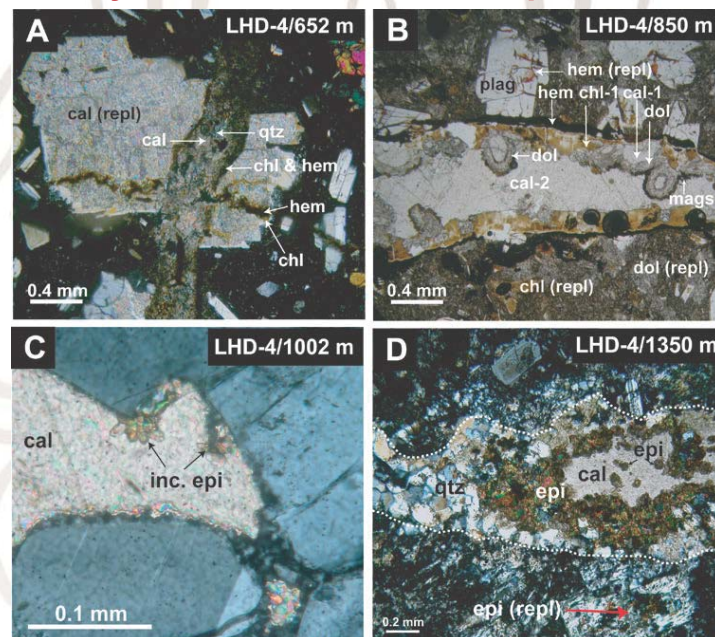


Active thermal manifestations in the shore of Lake Linau





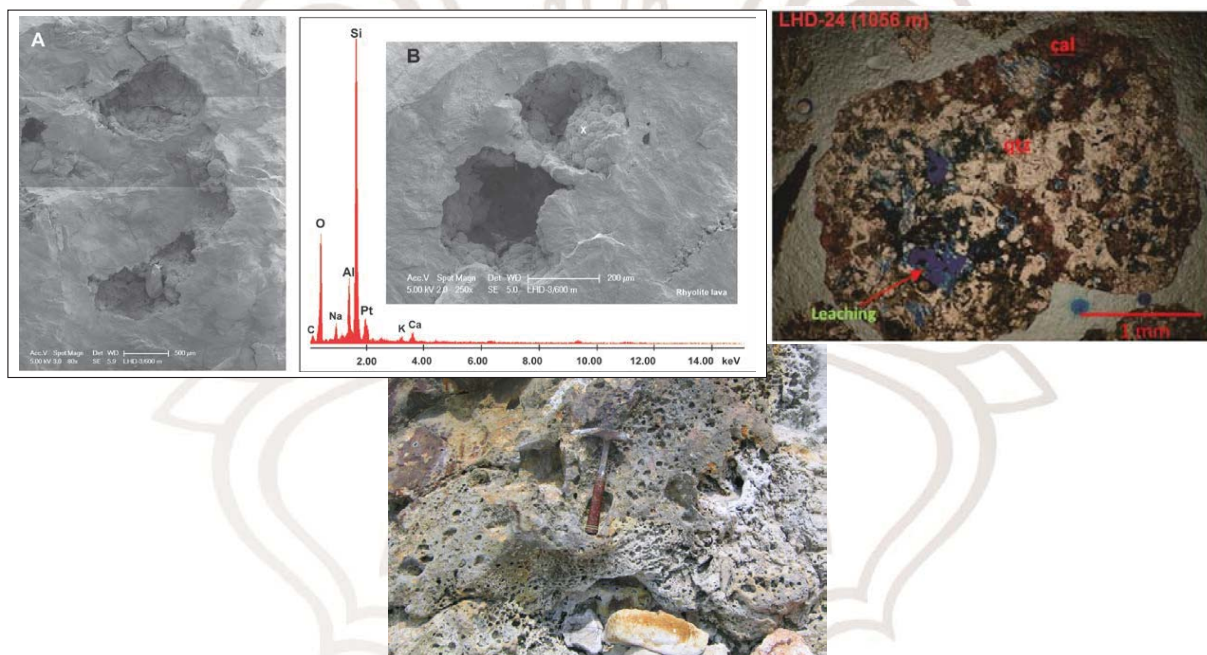
## Subsurface hydrothermal alteration: space-fill mineralogy



- Reflect processes affecting the circulating fluids



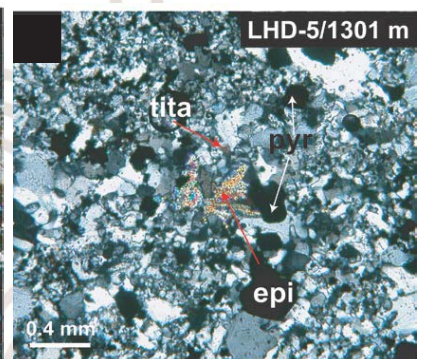
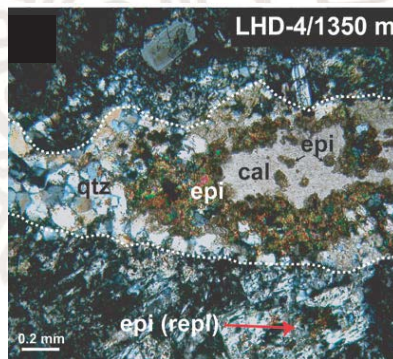
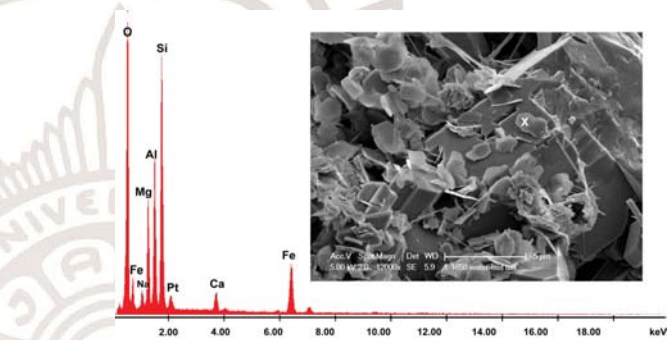
## Dissolution texture: result of interaction of rocks with reactive fluids





### Vein mineral paragenesis

- Simple veins are usually older or else, younger than those of complex texture.
- Chlorite is present field-wide, and commonly was the first deposited mineral.
- Calc-silicates tend to occur in veins with complex textures, which often cut the simpler veins, therefore they may have been formed after the simpler veins.
- Brecciated veins seem to be the youngest veins.



### Vein mineral paragenesis (example from well LHD-5)

Stage Depth (m)	1 <sub>5</sub>	2 <sub>5</sub>	3 <sub>5</sub>	4 <sub>5</sub>	5 <sub>5</sub>
500 - 501	hem	cal ± qtz ± chl ± hem			
650 - 651	chl	(chl ± cal ± anh)		tita	
652 - 653	chl chl →	cal cal	qtz qtz	anh cal tita	
750 - 751	chl →	cal →	chl →	cal	cha
900 - 902*	chl	(cal ± anh) →	(qtz ± pyr)		
1101 - 1102	chl		qtz →	epi	
1102 - 1103	chl	(ill → qtz)		czo epi tita	qtz
1301 - 1302			chl, ill, cal, qtz, epi, tita, adu, pyr)		micr. qtz
1331 - 1332	chl		(chl ± qtz)		
1404 - 1405	chl		(cal - qtz) (micr. qtz ± pyr ± epi) →	cal	





### Hydrothermal alteration stages

Subsurface vein mineral paragenesis observed in 14 wells indicate that Lahendong geothermal system has undergone at least five hydrothermal alteration stages:

1. Stage-1: development of mono-mineralic veins of chlorite in hot water-dominated reservoir.
2. Stage-2: deposition of calcite and second generation of chlorite.
3. Stage-3: deposition of calcite and quartz, and other carbonates.
4. Stage-4: deposition of calc-silicates and alkali silicates indicating the peak of the activity of the Lahendong hydrothermal system.
5. Stage-5:
  - Development of late calcite, late quartz and hematite veins.
  - Low temperature zeolite (mordenite and heulandite) developed at the margin of the system.
  - Development of brecciated veins at the central parts of the system and the deposition of chalcedony.
  - Rock leaching at the deep, central part of the system.

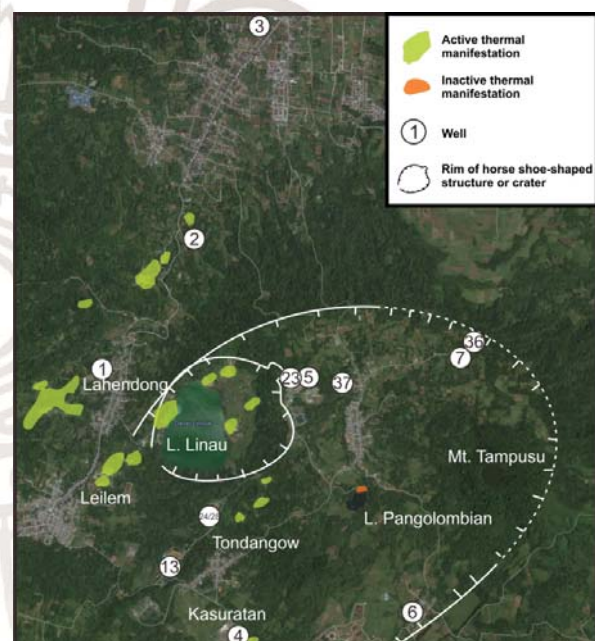


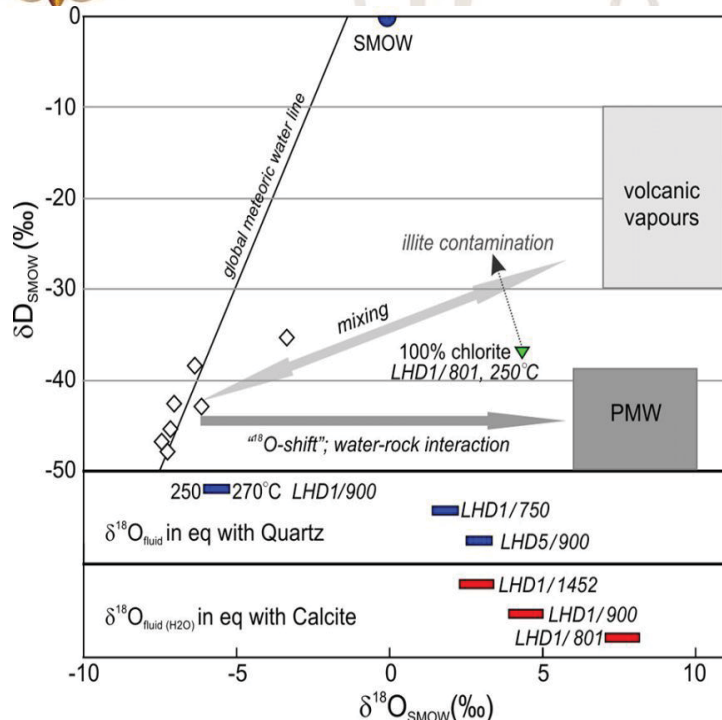
### Stable isotope analysis

Aim: to identify potential fluid source(s) of the geothermal fluids and investigate whether there could be a mixture of fluid components from magmatic and meteoric sources.

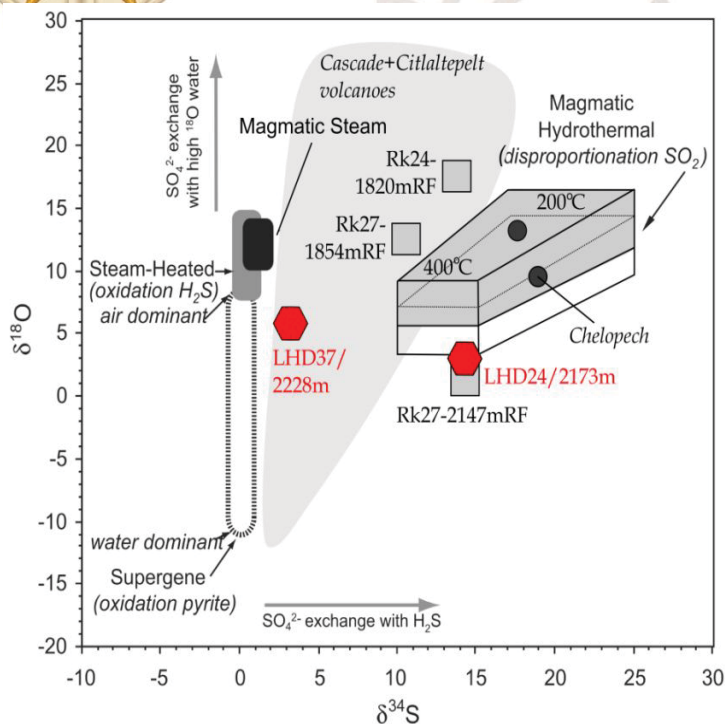
Isotope analysis was performed for 7 (seven) selected samples from Lahendong wells (LHD-1, LHD-5, LHD-24 and LHD-37).

Quartz, calcite and clays were analysed for isotope  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ , and  $\delta^{13}\text{C}$ , whereas anhydrite was for isotope  $\delta^{34}\text{S}$  and  $\delta^{18}\text{O}$ .





- Plot of  $\delta D$  and  $\delta^{18}O$  isotopic values of the calculated fluids in equilibrium with hydrothermal clays
- $\delta^{18}O$  values of hydrothermal fluid in equilibrium with quartz (blue bars) and calcite (red bars), calculated between 250 and 270°C.
- $\delta^{18}O$  in the quartz, clay, and calcite are enriched in oxygen isotope about 3‰, 4.8‰, and 2–7‰, respectively.
- The range of  $\delta^{18}O_{\text{fluid}}$  indicates mixing between meteoric water, chloride hot water and magmatic oxygen.

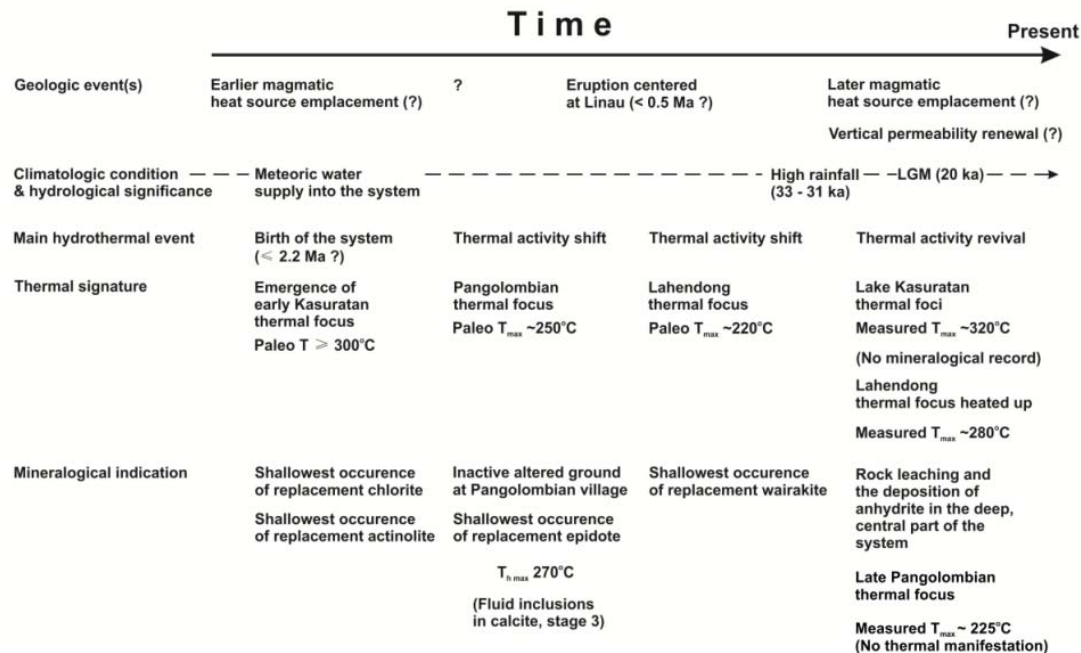


- Magmatic fluid influx during the deposition of anhydrite in the deep parts of LHD-24 and LHD-37.
- Similarity of isotopic signature of anhydrite from LHD-24 with hypogene anhydrite, associated with magmatic-hydrothermal fluid in the high sulfidation hydrothermal environment.
- Anhydrite from LHD-37 was deposited from  $SO_2$  magmatic gas or oxydation of magmatic  $H_2S$  gas in the magmatic-hydrothermal environment similar to the depositional environment of magmatic ore.





## Evolution of the Lahendong geothermal system



## Conclusions

Hydrothermal alteration studies on subsurface rocks combined with the field geology studies of reveal that:

- The Lahendong geothermal system has undergone natural changes, most notably relocation of thermal focus, and, changes in the composition of the altering fluid.
- The system was dynamic and different parts of the system have undergone different hydrothermal histories.
- Present thermal foci:
  - Major: Lahendong – Linau and the Late Kasuratan (both are expressed by active steam-heated manifestation).
  - Minor: Late Pangolombian (has not developed a manifestation).
- This finding, combined with the study of the composition of the present-day fluid, has to be taken account in making the field development strategy.
- The behavior of a geothermal system is better understood if both past and present conditions of the system are known. Reconstructing past conditions and the way a geothermal system changes through time – starting with observing the rocks – is therefore of similar importance to modelling of present-day and future conditions by means of reservoir simulation softwares.

## 04 Geothermal Fluids

Agung Harijoko  
(Universitas Gadjah Mada)



**GEOCHEMISTRY FOR GEOTHERMAL DEVELOPMENT**  
**UGM – UU – Geocap Capacity Building Program**  
**21 – 25 August, 2017**



## 04. GEOTHERMAL FLUIDS



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Adapted from geothermal lecture handouts by Agung Harijoko at Geological Engineering UGM.

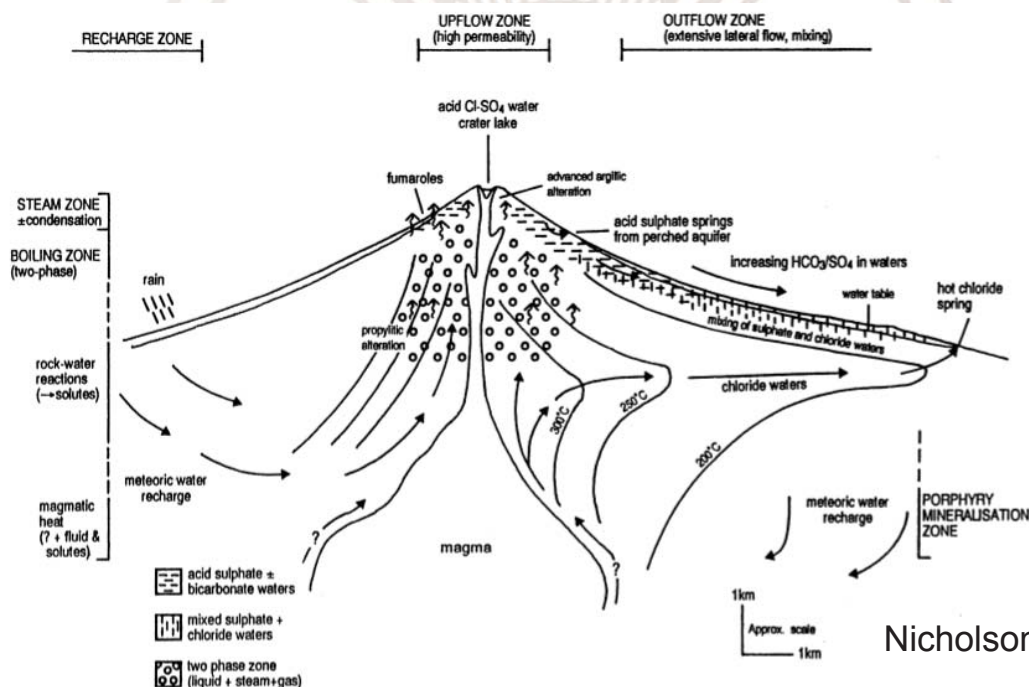


### Geothermal Fluids | Agung Harijoko



#### 4.1. Geothermal systems

- Geothermal energy is natural heat energy of the Earth that is transferred to the surface or near surface conductively and convectively.
- Water play important role as a media of convective heat transfer of the geothermal energy.



Nicholson, 1993



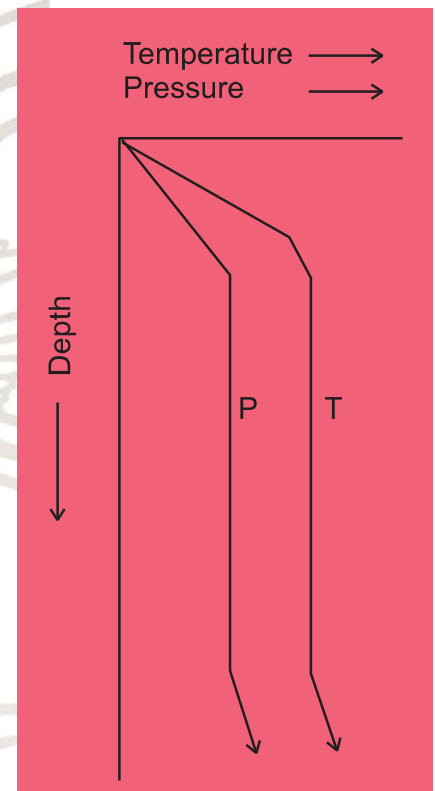


- The chemistry of the geothermal fluid may indicate the subsurface processes and physico-chemical condition, therefore it attracts researchers to study of the origin and evolution of the geothermal fluid.
- Craig (1963) showed that the deuterium content of geothermal waters are close to that of local groundwater.
- Ellis and Mahon (1964) showed that most of the chemical constituents of geothermal waters are resulted from leaching of crustal rocks.

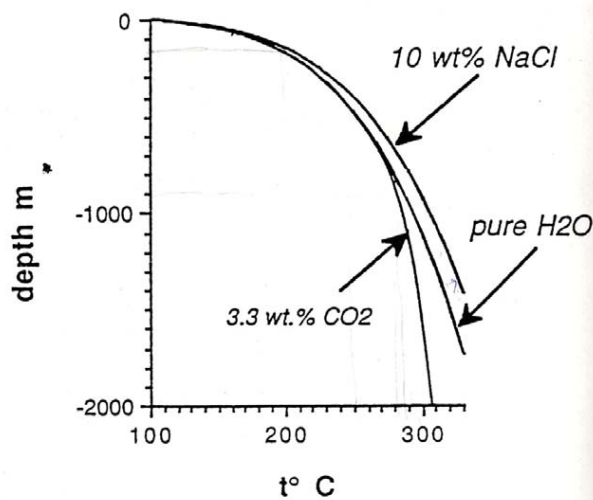


## 4.2. Characters of geothermal fluid

- On the surface, the temperature of geothermal water is higher than the ambient temperature of the surrounding air.
- Measured downhole temperatures in drilled geothermal systems range from ambient to over 400 °C
- Depending on  $P$  and  $T$  the fluids of geothermal systems may be single water phase or two-phase mixture of water and steam.







- In liquid-dominated systems, the fluid is dominantly liquid water by volume (White et al. 1971).
- In two-phase systems, pressure determines temperature at each depth, whereas under single phase conditions, temperature and pressure are independent variables.
- In vapor-dominated systems, vapor at ~240 °C fills permeable channels, although liquid water occupies inter-granular pore spaces.



- Very hot saline liquid (>400 °C) is known to exist below the vapor-dominated zone (Fournier 1991; Barelli et al. 1995; Gianelli and Ruggieri 2002).
- In systems where the temperature is lower than about 350 to 370 °C, pore fluid pressure is hydrostatic (Fournier 1991). Where higher temperatures have been encountered in drillholes, the pressure is above hydrostatic but probably still below lithostatic (Fournier 1991).



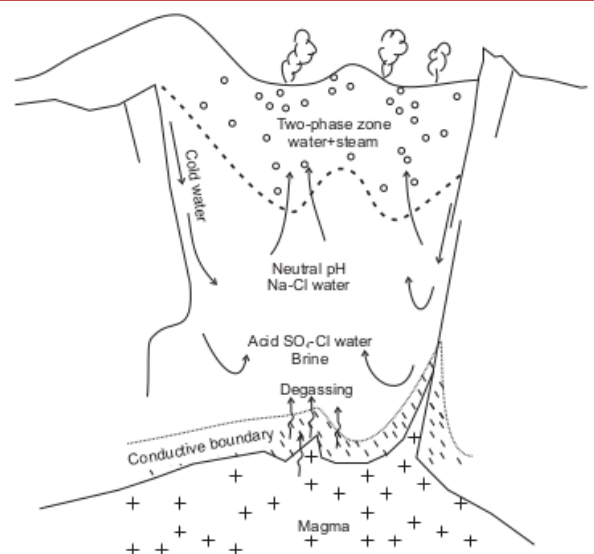
## Chemical characters

- Containing chemical elements in the form of aqueous, gases and isotopes
- One element may be a major element in the geothermal fluid but minor in rocks
- Chemical composition of geothermal fluids affected by:
  - Dissolution of primary mineral
  - Precipitation of secondary mineral



## Types of geothermal fluid

- Geothermal fluid is distinguished into primary and secondary geothermal fluid.
- Geothermal fluids at the bottom of the convection cell (base-depth) are termed primary geothermal fluids.
- When primary fluids rise towards the surface, they can undergo boiling and mixing to form secondary geothermal fluids.



Schematic of fluid flow within magmatic geothermal system (Arnorsson et al., 2007)





## Formation of secondary fluids

- Arnorsson et al., (2007) suggested the most important processes leading to the formation of secondary geothermal fluids are:
  - Depressurization boiling to yield boiled water and a steam phase with gas.
  - Phase separation of saline fluids into a hypersaline brine and a more dilute vapor.
  - Vapor condensation in shallow ground water or surface water to produce acid-sulfate, carbon-dioxide or sodium bicarbonate waters.
  - Mixing of CO<sub>2</sub> gas from a deep source with thermal ground water.
  - Mixing of geothermal fluids with shallower and cooler ground water.
- In the exploration stage we deal mostly with the secondary fluids, while during production we deal with primary fluid.



## Geothermal fluids

- Primary geothermal fluids
  - Na-Cl waters
  - Deep Acid-sulfate waters
  - High salinity waters.
- Secondary geothermal fluids
  - Steam-heated acid sulfate waters
  - Carbon-dioxide waters
  - Mixed waters



## Geothermal fluids

- Geothermal waters tend to have similar solute component in various concentration.
- Concentration difference is caused by the difference in:
  - Temperature
  - source of the water origin
  - magmatic input
  - rock type
  - condition and duration of water-rock interaction
  - boiling and mixing.



- Most of the solute components in the geothermal fluids:
  - Anions:  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{F}^-$ ,  $\text{I}^-$ ,  $\text{Br}^-$
  - Cations:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Li}^+$ ,  $\text{Mn}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{NH}_4^+$ , Unspecified As
  - Neutral species:  $\text{SiO}_2$ , B,  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ .





## Reactive and conservative components

Solute components of geothermal fluids are grouped as:

- Reactive/common rock-forming species: react with other elements to reach equilibrium, therefore their solubilities are controlled by temperature dependent mineral-fluid equilibria. Entering the solution after dissolution of the host minerals and the concentration decrease after the formation of secondary minerals.  $\text{SiO}_2$ , Ca, Na, K, Mg etc.
- Conservative/non reactive/solubles: non reactive, once dissolved in the water it will remain in the water therefore it is called also tracer elements. Cl, B, Br, Li, deuterium ( $\text{D}$ ,  $^2\text{H}$ ).



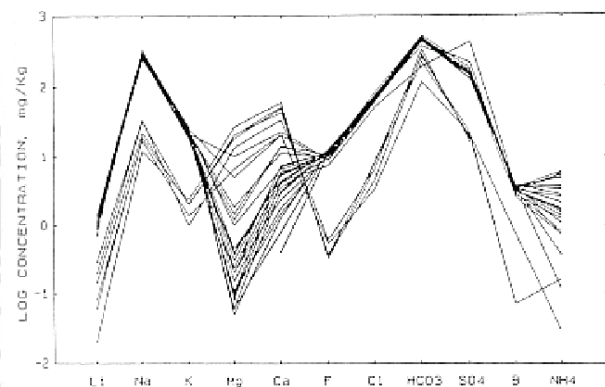
## Source of the components of geothermal waters

- The controlling process of the fluid composition is dissolution of primary minerals and the formation of secondary minerals.
- Rock dissolution increases concentration of conservative elements, such as :  $\rightarrow$  Cl, B, Br
- Formation of secondary minerals lowers concentration of reactive elements, such as : Al, Mg, Fe.
- Mineral-fluid equilibria control the major element concentrations and pH of deep geothermal fluids.
- Large-scale rock- water equilibria controlling fluid compositions and alteration assemblages in geothermal and fossil hydrothermal systems (Arnorsson et al., 1978; Bird and Norton, 1981; Giggenbach, 1981).



### 4.3. Classification of geothermal water

- The Schoeller plot displays the log concentration of several constituents for each water sample.
- The values are connected with a line, allowing comparison of the different waters plotted

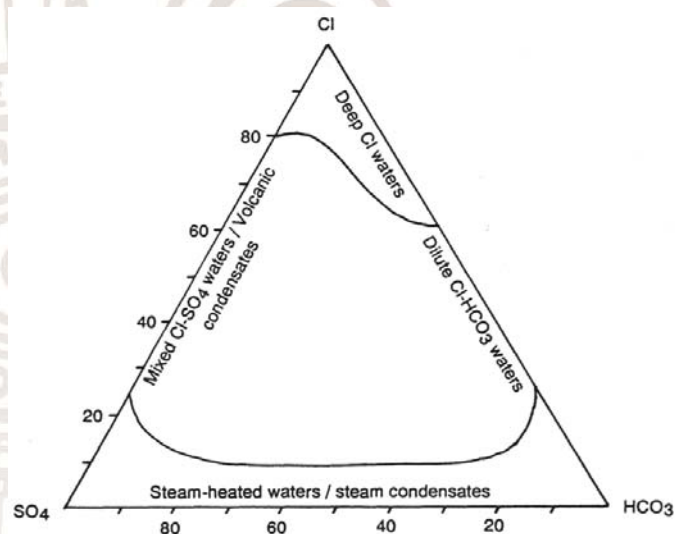


Example of Schoeller plot of thermal and cold waters from San Ignacio, Honduras (Truesdell, 1991)



### 4.3. Classification of geothermal water (cont'd)

- Giggenbach, (1998), proposed the use of ternary plot of three main anion of  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  to classify geothermal waters.
- The geothermal waters are classified as: chloride, bicarbonate and sulfat waters.
- Using this plot therefore we may identify deep geothermal water origin, volcanic water, steam heated water and mixing or peripheral water.







- The advantages of this diagram are:
  - the three main anion are plotted separately on the three vertices of the plot;
  - mixing lines are straight lines;
  - all available samples can be plotted; groupings and trends can be evaluated.
- Its limitations are:
  - relative ratios between Cl, SO<sub>4</sub> and HCO<sub>3</sub> are displayed; the content of each species relative to water is obliterated in this plot;
  - apparent correlations may be accidental; correlations have to be checked by means of additional independent data.



## Chloride water (Nicholson, 1993)

- *Occurrence.*
  - Also termed "alkali-chloride" or "neutral-chloride", is typical of the deep geothermal fluid found in most high-temperature systems.
- *Surface features.*
  - commonly discharged from hot springs and pools of good flow, and from most geysers.
  - The water in deep pools appears clear and blue-green in colour - a distinctive features of chloride waters.
- *Chemistry.*
  - Chloride is the dominant anion, up to about 10,000 mg/kg.
  - Other main constituents include sodium and potassium (often in a - 10:1 concentration ratio), as the principal cations, with significant concentrations of silica (higher concentrations with increasing temperature at depth) and boron.
  - Sulfate and bicarbonate concentrations are variable, but are commonly several orders of magnitude less than that of chloride.
  - Fe and Al concentration in the trace level.



## Acid sulfate waters

- *Occurrence.*
  - these are superficial fluids formed by the condensation of geothermal gases into near-surface, oxygenated groundwater.
- *Surface features.*
  - These acid waters are often found in turbid (cloudy) pools or mud pools but may also occur as springs.
- *Chemistry.*
  - Sulfate is the principal anion, and is formed by the oxidation of condensed hydrogen sulfide
$$\text{H}_2\text{S}_{(\text{g})} + 2\text{O}_{2(\text{aq})} = 2\text{H}^+_{(\text{aq})} + \text{SO}_4^{2-}_{(\text{aq})}$$
  - Fe and Al concentration is in detection limit indication for the near surface rock leaching.
  - Cl concentration is commonly very low except if there is influx of volcanic gas.



## Bicarbonate waters

- *Occurrence.*
  - Including those termed CO<sub>2</sub>-rich fluids and neutral bicarbonate-sulphate waters, are the product of steam and gas condensation into poorly-oxygenated sub-surface groundwaters.
  - Bicarbonate waters found in non-volcanogenic, high- temperature systems (eg. Turkey and Africa) are more problematic in origin and may constitute the deep reservoir fluid.
- *Surface features.*
  - Warm to hot springs and cool "soda" springs.
- *Chemistry.*
  - The waters are of near-neutral pH as reaction with the local rocks (either in the shallow reservoir or during lateral flow) neutralises the initial acidity of these waters (see above carbonate equilibrium).
  - Sulfate may be present in variable amounts, with chloride at low concentrations or absent (Mahon et al., 1980a). These waters are highly reactive, and their corrosive action on well casings needs to be taken into account in the development of a field (Hedenquist and Stewart, 1985).





## Summary of water types in geothermal systems

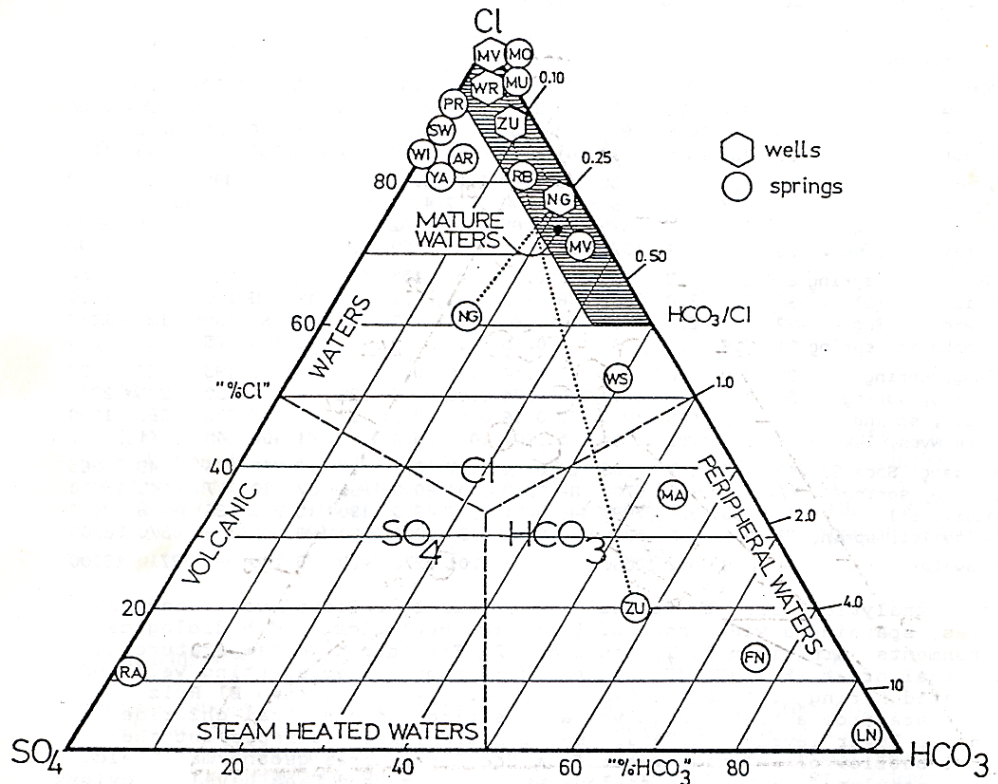
	Approximate pH range	Principle Anions
Groundwater	6 to 7.5	trace $\text{HCO}_3^-$
Chloride water	4 to 9	Cl, lesser $\text{HCO}_3^-$
Chloride-bicarbonate water	7 to 8.5	Cl, $\text{HCO}_3^-$
Bicarbonate water	5 to 7	$\text{HCO}_3^-$
Acid-sulfate water	1 to 3	$\text{SO}_4^{2-}$ , trace Cl
Acid-sulfate chloride water	1 to 5	$\text{SO}_4^{2-}$ , Cl



Table 5.1 (Giggenbach and Goguel, 1989; Giggenbach, 1991).

The chemical composition of thermal and mineralised waters from New Zealand (WK, NG, MO, MU, WI), Guatemala (ZU), Costa Rica (MV), Colombia (RA, RB), Mexico (AR), India (MA), Thailand (FN), Solomon Islands (PR), Vanuatu (YA) and Cameroon (LN) in mg/kg.

Area	°C	pH	Li	Na	K	Rb	Cs	Mg	Ca	B	$\text{HCO}_3$	$\text{SiO}_2$	$\text{SO}_4$	Cl
WK Wairakei, well	240	8.5	10.7	1170	167	2.20	2.00	0.01	20	26	5	590	35	1970
WK Wairakei, spring	99	7.7	14.5	1220	140	2.30	2.10	4.50	30	43	30	320	30	2100
NG Ngawha, well	230	7.1	10.9	880	75	0.30	0.75	0.10	3	895	310	385	26	1240
NG Ngawha, spring	80	7.2	10.4	910	64	0.29	0.60	1.40	11	850	330	150	446	1290
ZU Zunil, well	300	8.4	8.1	1030	210	1.90	2.00	0.01	11	45	150	890	61	1700
ZU Zunil, spring	87	8.7	0.6	260	37	0.08	0.02	43.0	43	5	500	200	195	170
MV Miravalles, well	245	7.5	5.7	1970	238	1.05	0.60	0.02	73	54	40	590	36	3300
MV Miravalles, spr.	73	8.5	3.4	1970	79	0.21	0.14	6.50	22	48	910	112	120	2600
RA Ruiz, acid spring	62	1.2	0.3	280	224	0.37	0.04	155	214	8	-	154	10670	1350
RB Ruiz, neutral s.	94	8.0	3.8	610	78	0.56	0.62	5.1	48	19	175	180	41	1000
AR Araro, spring	92	8.1	6.6	705	50	0.43	1.12	0.3	30	75	63	230	135	1010
MA Manikaran, spring	94	7.4	1.2	93	21	0.15	0.14	3.3	51	3	190	75	35	130
FN Fang, spring	99	9.0	0.6	122	8	0.14	0.29	0.1	1	<1	145	195	22	27
PR Paraso, spring	56	5.6	1.8	1210	178	0.74	0.09	26.6	289	16	6	150	205	2340
YA Yasur, spring	99	8.8	0.3	1270	73	0.16	0.01	0.3	17	21	75	270	280	1690
LN Lake Nyos, lake	23	5.4	.01	15	5	.004	.001	35.0	30	<1	400	45	<1	<1
WS Waitangi Soda Spr.	49	7.3	1.7	285	24	0.11	0.07	8.9	17	3	265	176	48	365
MO Morere, spring	47	7.0	4.6	6700	84	0.10	.004	80.0	2360	57	30	27	<3	15800
MU Maui, well	130	7.5	3.6	7880	440	0.71	0.08	48.0	190	15	630	36	18	12600
WI White Isl. spring	98	0.6	2.9	5910	635	5.40	0.36	3800	3150	160	<1	-	4870	38700
SW Seawater	4	7.8	0.2	10560	380	0.13	<.01	1270	400	5	140	-	2710	19000



## Brines

- It contains very high concentration of solute components.
- Chloride is the main component in the range of 10,000 – 100,000 ppm
- Concentration of Na, K, Ca is high to balance the charge.
- In geothermal system the formation can be:
  - Connate brines trapped in the sedimentary basin
  - Dissolution of the evaporate by meteoric water





- **Geothermal fluid different because:**
  - Sources of recharge water in geothermal system
  - Contribution of volatile magmatic and metamorphic
  - Hydrology → mixing and boiling



#### 4.4. Origin of geothermal water

- One of the main goals of geothermal geochemistry research is to identify the origin of geothermal fluids.
- Water recharge derived from:
  - Meteoric water
  - Sea water
  - Connate water
  - Magmatic water
- They may constitute a mixture of two or more fluids, such as water of meteoric origin, seawater and magmatic volatiles.
- Origin of geothermal water therefore can be identified by:
  - Character of the chemical composition of conservative constituents
  - Stable isotope of water,  $^{18}\text{O}$  and  $^2\text{H}$ .



## Identifying the source(s) of water using Cl /B ratios

- Cl/B ratio is often used to indicate a common reservoir source for waters
- Some caution is required, since waters from the same reservoir can show differences in this ratio
- Differences can be induced by a change in lithology at depth over a field or by the adsorption of B onto clays during lateral flow

**Approximate Ranges In Chemical Components of Ocean Water, Oil-Field Brines Dominated by Chloride, and Volcanic Sodium-Chloride Springs**

Ratios, by weight	Ocean*	Oil-field brines+	Volcanic hot springs**
HCO <sub>3</sub> /Cl++	0.0074	0.0001-1	0.01-3
SO <sub>4</sub> /Cl	0.14	0.00000-1	0.01-0.5
F/Cl	0.00007	0.00001-0.001	0.0005-0.1
Br/Cl	0.0034	0.0001-0.01	0.0001-0.001
I/Cl	0.000003	0.00003-0.02	0.00001-0.0005
<b>B/Cl</b>	<b>0.00024</b>	<b>0.00001-0.02</b>	<b>0.01-0.1</b>
K/Na	0.036	0.001-0.03	0.03-0.3
Li/Na	0.00001	0.0001-0.003	0.003-0.03
Ca + Mg/Na + K	0.153	0.01-5	0.001-0.2

(White, 1957)



## Measuring isotopes

- It is difficult to get accurate measurement of absolute composition, however more accurate result can be get by comparing to the standart.
- R is the ratio in number of atoms between a given isotope and the most abundant isotope of that element.
- $R_{\text{unknown}} (= {}^{18}\text{O}/{}^{16}\text{O} \text{ or } \text{D}/\text{H})$
- To get accurate number of ratio, we compare to the standart.
- $(R_{\text{unknown}} - R_{\text{standar}})/R_{\text{standar}}$
- The ratio is symbolized with “del” (δ) as deviation per mil (‰).





- $\delta$  is “delta”, and is the isotope ratio of a particular thing (molecule, mineral, gas) relative to a standard times 1000. sometimes called ‘del’.

$$\delta^{18}O = \left( \frac{R_{sample} - R_{standard}}{R_{standard}} \right) \times 10^3$$

$$\delta = 1000 \{ (R_{unk}/R_{std}) - 1 \}$$



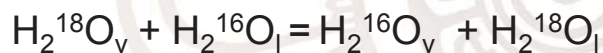
- Isotopes of the same element have almost identical properties but, because of their differences in mass, they have different rates and different distribution in two chemical compounds or phases in mutual isotopic exchange.
- Some physical processes, such as, diffusion, evaporation, condensation, melting, etc. also produce isotopic differentiation.
- All these variations in the isotopic composition produced by chemical or physical processes, in compounds or phases, present in the same system, are called isotopic fractionations.
- The fractionation factor “a” is the ratio between the isotopic ratios in the different species or phases of a system.
- At equilibrium “a” is related to the very good approximation that the isotopes are randomly distributed among all possible sites in the molecule, to the equilibrium constant K for the isotope exchange reaction between the two substances.



$$\alpha_b^a = \frac{R_a}{R_b}$$

Where  $R_a$  is the ratio of heavy/light isotope and  $a$  is the fractionation factor

Example water in liquid and vapor



So:

$$K = (\text{H}_2^{16}\text{O}_v) (\text{H}_2^{18}\text{O}_l) / (\text{H}_2^{18}\text{O}_v) (\text{H}_2^{16}\text{O}_l)$$



$$a = (\text{H}_2^{16}\text{O}_v \text{H}_2^{18}\text{O}_l) / (\text{H}_2^{18}\text{O}_v \text{H}_2^{16}\text{O}_l) = R_l / R_v$$

$$\alpha_{wv}(^{18}\text{O}) = \frac{R^{18}\text{O}_{\text{water}}}{R^{18}\text{O}_{\text{vapour}}}$$

$$1000 + (d) = 1000 (R_{\text{unk}} / R_{\text{std}})$$

$$\alpha = \frac{1000 \left( \frac{R_l}{R_{\text{std}}} \right)}{1000 \left( \frac{R_v}{R_{\text{std}}} \right)} = \frac{1000 + \delta_l}{1000 + \delta_v}$$





$$\alpha_{liquid-vapor}(O) = \frac{1000 + \delta^{18}O_l}{1000 + \delta^{18}O_v}$$



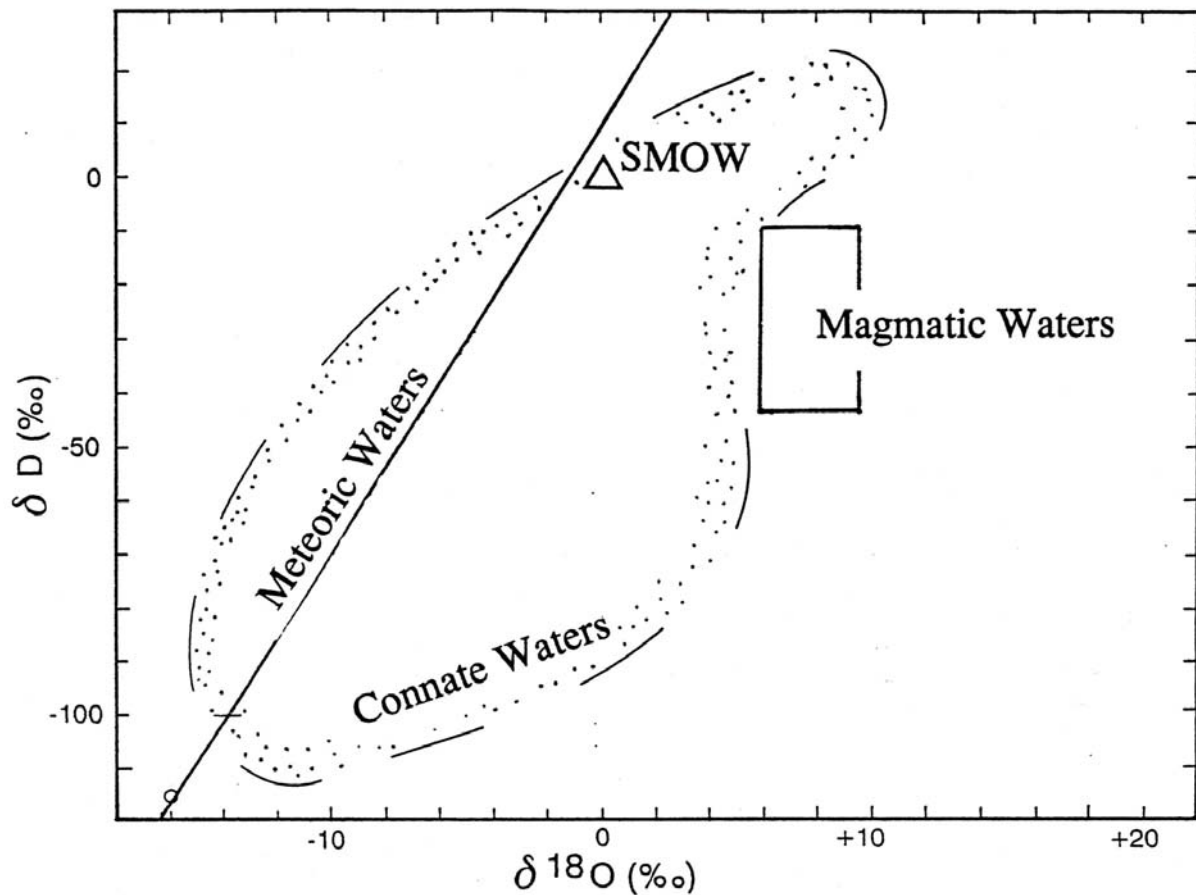
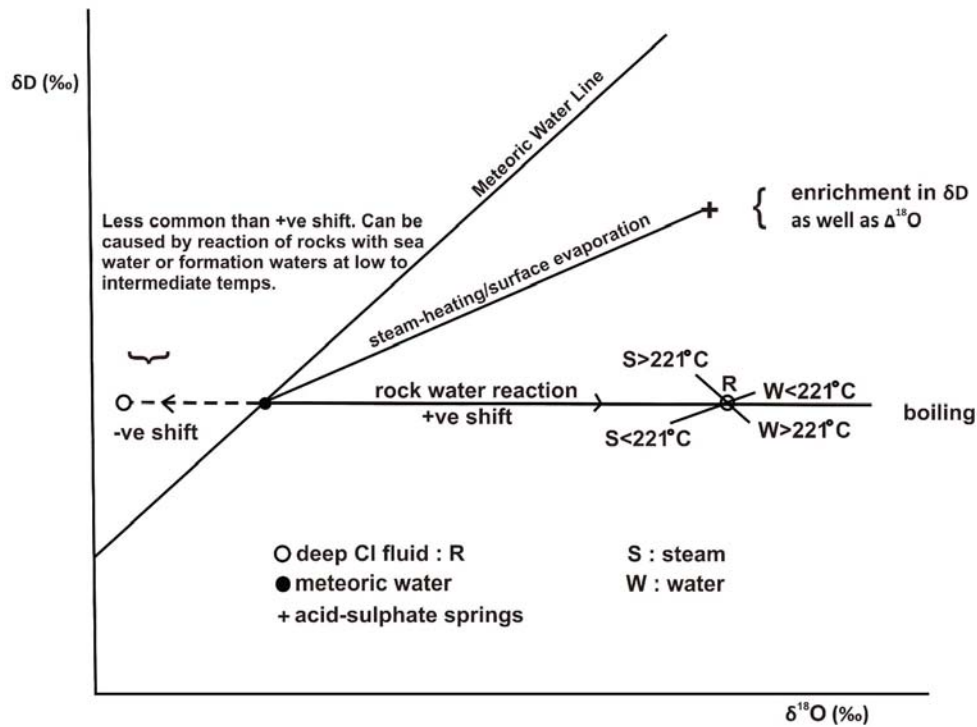
Because of the high rate at which isotopic equilibrium is attained between the liquid and vapor phases (Giggenbach, 1971), the distribution of isotopes can be assumed to be close to equilibrium and, therefore, to be governed by the equilibrium constant  $\alpha$ . The measured isotope contents  $\delta_w$  and  $\delta_s$  in the liquid and vapor phases are then related for either deuterium or oxygen-18 through:

$$1000 \ln \alpha \approx 1000(\alpha - 1) \approx \delta_w - \delta_s \quad (20)$$

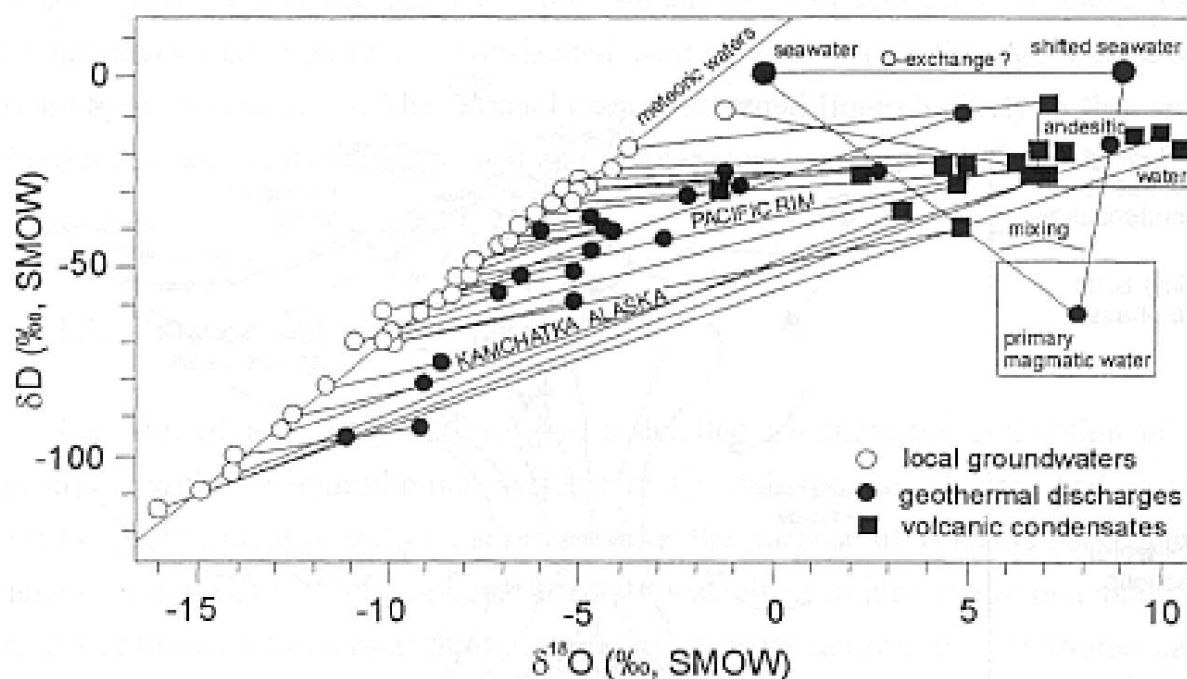
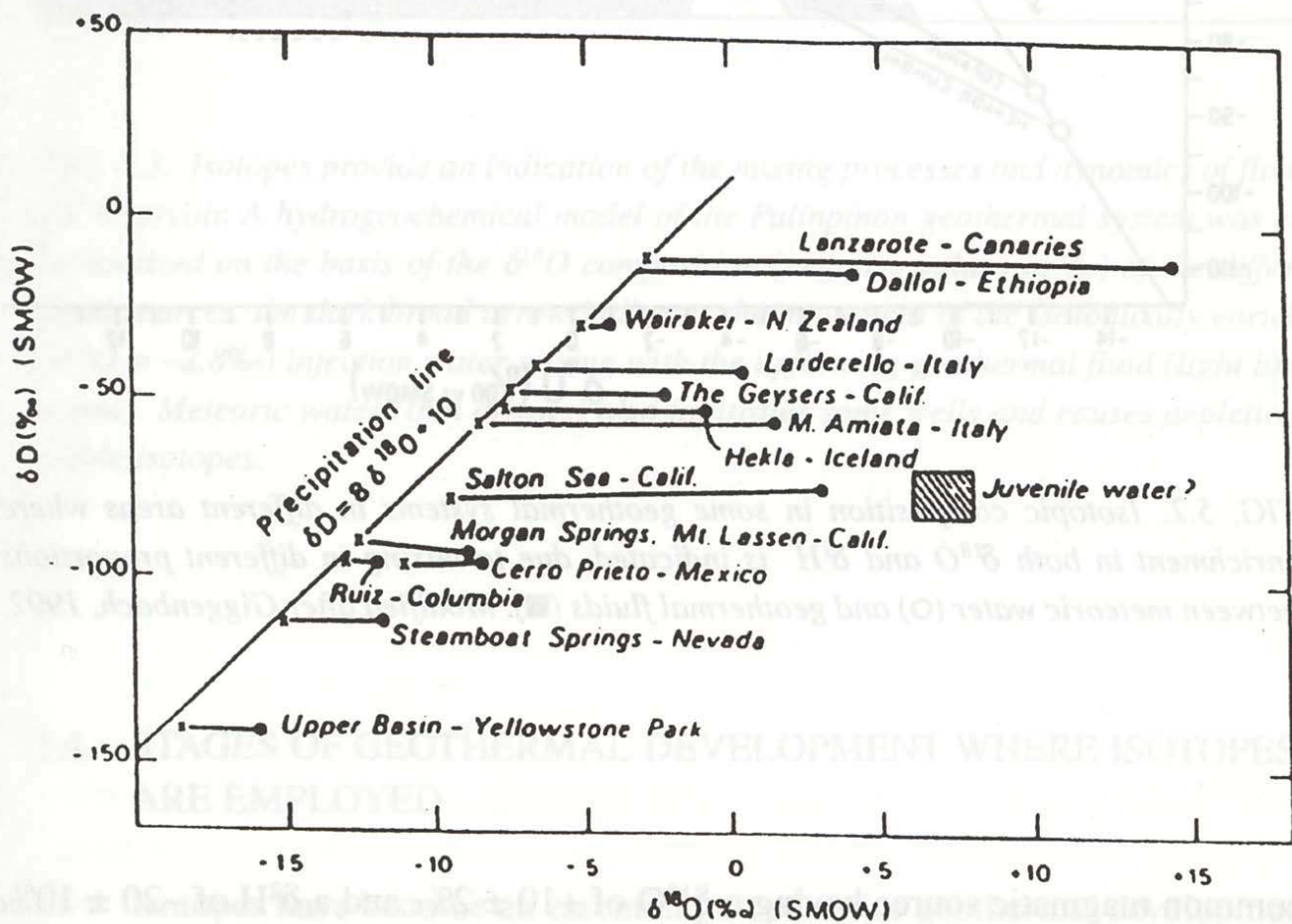
$$10^3 \ln \alpha_b^a \approx \delta_a - \delta_b = \Delta_b^a$$



## Identification source of water using stable isotope







## **05 Interpretation of Water Chemistry**

Pri Utami & Agung Harijoko  
(Universitas Gadjah Mada)





## **05. INTERPRETATION OF WATER CHEMISTRY (PART-1)**



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Adapted from geothermal lecture handouts by Pri Utami at the  
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and Geothermal Institute, The University of Auckland.



### **Interpretation of Water Chemistry | Pri Utami**

#### **5.1. Introduction**

- In the interpretation of water chemistry, it is important to note that not all springs will give reliable information about the conditions at depth.
- Hot, boiling chloride springs with strong outflows experience least contamination and therefore, become the most useful for reservoir-related investigations.
- Recording the composition of spring discharges across the field is very important to reveal the details of hydrology and processes.
- The deep chloride reservoir fluids of most geothermal systems tend to have similar dissolved constituents; the variations are due to the variation in temperature, gas content, heat source, rock type, permeability, source of recharge fluids, and the duration of hydrothermal activity.
- Since fluid-rock interaction is one of the factors determining the compositions of hydrothermal fluids, the knowledge of chemical composition of rocks will help understand the fluid geochemistry.



## 5.2. Interpretation of geothermal fluid chemistry

### pH

pH scale is based on water dissociation equilibrium,  $\text{pH} = -\log [\text{H}^+]$ . The pH of surface geothermal waters is basically determined by the loss of  $\text{CO}_2$  on boiling which causes the solution to be progressively more alkaline.

- Temperature: at the surface the neutral pH is about 7, but at high temperature reservoir it may be around 5.5.
- Salinity: greater fluid salinity produces a lower pH.
- Gas content: lost of gas from the liquid phase consumes proton, therefore pH increases.
- Mineral buffers: pH (hydrogen ion activity) can be buffered by reactions with silicate minerals.



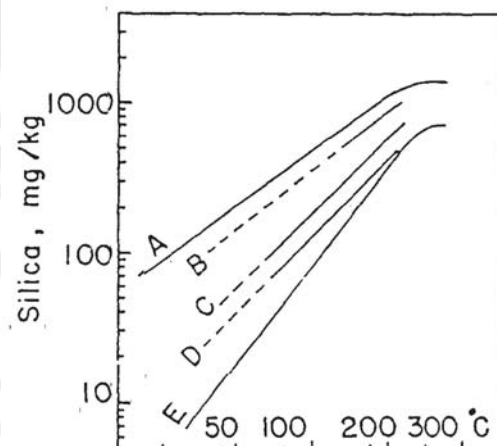
## 5.3. Common solutes and their behavior

- Anions:  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^-$ ,  $\text{F}^-$ ,  $\text{B}^-$ ,  $\text{I}^-$
- Cations:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$
- Neutral:  $\text{SiO}_2$ ,  $\text{NH}_3$ , As, B, and Noble gases.

### Silica ( $\text{SiO}_2$ )

Silica concentrations in geothermal fluids are controlled by the solubility of different silica minerals.

Silica in geothermal systems occur in various polymorph: quartz, chalcedony, cristobalite, opal, amorphous silica.

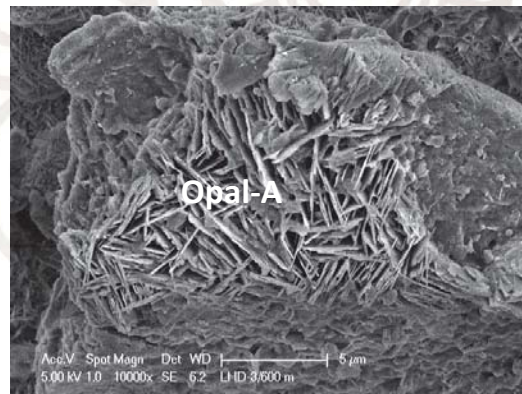
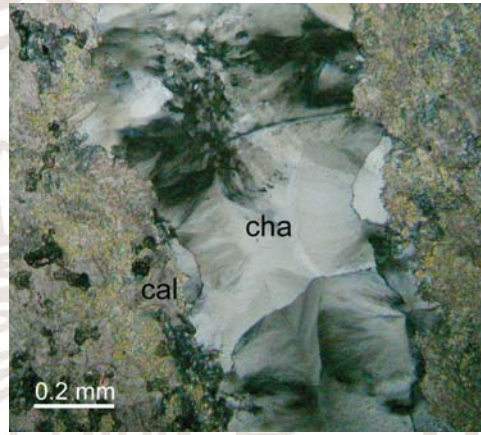


- A: Amorphous silica
- B: Opal-CT
- C: Cristobalite
- D: Chalcedony
- E: Quartz





Quartz



Opal-A



### Amonia ( $\text{NH}_3$ )

Amonia as either gas ( $\text{NH}_3$ ) or solute (amonium ion  $\text{NH}_4^+$ ) is common, although relatively minor, in geothermal fluids.

High level of  $\text{NH}_3$  can be the product of steam heating as the gas condenses out of the vapor phase.

High level of  $\text{NH}_3$  can also be found in deep geothermal fluids associated with sedimentary horizons.

### Arsenic (As)

In solution As occurs predominantly as uncharged species (arsenous acid/ $\text{H}_3\text{AsO}_3$  and arsenic acid/ $\text{H}_3\text{AsO}_4$ ), however in hot springs and reservoir fluids As present as As(III).





## Boron (B)

- Boric acid  $\text{H}_3\text{BO}_3$  or  $\text{HBO}_2^-$
- Springs with very high concentration of boron (~ 800 to 1000 mg/kg) are found in waters associated with organic-rich sedimentary rocks.
- Cl/B ratios are used to indicate common reservoir, however differences can occur due to a change in lithology at greater depths, for example the introduction of sedimentary horizon, or by adsorption of B into clays due to lateral outflow.
- Leaching of evaporite sequence in the reservoir can increase the concentration of Boron.



## Noble gases

- The noble gases (Ar, He, Kr, Ne, Xe) are largely atmospheric, being contributed to geothermal systems through the meteoric water recharge.
- Ar and He can also be of radiogenic origin:  $^4\text{He}$  is formed by the decay of uranium and thorium; while decay of  $^{40}\text{K}$  produces  $^{40}\text{Ar}$ . These isotopes enter geothermal system through direct magmatic input or by leakage of gases from the mantle.
- Rn (Radon) is the heaviest noble gas, it is radioactive, and is radiogenic in origin.
- Noble gases remain in the liquid phase until the boiling occurs, after which they enter steam phase and the residual waters become heavily depleted in noble gases. Therefore, the concentration of the gases dissolved in spring and well discharges can be used as indicators of meteoric origin of the geothermal fluids, and of near-surface boiling episodes.



The chemical composition of thermal and mineralized waters from New Zealand (WK,NG,MO,MU,WI), Guatemala (ZU), Costa Rica (MV), Colombia (RA,RB), Mexico (AR), India (MA), Thailand (FN), Solomon Islands (PR), Vanuatu (YA) and Cameron (LN) in mg/kg (Giggenbach, 1991).

Area	°C	pH	Li	Na	K	Rb	Cs	Mg	Ca	B	HCO <sub>3</sub>	SiO <sub>2</sub>	SO <sub>4</sub>	Cl
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MV Miravalles, well	245	7.5	5.7	1970	238	1.05	0.60	0.02	73	54	40	590	36	3300
MV Miravalles, spr.	73	8.5	3.4	1970	79	0.21	0.14	6.50	22	48	910	112	120	2600
RA Ruiz, acid spring	62	1.2	0.3	280	224	0.37	0.04	155	214	8	-	154	10670	1350
RB Ruiz, neutral s.	94	8.0	3.8	610	78	0.56	0.62	5.1	48	19	175	180	41	1000
AR Araro, spring	92	8.1	6.6	705	50	0.43	1.12	0.3	30	75	63	230	135	1010
MA Manikaran, spring	94	7.4	1.2	93	21	0.15	0.14	3.3	51	3	190	75	35	130
FN Fang, spring	99	9.0	0.6	122	8	0.14	0.29	0.1	1	<1	145	195	22	27
PR Paraso, spring	56	5.6	1.8	1210	178	0.74	0.09	26.6	289	16	6	150	205	2340
YA Yasur, spring	99	8.8	0.3	1270	73	0.16	0.01	0.3	17	21	75	270	280	1690
LN Lake Nyos, lake	23	5.4	.01	15	5	.004	.001	35.0	30	<1	400	45	<1	<1
WS Waitangi Soda Spr.	49	7.3	1.7	285	24	0.11	0.07	8.9	17	3	265	176	48	365
MO Morere, spring	47	7.0	4.6	6700	84	0.10	.004	80.0	2360	57	30	27	<3	15800
MU Maui, well	130	7.5	3.6	7880	440	0.71	0.08	48.0	190	15	630	36	18	12600
WI White Isl. spring	98	0.6	2.9	5910	635	5.40	0.36	3800	3150	160	<1	-	4870	38700
SW Seawater	4	7.8	0.2	10560	380	0.13	<.01	1270	400	5	140	-	2710	19000

## Common Rock Forming Minerals and their chemical compositions

Name	Chemical composition	Name	Chemical composition
<b>Feldspar group</b>		<b>Silicates</b>	
Plagioclase	Ca and Na Al silicate	Olivine	Mg, Fe silicate
Potassium feldspar (orthoclase, microcline)	K Al silicate	Garnet group	Complex silicate
<b>Pyroxene group</b>	Fe, Mg silicate (some with Al, Na, Ca)	Clay minerals group	Complex Al silicate hydroxide
(augite most common)		<b>Non-silicates</b>	
<b>Amphibole group</b>	Complex Fe, Mg Al silicate hydroxide	Calcite	CaCO <sub>3</sub>
(hornblende most common)		Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>
<b>Quartz</b>	Silica	Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O
<b>Mica group</b>			
Muscovite	K Al silicate hydroxide		
Biotite	K Fe Mg Al silicate hydroxide		



## Cations

### Sodium ( $\text{Na}^+$ ) and Potassium ( $\text{K}^+$ )

- The concentration of these cations are controlled by fluid-mineral equilibria, that becomes the basis of Na/K geothermometry.
- K concentrations are typically 1/10 of those of Na.
- Low Na/K (<15) tend to occur in water which have reached the surface rapidly----- upflow or more permeable zones ---  
- presence of adularia !
- Low Na/K indicative of lateral flow, or near surface reactions and conductive cooling.



### Calcium ( $\text{Ca}^{2+}$ )

Calcite ( $\text{CaCO}_3$ ), anhydrite ( $\text{CaSO}_4$ ), and fluorite ( $\text{CaF}_2$ ) – the retrograde solubility minerals, control the concentration of Ca.

Calcite, for example deposits in response to loss of  $\text{CO}_2$  on boiling

Na/Ca can be used like Na/K, where the highest values indicating a more direct feed from reservoir.

### Lithium ( $\text{Li}^+$ ), Rubidium ( $\text{Rb}^+$ ) and Caesium ( $\text{Cs}^+$ )

- Collectively termed the "rare alkali".
- Readily incorporated into hydrothermal minerals (chlorite, quartz, clays).
- Highest concentrations in areas with rhyolitic and andesitic host rocks, but significantly lower in basaltic rocks (Ellis, 1979).





### Magnesium ( $\text{Mg}^{2+}$ )

- Magnesium concentration is usually low (0.01 – 0.1 mg/kg) as magnesium is readily incorporated into secondary minerals (especially chlorite).
- Higher Mg concentrations indicate near surface reactions leaching Mg from rocks, or dilution by groundwater that is already rich in Mg.

### Aluminium ( $\text{Al}^{3+}$ )

In chloride-type fluids Al is low ( $< 0.02$  mg/kg), usually undetectable, but acid sulfate type water can contain several hundreds mg/kg of Al through leaching of rocks.

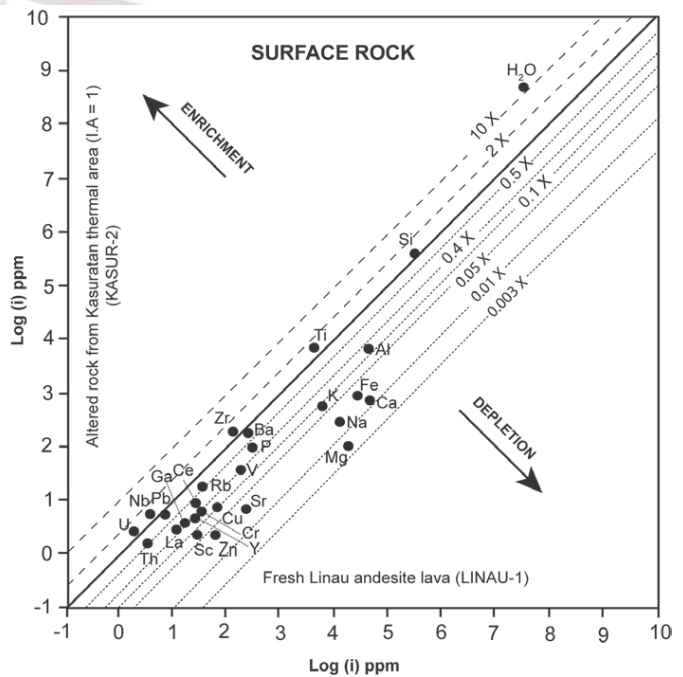
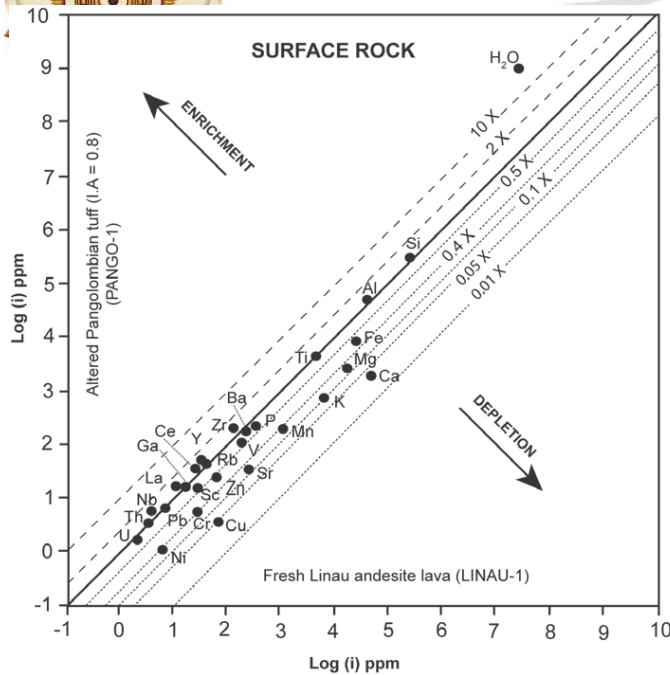


### Iron ( $\text{Fe}^{2+}$ , $\text{Fe}^{3+}$ )

- The concentration of iron in chloride-type fluid is invariably low (0.001 to 1.0 mg/kg).
- Higher level of iron in the surface waters indicate leaching.
- Contamination from casing and well head equipment is usually insignificant (Gunnlaugsson and Arnorsson, 1982).

### Manganese ( $\text{Mn}^{2+}$ , $\text{Mn}^{4+}$ )

Considered as trace constituent in geothermal waters ( $\sim 0.01$  mg/kg), however there are some springs in Japan and USA that have excess Mn.



Leaching of surface rocks at Lahendong thermal areas that causes the lost of cations from the primary minerals; these are concentrated in fluids (From Utami, 2011).



## Anions

### Fluoride

- Fluoride concentration rarely exceeds 10 mg/kg.
- Waters from reservoir associated with volcanic rocks (rhyolite, pumice, obsidian) has higher fluoride concentration compare to those of sedimentary lithology.

### Chloride

- High chloride concentrations in hot springs indicate that water fed directly from deep reservoir, with minimum mixing or conductive cooling.
- Low Cl but without characteristics of steam-heating, may indicate dilution by groundwater).
- Iso-Cl map can be constructed to recognise the margin of the system, and zones of groundwater inflow.





### Bromide (Br<sup>-</sup>)

- Very low level in hydrothermal fluids, except where sea water is incorporated into the reservoir fluids.
- Br/Cl and Br/I are used as indicators of mixing with sea water.

### Iodide (I<sup>-</sup>)

- Attains highest value in water from organic-rich sedimentary rock reservoir.
- May also be due to contribution of Iodide from shallow organic materials.



### Bicarbonate

- Reactions between the dissolved CO<sub>2</sub> and the host rocks form the bicarbonate fluids.
- Boiling springs fed directly from reservoir tend to have lowest HCO<sub>3</sub> concentration.
- HCO<sub>3</sub>/SO<sub>4</sub> can be used to indicate flow direction.
- HCO<sub>3</sub>/SO<sub>4</sub> increases away from upflow direction.

### Sulfate (SO<sub>4</sub><sup>2-</sup>)

- Sulfate concentration in the deep reservoir is usually low (<50 mg/kg).
- Increase of concentration may be due to steam condensate.



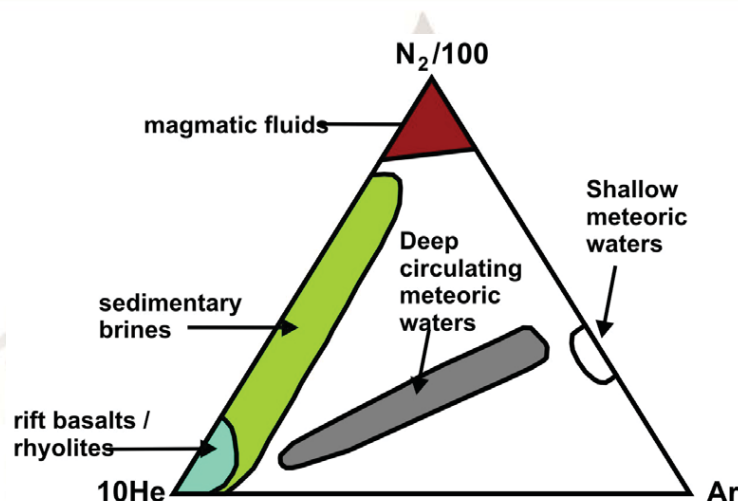
## Gas

Steam-heated springs inherit only a few of the characteristics of the deep reservoir fluid because they are largely products of surface oxidation and rock leaching, therefore they are not useful for liquid geothermometry.

Gas chemistry is employed to obtain the information about deep reservoir conditions.

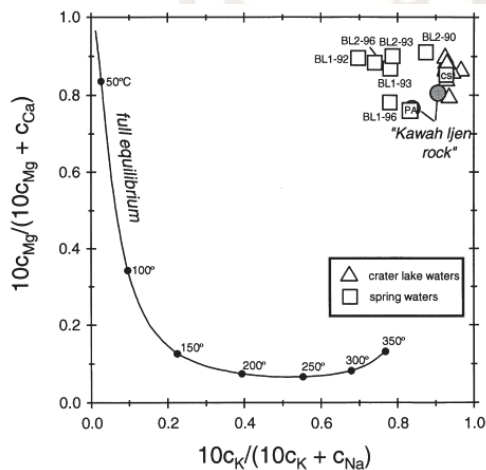
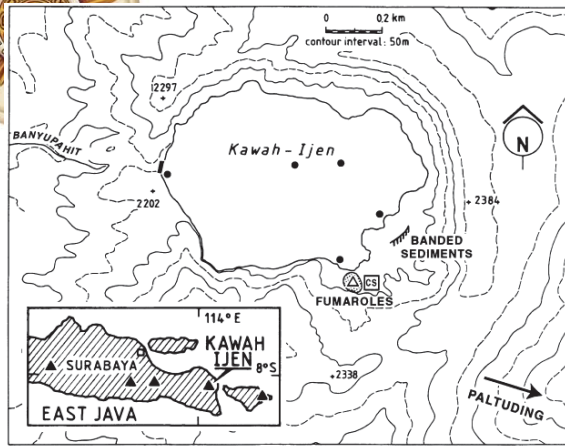
The presence of steam at the surface is a positive indicator of hot subsurface. Commonly geothermal resources with fumaroles have high temperature.

Trends in gas concentration ratios give valuable information about the location of the system, the reservoir and hydrology.

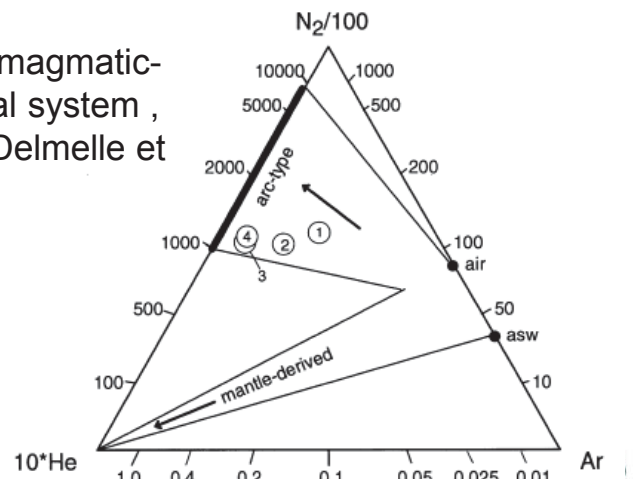


- Origin of water and accompanying gas in a geothermal system is revealed by the relative proportion of unreactive Ar, He, and N in steam discharges.
- The proportion are presented on tri-linear diagram.
- Contrast in  $N_2$  and He proportion depends on tectonic setting.





Kawah Ijen magmatic-hydrothermal system, East Java (Delmelle et al, 2000).



## GEOCHEMISTRY FOR GEOTHERMAL DEVELOPMENT

### UGM – UU – Geocap Capacity Building Program

21 - 25 August, 2017



## 05. INTERPRETATION OF WATER CHEMISTRY (PART-2)



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- Ion Balance calculation is performed to evaluate and QC the laboratory analyses.



## Data presentation

- The result of chemical analysis is presented in the unit of milligram/kilogram (mg/kg) or milligram/Liter solution (mg/L).
- Calculation commonly is conducted in the unit mole/kg solution (generally water or condensate).





## Conversion

- Conversion from weight base (mg/kg or ppm) to mole base (mole) :  
molality (m) =  $(\text{mg/kg}) / (\text{BAG} \cdot 1000) \times 1000 / (1000 - \Sigma(\text{mg/kg}) / 1000)$   
molarity (M) =  $(\text{mg/L}) / (\text{BAG} \cdot 1000) \times 1000 / (1000 - \Sigma(\text{mg/L}) / 1000)$
- As geothermal water usually dilute water therefore the value of the second part is almost 1 therefore we may neglect the second part.



## Fluid Chemistry Analysis

- One of the most important assumption is: chemical/isotope analysis has been done correctly and accurate.
- In order to reassure the accuracy of chemistry analysis, ionic balance must be calculated.
- Using equivalent concentrations of the ions, the error in charge balance was calculated from the absolute difference between the sums of cations and of anions divided by the average of the total cations and anions.



- The ionic species were expressed as equivalent concentrations from the following calculation.

$$\text{Equivalent Concentration} = \frac{(\text{concentration}) \times (\text{ionic charge})}{\text{molecular weight}}$$

- where molecular weight is in gram/mole, concentration is in milligrams per liter (mg/L), and equivalent concentration is in milliequivalents per liter (meq/L).



## 5.4. Ion Balance

- $\sum z_i m_i = 0$ , where  $m$  = molality,  $z$  = charge
- In water geochemistry, the dominant ions are:  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$ .
- Thus:
  - $m\text{Na} + m\text{K} + 2m\text{Ca} + 2m\text{Mg} = m\text{Cl} + m\text{HCO}_3 + 2m\text{SO}_4$
- Analysis result can be considered as “good enough” if
  - $\Delta\text{charge} < 10\%$
  - $$\Delta\text{charge} (\%) = \frac{|\sum \text{cations} - \sum \text{anions}|}{(\sum \text{cations} + \sum \text{anions})/2} \times 100$$
  - Or 
$$\Delta\text{charge} (\%) = \frac{|\sum \text{cations} - \sum \text{anions}|}{(\sum \text{cations} + \sum \text{anions})} \times 200$$





## 5.5. Mass Balance

- In order to calculate mass balance, then TDS (Total Dissolved Solid) must be measured
- Calculation of mass balance can be done with equation:

$$\bullet \text{ Mass Balance} = \frac{TDS \left(\frac{mg}{kg}\right)}{\sum \text{solute concentrations} \left(\frac{mg}{kg}\right)}$$



## 5.6. Conductivity Balance

- Calculation of error can also be derived from conductivity balance, with calculation:

$$\bullet \text{ Error}(\%) = \frac{100|\text{conductivity} - (100 \sum \text{cations})|}{\text{conductivity}}$$



## Example

- This is an example of chemical analysis result, please determine whether the result is accurate.

Location	Na	K	Mg	Ca	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	Sci
Wairakei	1070	102	0.4	26	1770	26	76	3070
Waitangi	285	24	9	17	364	49	202	950

- Unit in ppm



## **06 Fluid Geothermometer**

Agung Harijoko  
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## **05. FLUID GEOTHERMOMETER**



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Adapted from geothermal lecture handouts by Agung Harijoko at Geological Engineering UGM.



### **Fluid Geothermometers | Agung Harijoko**

#### **5.1. Introduction**

- One of the tasks in geothermal exploration is to infer the reservoir temperature.
- Temperature-dependent process.
  - Solubility of individual minerals
  - Exchange reaction which fix ratios of certain dissolved constituent
- In the geothermal system there is hydrothermal alteration process that is basically chemical reaction of hot water and primary minerals resulted in secondary minerals.
- Assumption: the chemical reaction achieve equilibrium state



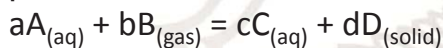


- An equilibrium reaction can be approached using the concentration of the solutes and changes in energy, therefore the process is dependent in temperature.
- Energy changes can described with thermodynamics, involving enthalpy, entropy, temperature. To include all these parameters we use the Gibb's Free Energy (G).



- **Equilibrium constant**

If there are two substances (material) mixed at a certain temperature and pressure, whether the reaction will be run?



Reaction shift to the right:  $k_1 [A]^a [B]^b$

Reaction shift to the left:  $k_2 [C]^c [D]^d$

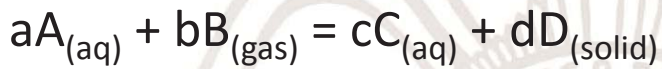
$$k_1 [A]^a [B]^b = k_2 [C]^c [D]^d$$

$$K = \frac{k_1}{k_2} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$



## Equilibrium reaction

- Gibbs-free energy



$$\Delta G_R^o = \sum n_i G_{f,prod}^o - \sum n_i G_{f,}^o$$

$$\Delta G_R = \Delta G^o + RT \ln \left( \frac{a_C^c a_D^d}{a_A^a a_B^b} \right)$$

## Equilibrium

$$\Delta G_R = 0$$

$$-\Delta G_R^o = RT \ln \left( \frac{a_C^c a_D^d}{a_A^a a_B^b} \right)$$

$$\exp \left( \frac{-\Delta G_R^o}{RT} \right) = \left( \frac{a_C^c a_D^d}{a_A^a a_B^b} \right) = K_{eq}$$

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



$$\Delta G_R^o = -RT \ln K$$

K=equilibrium constant at standard T (25°C)

T in Kelvin 298.15°K

R=gas constant=1.987 cal/mol°

$$\Delta G_R^o = -1.364 \log K$$

$\Delta G_R^o$ : in kcal/mol°



**What if  $T \neq 25^\circ\text{C}$ ?**

Use the Van't Hoff Equation

By differentiating the equation with respect to T

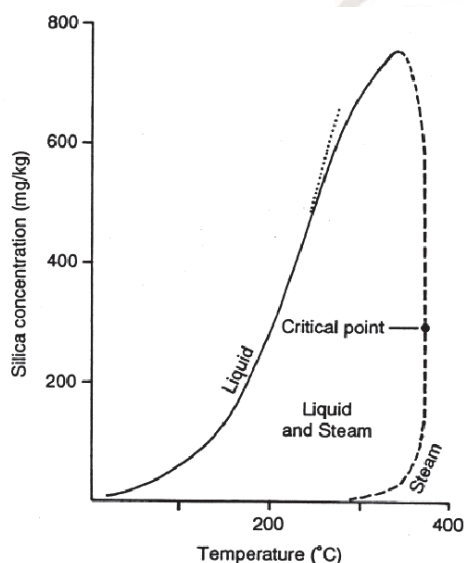
$$\ln K = -\frac{\Delta G_R^\circ}{RT}$$

$$\log K_T = \log K_T^\circ - \frac{\Delta H_R^\circ}{2.3025R} \left( \frac{1}{T} - \frac{1}{298.15} \right)$$

 $\Delta H_R^\circ$  Enthalpy of reaction

R: 1.987 cal/deg-mol

T in Kelvin

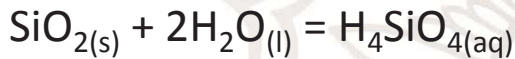
**5.2. Cation Geothermometers****Silica geothermometer**

The solubility of quartz in water at the vapour pressure of the solution calculated from Fournier and Potter (1982a,b).

- Silica is abundant and is a common solute in geothermal water.
- The solubilities of silica minerals decrease as temperature decrease below  $340^\circ\text{C}$ .
- Geothermal water becomes saturated with respect to silica in a geothermal reservoir after prolonged water-rock interaction at constant temperature.
- Silica will polymerize and precipitate during fast upward movement to the earth's surface.
- Precipitation will be significant if it is exceeded the amorphous silica solubility.



The solubility of silica is controlled by the reaction:



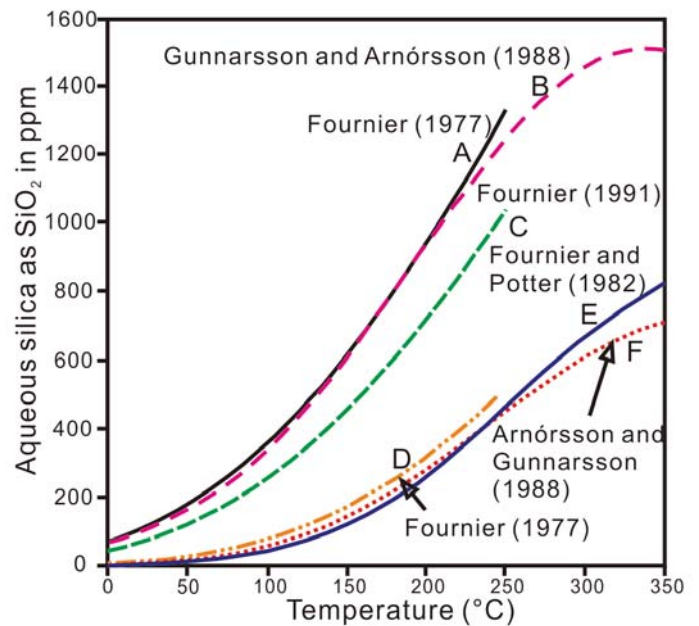
$$K = [\text{H}_4\text{SiO}_4]$$

**Amorphous silica**

$$T(^{\circ}\text{C}) = \frac{731}{452 - \log c_{\text{SiO}_2}} - 273.15$$

**Chalcedony**

$$T(^{\circ}\text{C}) = \frac{1032}{4.69 - \log c_{\text{SiO}_2}} - 273.15$$



### Silica Polymorphs

- A&B: amorphous silica
- C: opal
- D: chalcedony
- E & F: quartz



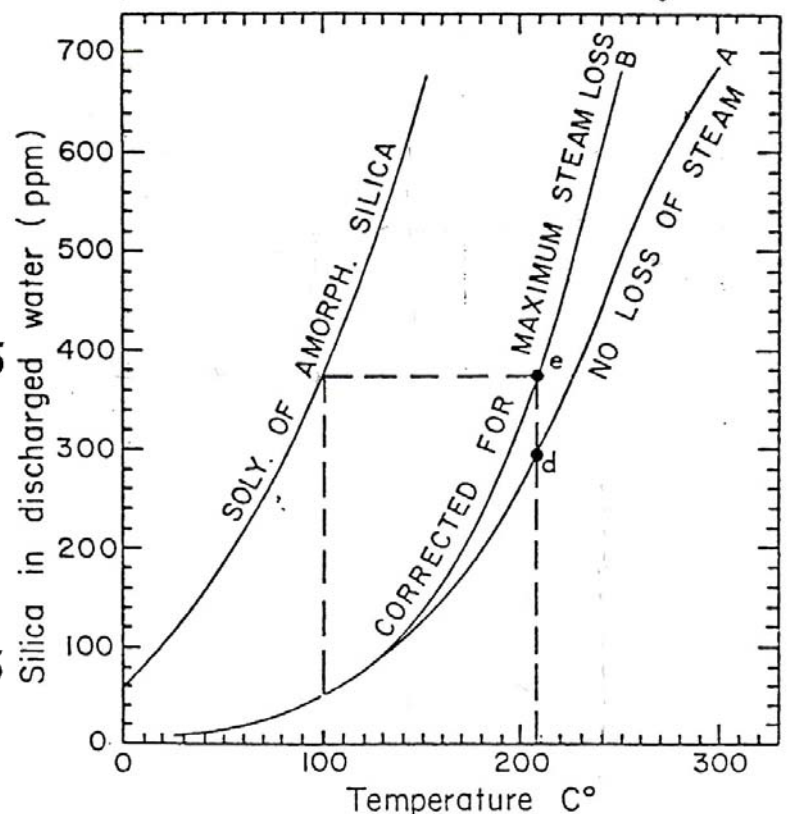
No steam loss

$$t^{\circ}\text{C} = \frac{1309}{5.19 - \log \text{SiO}_2} - 273.15$$

(Fournier, 1981)

Maximum steam loss

$$t^{\circ}\text{C} = \frac{1522}{5.75 - \log(\text{SiO}_2)} - 273.15$$



- Fast equilibration at  $T > 230^{\circ}\text{C}$
- Can be affected by concentration and dilution
- Close to well bore temperature





## Na/K Geothermometers

- Reaction between alkali feldspars.
- $\text{NaAlSi}_3\text{O}_8 + \text{K}^+ \leftrightarrow \text{KAlSi}_3\text{O}_8 + \text{Na}^+$
- Very slow equilibration at  $< 300^\circ\text{C}$ .
- Solubilities of albite and K-feldspar decrease with decreasing temperatures, tend to precipitate in geothermal up flow zones.
- Albite and K feldspar are widespread as secondary minerals in rocks of geothermal systems with a quite variable composition
- Deeper reservoir temperature.
- Unaffected by boiling and dilution.
- At lower temperatures other reactions may control the Na/K.
- Na/K ratio is indicative for reservoir temperature.



Adularia



Albite



**Na – K** (works best at  $> 180^\circ\text{C}$ )

$$T(^{\circ}\text{C}) = \frac{1217}{\log(c_{\text{Na}}/c_{\text{K}}) + 1.483} - 273 \quad (\text{Fournier, 1981})$$

$$T(^{\circ}\text{C}) = \frac{1390}{\log(c_{\text{Na}}/c_{\text{K}}) + 1.75} - 273 \quad (\text{Giggenbach, 1988})$$



## Potassium/Magnesium ( $T_{K/Mg}$ )

- Mg concentration is typically <0.01 mg/kg in Cl-waters.
- Higher Mg (several ppm) occurs in cool marginal waters.
- Muscovite-clinocllore-K-feldspar assemblage controls K, Mg.

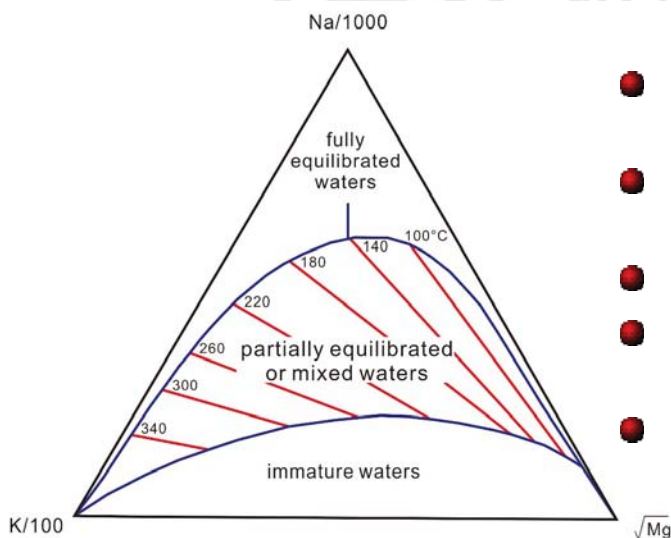


**K – Mg** ( $T = \sim 100^\circ\text{C}$  to  $300^\circ\text{C}$ )

$$t (^{\circ}\text{C}) = \frac{4410}{14 + \log \left( C_K^2 / C_{Mg} \right)} - 273.15 \text{ (Giggenbach, 1988)}$$



## Tri-linear $T_{Na-K-Mg}$ Indicator diagram (Giggenbach 1983)



- Allows evaluation of deep temperature and shallow equilibration temperatures.
- Allows visualisation of a large number of samples.
- Qualitative approach.
- Combines Na-K and K-Mg geothermometer equations.
- Represents slow (Na/K) and fast (K-Mg) equilibration.





### Cation geothermometer limitation

- A geothermometer records the temperature of the last equilibrium (which is not necessarily that of the deep reservoir); unravel results from different geothermometers may therefore reflect differences in the degree of equilibrium.
- The silica geothermometer is based on absolute concentrations, not concentration ratios, and is therefore influenced by boiling and dilution more than the alkali geothermometers.



### 5.3. Gas Geothermometers

In many geothermal fields, surface manifestations consist only of hot ground, acid surface waters and fumaroles. In these fields the thermal groundwater table is subsurface. When this is the case, water geothermometers cannot be applied. This has called for the development of gas geothermometers for geothermal exploration. The first gas geothermometer developed is that of D'Amore and Panichi (1980). Later geochemical methods involving gas chemistry have been developed to estimate steam to water ratios in geothermal reservoirs (e.g. D'Amore and Truesdell, 1985; Arnórsson et al., 1990).



### Kinds of geothermal gas

- $\text{CO}_2$
- $\text{H}_2\text{S}$
- $\text{NH}_3$
- $\text{N}_2$
- $\text{H}_2$
- $\text{CH}_4$
- Known as “Non Condensable Gases” (NCG)



- Gas geothermometry requires an assumption for the data ratio of gas / steam, steam / water ratio because these ratios in the manifestation are unknown
- Hot springs manifestation or fumarole usage restricted usually only on well data, except gas geothermometer
- D'Amore & Panichi based empirically  $\text{CO}_2\text{-H}_2\text{S-H}_2\text{-CH}_4$





- $2\text{CH}_4 + 2\text{H}_2\text{O} = \text{C} + \text{CO}_2 + 6\text{H}_2$
- $\text{FeS}_2 + \text{CaSO}_4 + 3\text{H}_2\text{O} + \text{CO}_2 = \text{CaCO}_3 + \text{Fe}_3\text{O}_4 + 1/3 + 7/3 \text{O}_2 + 3\text{H}_2\text{S}$
- $\log \text{PCO}_2 = 8.2 \text{ to } 23,643 / T$
- $\text{CO}_2 < 75\% \rightarrow \text{PCO}_2 = 0.1$
- $\text{CO}_2 > 75\% \rightarrow \text{PCO}_2 = 1$
- $\text{CO}_2 > 75\% \text{ and } \text{CH}_4 > \text{and } \text{H}_2\text{S} \rightarrow \text{PCO}_2 = 10$
- $T = 24\,775 / (2 \log (\text{CH}_4 / \text{CO}_2) - 6 \log (\text{H}_2 / \text{CO}_2) - 3 \log (\text{H}_2\text{S} / \text{CO}_2) - 7 + 36.05 \log \text{PCO}_2) \rightarrow \text{in Kelvin}$
- Operates on simple gas ratios and an assumed value for the partial pressure of carbon dioxide ( $\text{PCO}_2$ ); intended to be applied to fumaroles, gas seeps and hot springs alike.
- Problem with this geothermometer is that it seems to work in some fields, but not in others.



### Complexity In the Analysis and Interpretation of Gas

- Required accuracy in sampling
- Variations in composition of the gas
- Sensitivity to pressure
- Vapor-liquid fractionation process
- Effect of temperature
- Chemical gas geochemistry is less frequently supplied than water geochemistry



## Manifestations Associated With Gas

- Fumaroles
- Kaipohan
- Solfatara
- Steaming ground
- Hot pools
- Well discharges



## 5.4. Concluding Remark

- Geothermometry provides a tool to infer the reservoir temperature
- Care must be taken when we apply any geothermometer
- The result of the geothermometer calculation has no meaning if basic requirements are not fulfilled



## **07 Stable Isotope & Application in Geothermal Exploration**

Manfred van Bergen  
(Utrecht University)

**GEOCHEMISTRY FOR GEOTHERMAL DEVELOPMENT**  
**UGM – UU – Geocap Capacity Building Program**  
**21 - 25 August, 2017**



**07. STABLE ISOTOPES AND APPLICATIONS IN GEOTHERMAL EXPLORATION**

Manfred van Bergen  
 Utrecht University



**Stable isotopes and applications in geothermal exploration**

**Contents**

- Background and theory
- Stable isotope systematics of active volcanic lakes with examples from East Indonesia
- Geochemistry of spring waters from geothermal systems on Java
- Stable isotope signals of water-rock interactions – an example from the Los Azufres geothermal field (Mexico)







## Stable isotopes and applications in geothermal exploration

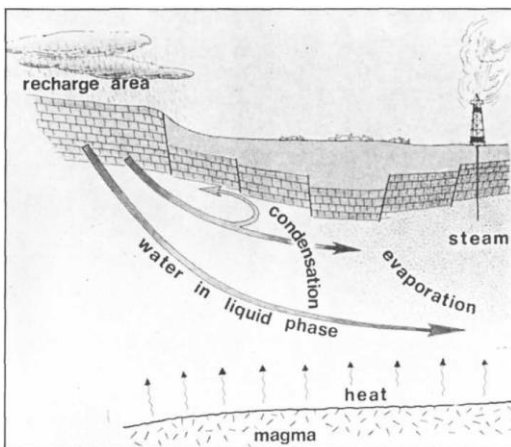
### Key features of stable isotopes (H, Li, B, C, N, O, Si, S, Cl)

- Low atomic mass
- Large relative mass difference between isotopes
- Bonds are highly covalent in character
- More than one oxidation state (C, N, S), variety of compounds (O), important constituents of solids and fluids
- Rare isotope sufficiently abundant for analysis



## Stable isotopes and applications in geothermal exploration

### Principal applications



- Process identification
- Geothermometry
- Provenance tracing





## Stable isotopes and applications in geothermal exploration

### Isotope ratios of stable isotopes

Element	Notation	Ratio	Standard	Absolute Ratio
Hydrogen	$\delta D$	D/H ( $^2H/^1H$ )	SMOW	$1.557 \times 10^{-4}$
Lithium	$\delta^6Li$	$^6Li/^7Li$	NBS L-SVEC	0.08306
Boron	$\delta^{11}B$	$^{11}B/^10B$	NBS 951	4.044
Carbon	$\delta^{13}C$	$^{13}C/^12C$	PDB	$1.122 \times 10^{-2}$
Nitrogen	$\delta^{15}N$	$^{15}N/^14N$	atmosphere	$3.613 \times 10^{-3}$
Oxygen	$\delta^{18}O$	$^{18}O/^16O$	SMOW, PDB	$2.0052 \times 10^{-3}$
	$\delta^{17}O$	$^{17}O/^16O$	SMOW	$3.76 \times 10^{-4}$
Sulfur	$\delta^{34}S$	$^{34}S/^32S$	CDT	$4.43 \times 10^{-2}$

### $\delta$ notation

$$\delta^{18}O = \left[ \frac{(^{18}O/^16O)_{\text{sam}} - (^{18}O/^16O)_{\text{SMOW}}}{(^{18}O/^16O)_{\text{SMOW}}} \right] \times 10^3$$

SMOW: Standard Mean Ocean Water  
PDB: Pee Dee Belemnite

$$\delta^{18}O_{\text{PDB}} = 1.03086 \delta^{18}O_{\text{SMOW}} + 30.86$$

Adapted from White (2015)



## Stable isotopes and applications in geothermal exploration

*fractionation factor,  $\alpha$*

$$\alpha_{A-B} \equiv \frac{R_A}{R_B}$$

*fractionation of isotopes between two phases*  $\Delta_{A-B} = \delta_A - \delta_B$

$$\Delta \approx (\alpha - 1)10^3 \quad \Delta \approx 10^3 \ln \alpha$$

*at equilibrium:*  $\alpha_{A-B} = (K/K_{\infty})^{1/n}$

$n$ : number of atoms exchanged

$K$  equilibrium constant

$K_{\infty}$  equilibrium constant at infinite temperature

Adapted from White (2015)



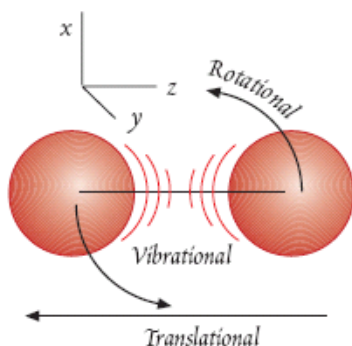




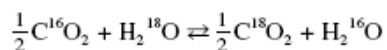
## Stable isotopes and applications in geothermal exploration

Equilibrium fractionations from:

Translational – **Vibrational** – Rotational motions of molecules



Effects are small, e.g.:



equilibrium constant 1.04 at 25°C

Adapted from White (2015)

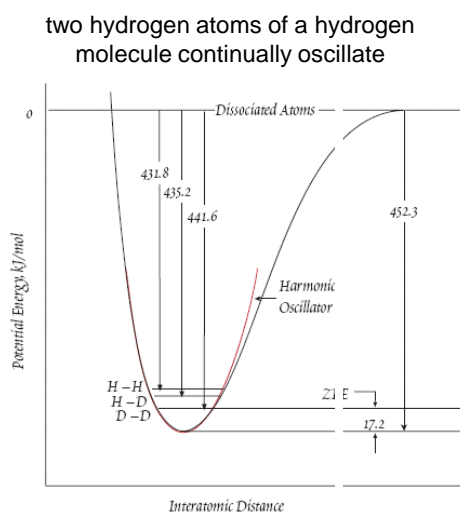


## Stable isotopes and applications in geothermal exploration

Oscillation – bond strength - isotopic fractionation

Frequency of oscillation is quantized

Energy-level diagram for hydrogen molecule



So why does equilibrium fractionation occur?

- a molecule with a heavy isotope (D) sits at a lower zero point energy level than the same molecule with all light isotopes (H)
- bonds with high potential energies are broken more readily
- bond strengths vary for light and heavy isotopes of an element

What about temperature?

- the difference in zero point energies for light vs. heavy molecules decreases with increasing T
- bond strengths converge at high T, fractionation factor goes to 1 at high T

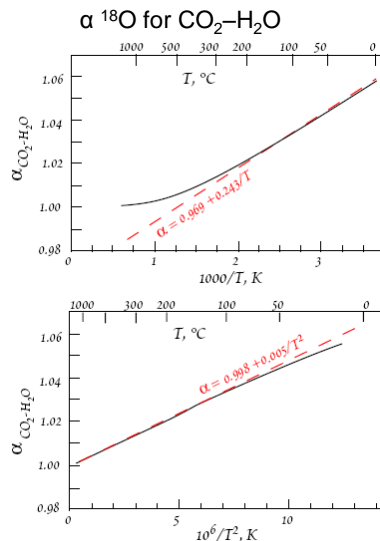
Adapted from White (2015)





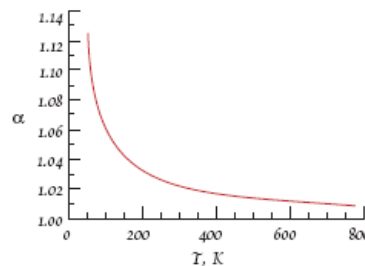
## Stable isotopes and applications in geothermal exploration

### Temperature dependence of the fractionation factor



Adapted from White (2015)

Exchange of  $^{18}\text{O}$  and  $^{16}\text{O}$  between carbon monoxide and oxygen:  
 $\text{C}^{16}\text{O} + ^{16}\text{O}^{18}\text{O} \leftrightarrow \text{C}^{18}\text{O} + ^{16}\text{O}_2$



## Stable isotopes and applications in geothermal exploration

### Composition dependence 1

*The heavy isotope goes into the phase in which it is most strongly bound*

**Quartz**,  $\text{SiO}_2$  is typically the most  $^{18}\text{O}$  rich mineral and **magnetite** the least

Oxygen is dominantly *covalently* bonded in **quartz**, but dominantly *ionically* bonded in **magnetite**

The O is bound *more strongly* in **quartz** than in **magnetite**, so **quartz** is enriched in  $^{18}\text{O}$

Adapted from White (2015)







## Stable isotopes and applications in geothermal exploration

### Composition dependence 2

Substitution of cations in a dominantly ionic site (typically the octahedral sites) in silicates has only a secondary effect on the O bonding, so that ***isotopic fractionations of O isotopes between similar silicates are generally small.***

Similar fractionation between the end-members of the **alkali feldspar series and water**, since only the substitution of  $K^+$  for  $Na^+$  is involved

Substitutions of cations in sites that have a strong covalent character (generally tetrahedral sites) result in greater O isotope fractionations

greater fractionation factors between end-members of the **plagioclase series and water**, since the substitution of Al for Si as well as Ca for Na is involved, and the bonding of O to Si and Al in tetrahedral sites has a large covalent component

Adapted from White (2015)



## Stable isotopes and applications in geothermal exploration

### Composition dependence 3

**Carbonates** are  $^{18}O$  rich because O is bonded to a small, highly charged atom,  $C^{4+}$

The fractionation,  $\Delta^{18}O_{cal-water}$ , between calcite and water is about 30 ‰ at 25°C

The cation in the carbonate has a secondary role (due to the effect of the mass of the cation on vibrational frequency).

The  $\Delta^{18}O_{carb-H_2O}$  decreases to about 25 ‰ when Ba replaces Ca (Ba has about 3 times the mass of Ca)

Adapted from White (2015)





## Stable isotopes and applications in geothermal exploration

### Other effects on isotopic fractionations

**Crystal structure** plays a secondary role. The  $\Delta^{18}\text{O}$  between aragonite and calcite is about 0.5 ‰.

However, there is a large fractionation (10 ‰) of C between graphite and diamond

**Pressure effects** on fractionation factors are small, no more than 0.1 ‰ over 20 kbars

Adapted from White (2015)



## Stable isotopes and applications in geothermal exploration

### Kinetic isotope fractionations

associated with *fast, incomplete, or unidirectional* processes like **evaporation, diffusion, dissociation reactions, and biologically mediated reactions.**

Temperature is related to the average kinetic energy  $E = 1/2 mv^2$

$^{12}\text{C}^{16}\text{O}_2$  and  $^{13}\text{C}^{16}\text{O}_2$  in carbon dioxide gas (ideal gas)

If their energies are equal, the ratio of their velocities is  $(45/44)^{1/2}$ , or 1.011

Thus  $^{12}\text{C}^{16}\text{O}_2$  can diffuse 1.1% further in a given amount of time than  $^{13}\text{C}^{16}\text{O}_2$

*Where reactions do not achieve equilibrium the lighter isotope will usually be preferentially concentrated in the reaction products*

Adapted from White (2015)





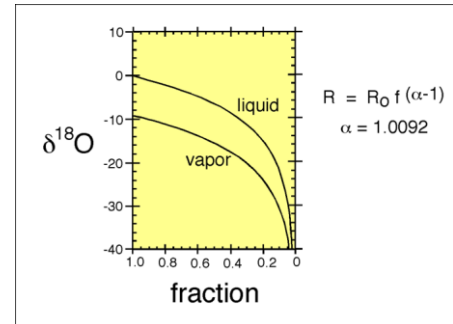
## Stable isotopes and applications in geothermal exploration

Rayleigh fractionation occurs when the reaction product is removed from the system

Equation for **Rayleigh** processes:

$$R_t = R_0 f^{(1-a)}$$

**R** and **R<sub>0</sub>** are the ratios at **t** and at **t=0**  
**f** is the fraction remaining at **t**  
**a** is the equilibrium fractionation factor



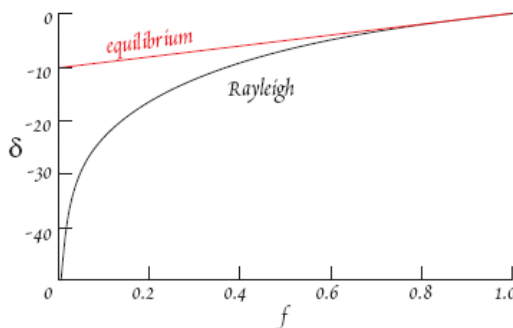
Condensation example

condensate is formed from a vapor mass and fraction remaining of original vapor declines



## Stable isotopes and applications in geothermal exploration

Fractionation of isotope ratios during **Rayleigh** and **equilibrium** condensation



$\delta$  is the ‰ difference between the isotopic composition of original vapor and the isotopic composition when fraction  $f$  of the vapor remains

Adapted from White (2015)







## Stable isotopes and applications in geothermal exploration

### Isotope geothermometry

$$\ln K = \ln a = A + B/T^2$$

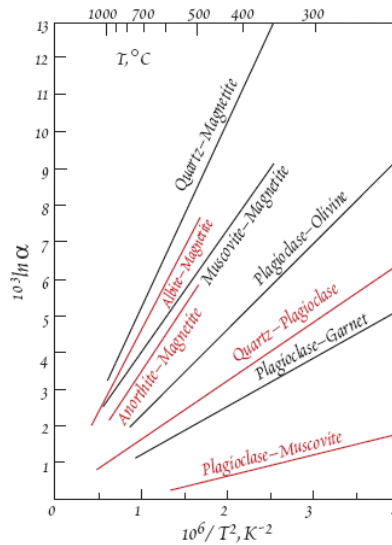
(at low temperatures)

Coefficients for oxygen isotope fractionation at low temperatures

$$\Delta_{QZ-\phi} = A + B \times 10^6/T^2$$

$\phi$	A	B
Feldspar	0	$0.97 + 1.04b^*$
Pyroxene	0	2.75
Garnet	0	2.88
Olivine	0	3.91
Muscovite	-0.60	2.2
Amphibole	-0.30	3.15
Biotite	-0.60	3.69
Chlorite	-1.63	5.44
Ilmenite	0	5.29
Magnetite	0	5.27

(relative to quartz)



Adapted from White (2015)



## Stable isotopes and applications in geothermal exploration

### Isotope geothermometry

Coefficients for oxygen isotope fractionation at elevated temperatures (600-1300 °C)

$$1000\alpha = B \cdot 10^6/T^2$$

(at high temperatures)

	Cc	Ab	An	Di	Fo	Mt
Qz	0.38	0.94	1.99	2.75	3.67	6.29
Cc		0.56	1.61	2.37	3.29	5.91
Ab			1.05	1.81	2.73	5.35
An				0.76	1.68	4.30
Di					0.92	3.54
Fo						2.62

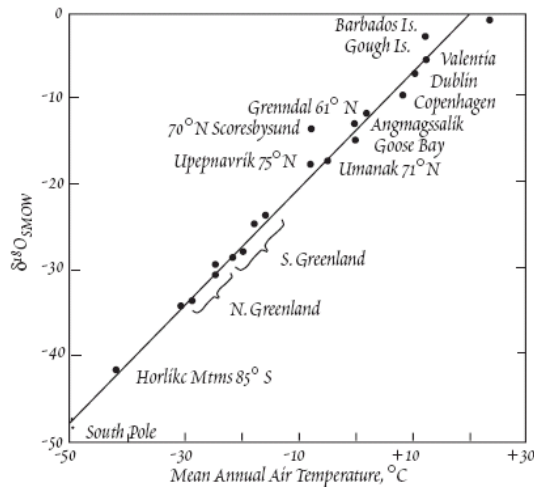
Adapted from White (2015)





## Stable isotopes and applications in geothermal exploration

### Isotope fractionation in the hydrologic system



Variation of  $\delta^{18}\text{O}$  in precipitation as a function of mean annual temperature

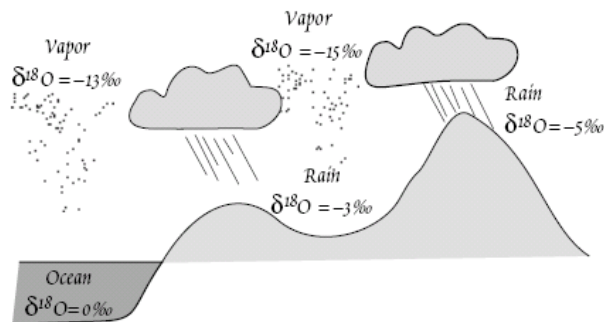
$$\ln a = A - B/T^2$$

Adapted from White (2015)



## Stable isotopes and applications in geothermal exploration

### Rayleigh fractionation and the decreasing $\delta^{18}\text{O}$ in rain as it moves inland



$$\Delta = 1000(f^{\alpha-1} - 1)$$

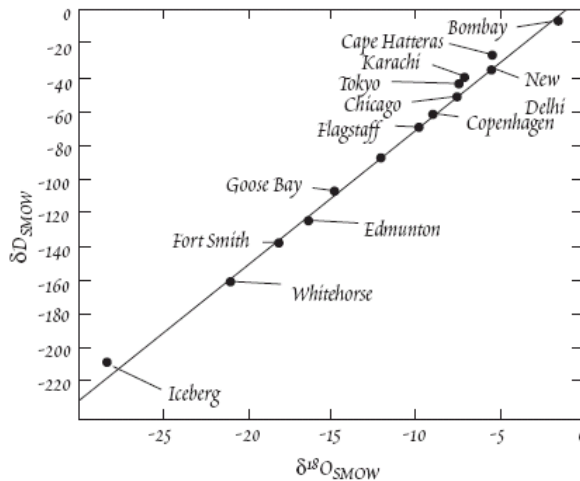
Adapted from White (2015)





## Stable isotopes and applications in geothermal exploration

### Northern hemisphere variation in $\delta D$ and $\delta^{18}O$ in precipitation and meteoric waters



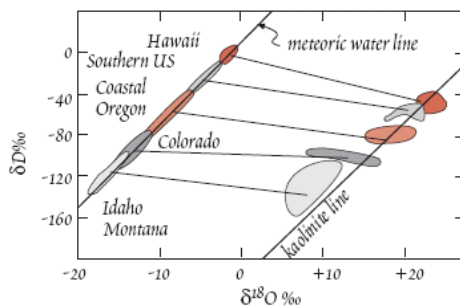
The relationship between  $\delta D$  and  $\delta^{18}O$  is approximately  $\delta D = 8 \cdot \delta^{18}O + 10$

Adapted from White (2015)



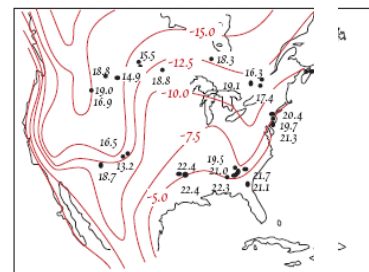
## Stable isotopes and applications in geothermal exploration

### Clays in soil



$\delta D$  and  $\delta^{18}O$  in modern meteoric water and kaolinites

Kaolinites are enriched in  $^{18}O$  by about 27‰ and  $^2H$  by about 30‰



$\delta^{18}O$  in Cretaceous kaolinites from North American (black) compared with contours of  $\delta^{18}O$  (in red) of present-day meteoric water

Adapted from White (2015)







## Stable isotopes and applications in geothermal exploration

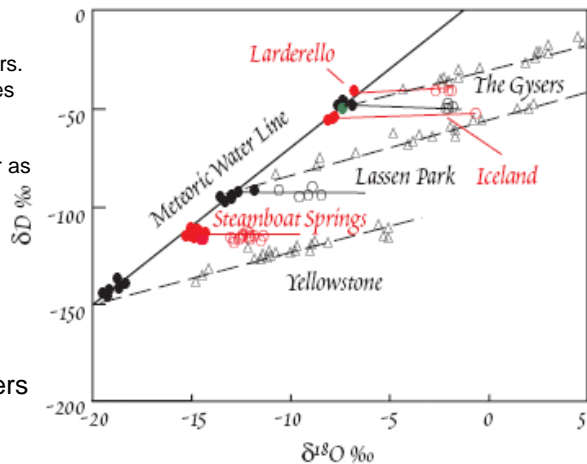
### Stable isotope effects from water-rock interaction and mixing in hydrothermal systems

The  $\delta D$  shift in acidic, sulfur-rich waters occurs when H isotopes are fractionated during boiling of geothermal waters. The steam produced is enriched in sulfide. The steam mixes with cooler meteoric water, condenses, and the sulfide is oxidized to sulfate, resulting in their acidic character. The mixing lines reflect mixing of the steam with meteoric water as well as the fractionation during boiling

- Meteoric water
- Chloride-type geothermal waters
- △ Acidic, sulfide-rich geothermal waters

Horizontal lines: mixing between meteoric water and chloride-type geothermal waters  
Inclined lines: mixing between meteoric water and acidic waters

Adapted from White (2015)

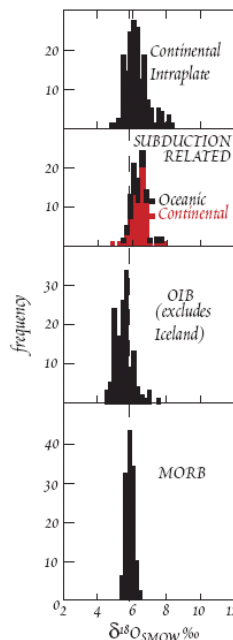


The shift in  $\delta^{18}O$  results from high temperature ( $\sim 300^\circ C$ ) reaction of the local meteoric water with hot rock. Because the rocks contain almost no hydrogen, there is little change in  $\delta D$  of the water.

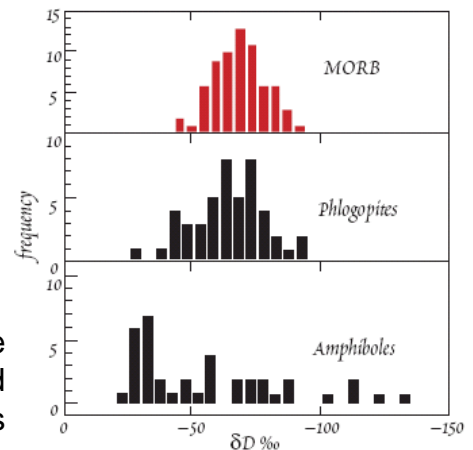


## Stable isotopes and applications in geothermal exploration

### Oxygen isotope data for different basalt types



### Hydrogen isotope data for MORB and hydrous minerals



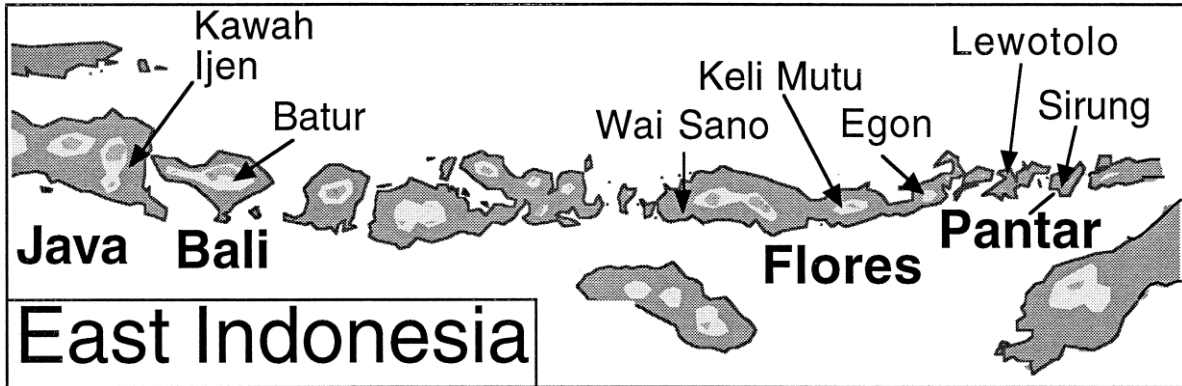
Adapted from White (2015)





### Stable isotopes and applications in geothermal exploration

Sampling sites of crater lake water and gas samples in Eastern Indonesia

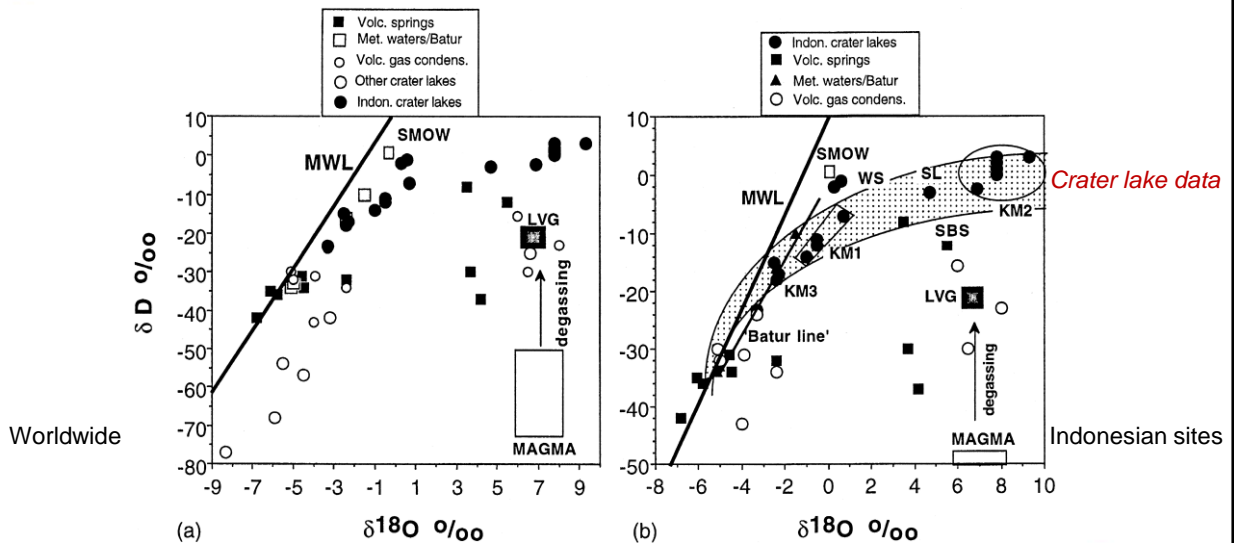


Varekamp and Kreulen (2000)



### Stable isotopes and applications in geothermal exploration

Analytical data for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in volcanic and meteoric water samples



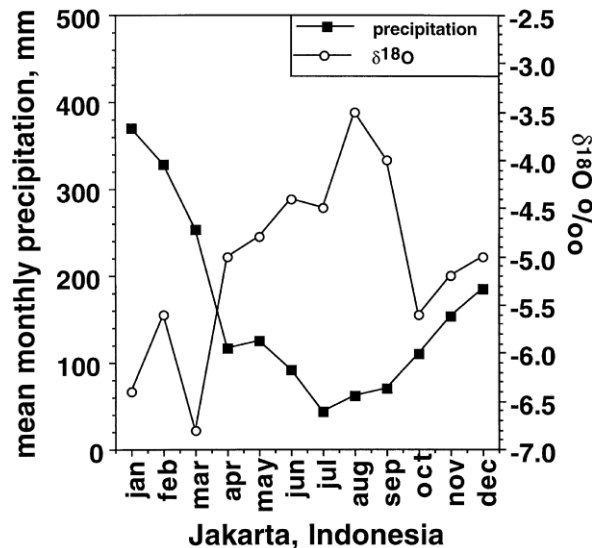
Varekamp and Kreulen (2000)





### Stable isotopes and applications in geothermal exploration

#### Variation in precipitation rate and isotopic composition of precipitation in Jakarta (1985)



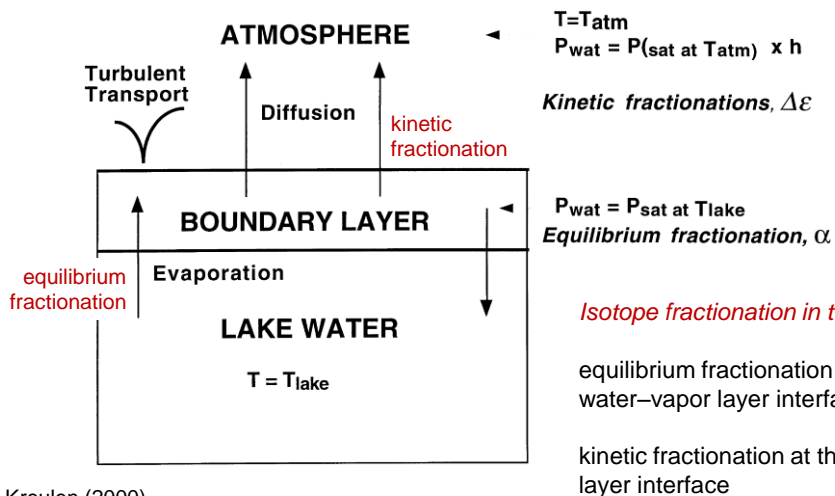
Varekamp and Kreulen (2000)

Jakarta, Indonesia



### Stable isotopes and applications in geothermal exploration

#### Processes at the water–air interface during evaporation



Varekamp and Kreulen (2000)

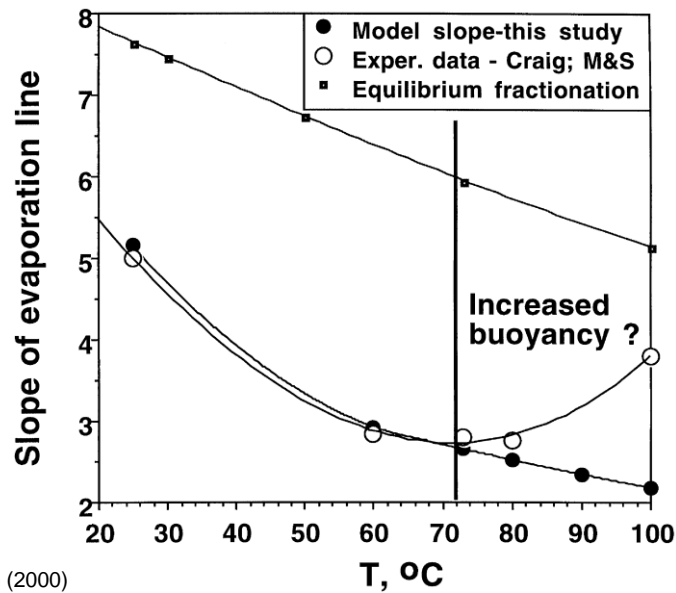






# Stable isotopes and applications in geothermal exploration

## Slopes of evaporation lines as a function of lake water temperature

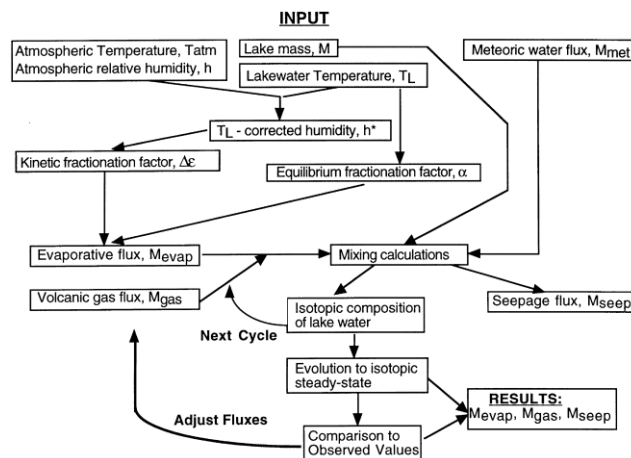


Varekamp and Kreulen (2000)



# Stable isotopes and applications in geothermal exploration

## Flow sheet of the numerical routine for the isotopic evolution of volcanic lakes



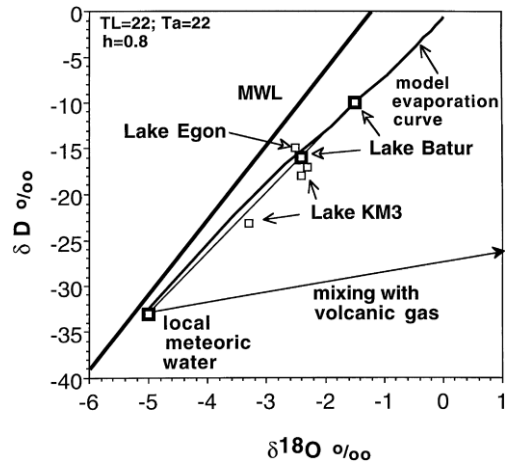
Varekamp and Kreulen (2000)





# Stable isotopes and applications in geothermal exploration

Isotopic evolution of “meteoric” volcanic lakes in Indonesia such as Lake Batur by evaporation only

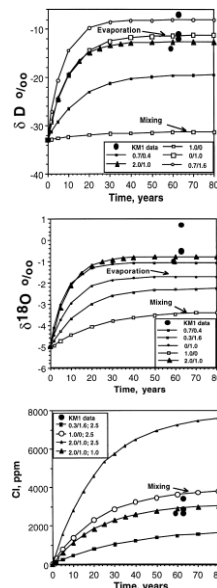


Varekamp and Kreulen (2000)



# Stable isotopes and applications in geothermal exploration

Isotopic evolution diagrams for lake KM1 for various  $M_{\text{gas}}/M_{\text{evap}}$  ( $\times 10^8$  g/day) and  $\text{Cl}^-$  contents of the volcanic input at 2.5 or 1%;



Varekamp and Kreulen (2000)





## Stable isotopes and applications in geothermal exploration

### Isotope data for a cool (KM1) and a warm crater lake (KM2) and local meteoric waters

ev-1 and ev-2:

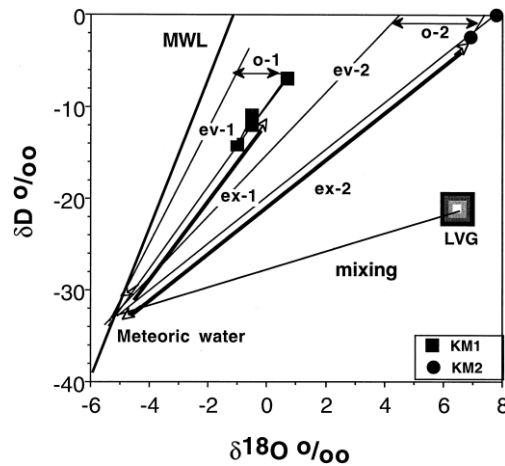
local, pure evaporation lines for lakes KM1 and KM2

o-1 and o-2:

off sets from the pure evaporation lines as a result of mixing with volcanic gas of composition LVG



Varekamp and Kreulen (2000)



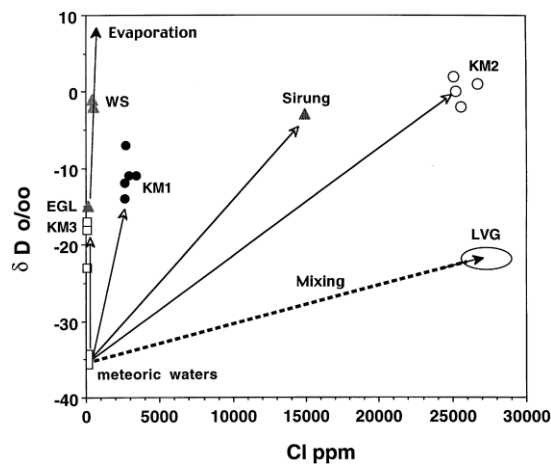
The slope of the pure evaporation lines is determined by the lake water temperature at given atmospheric conditions, and the slope of the isotopic evolution lines depends on  $M_{\text{gas}}/M_{\text{evap}}$



## Stable isotopes and applications in geothermal exploration

### Increasing degree of evaporation with increases in admixed volcanic gas (higher $Cl^-$ ) for Keli Mutu (KM), Egon (EGL) and Sirung lakes

Composition of lake Wai Sano results from extensive evaporation, given its high surface-to-mass ratio



Varekamp and Kreulen (2000)

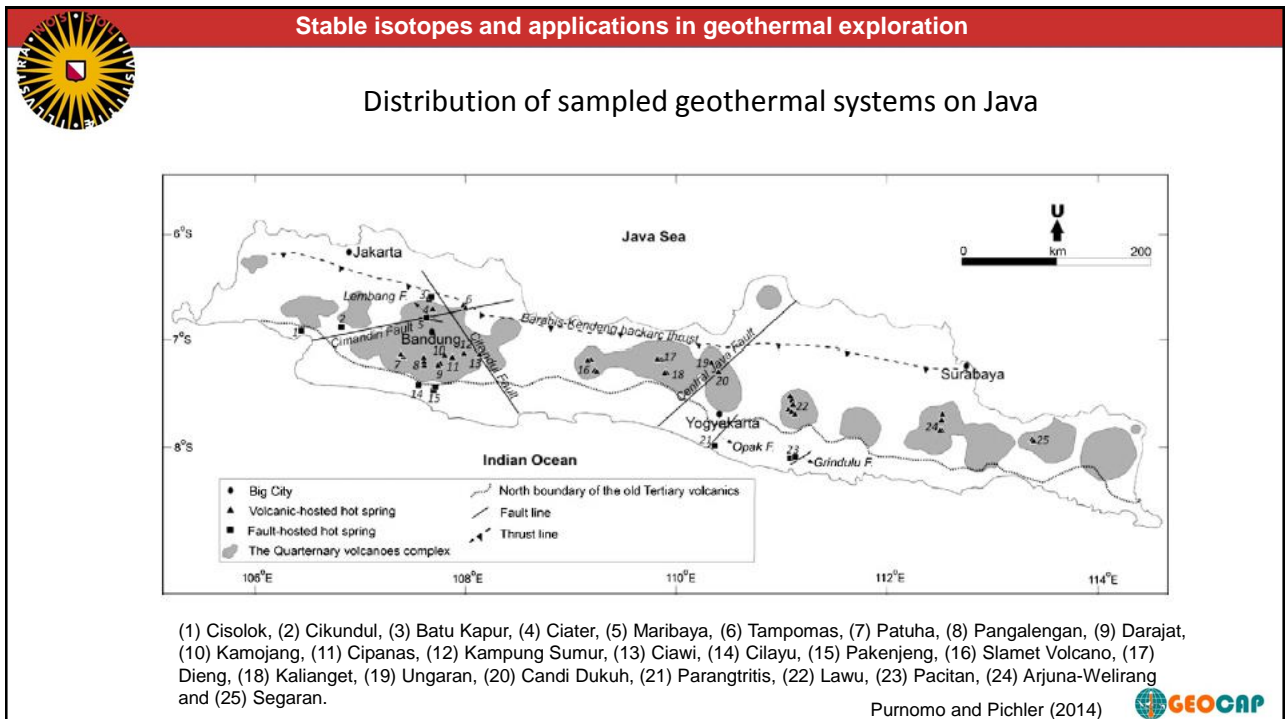






### Stable isotopes and applications in geothermal exploration

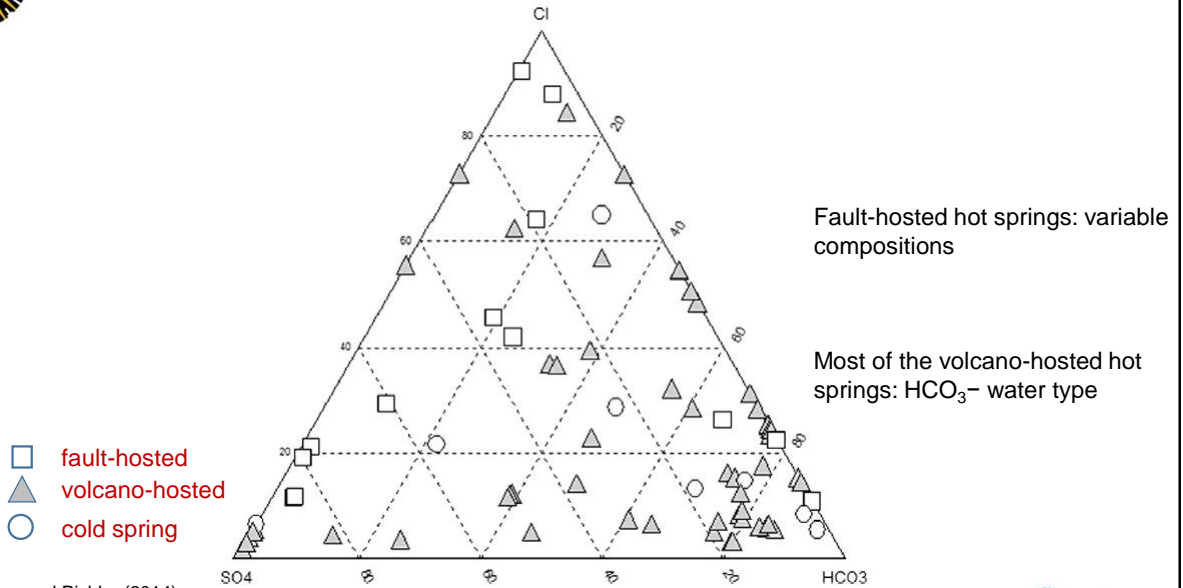
#### Keli Mutu (Flores)





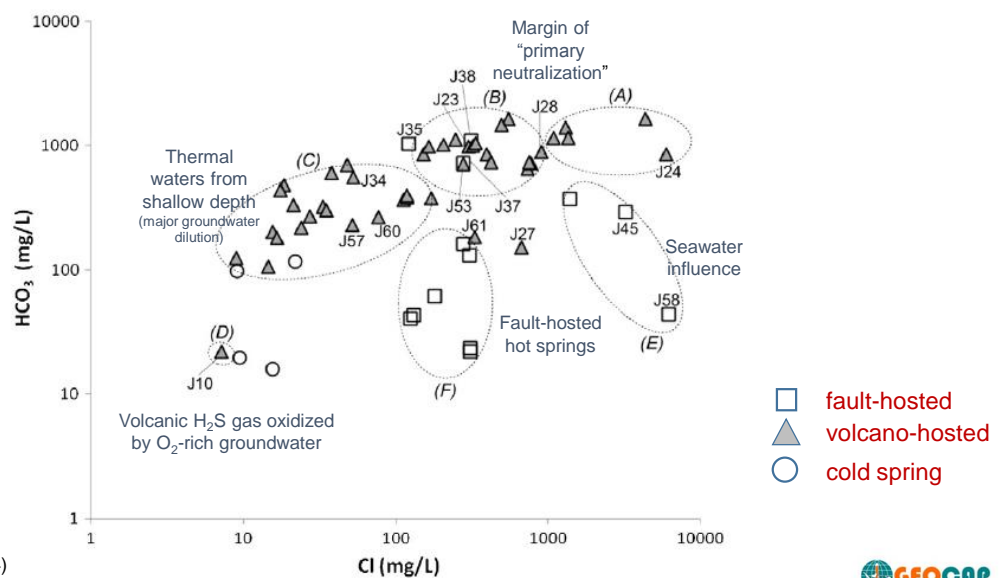
### Stable isotopes and applications in geothermal exploration

#### $\text{SO}_4$ - $\text{HCO}_3$ -Cl ternary diagram of cold and hot springs



### Stable isotopes and applications in geothermal exploration

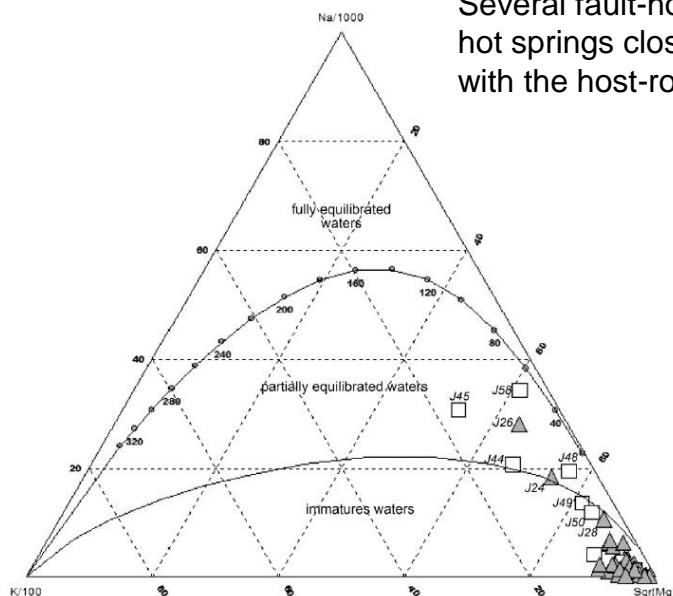
#### $\text{HCO}_3$ vs. Cl diagram for cold and hot springs on Java





### Stable isotopes and applications in geothermal exploration

Several fault-hosted and a few volcano-hosted hot springs close to or in partial equilibrium with the host-rock



Purnomo and Pichler (2014)

□ fault-hosted  
▲ volcano-hosted



### Stable isotopes and applications in geothermal exploration

#### Compilation of calculated geothermal reservoir temperatures on Java

Geothermal systems	Geothermal types	T (°C)	Geothermometer
Slamet M.	V	258 to 380	Si parent and Na-K
Ciawi	V	188 to 313	Si parent and Na-K
Cipanas	V	202 to 287	Na-K and Na-K-Ca
Arjuna-Welirang M.	V	217 to 305	Na-K and Na-K-Ca
Segaran	V	221 to 283	Na-K and Na-K-Ca
Lawu M.	V	127 to 150	Na-K
Candi Dukuh	V	165 to 204	Na-K and Na-K-Ca
Pangalengan	V	221 to 323	Si parent and Na-K
Kalianget	V	216 to 310	Na-K and Na-K-Ca
Patuha	V	205 to 301	Na-K and Na-K-Ca
Tampomas	V	172 to 212	Na-K and Na-K-Ca
Kampung Sumur	V	196 to 263	Na-K and Na-K-Ca
Dieng	V	236 to 349	Na-K and Na-K-Ca
Pacitan	V	<100	Si
Maribaya	F	203 to 299	Na-K and Na-K-Ca
Batu Kapur	F	180 to 278	Si parent and Na-K
Pakenjeng	F	<100	Si
Cilayu	F	125 to 177	Na-K
Cikundul	F	111	Na-K
Cisolok	F	139 to 143	Na-K
Parangtritis	F	88	Na-K

V = volcano-hosted, F = fault-hosted.

Purnomo and Pichler (2014)

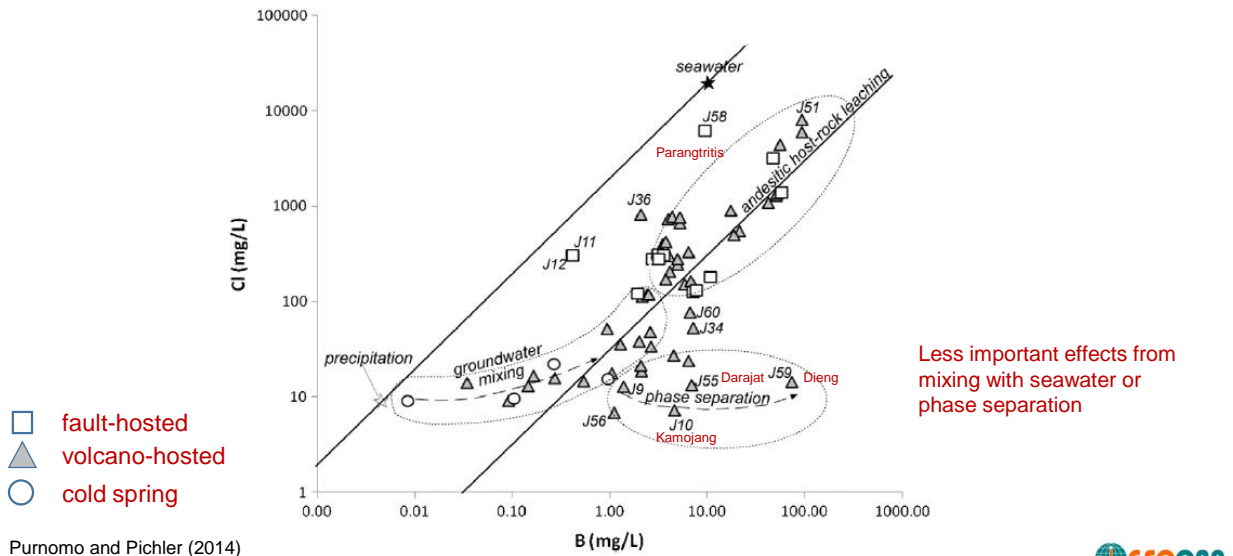






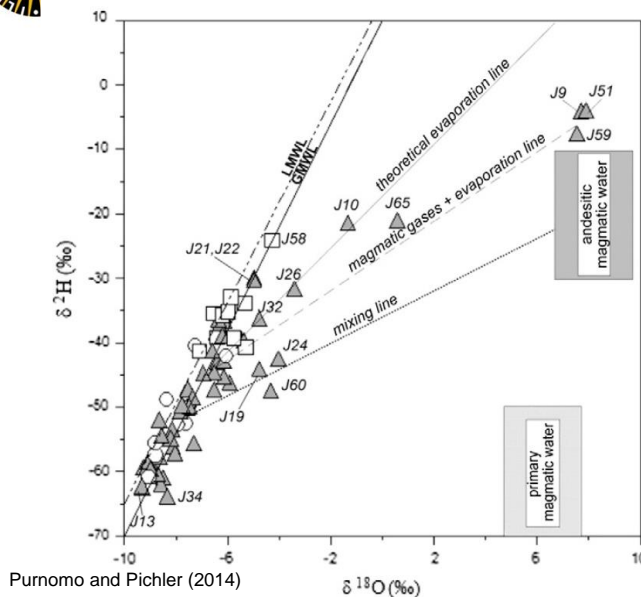
### Stable isotopes and applications in geothermal exploration

#### Cl/B ratio of volcano-hosted and fault-hosted hot springs controlled by water–rock interaction



### Stable isotopes and applications in geothermal exploration

#### $\delta^2\text{H}$ ( $=\delta\text{D}$ ) and $\delta^{18}\text{O}$ compositions of cold and hot springs

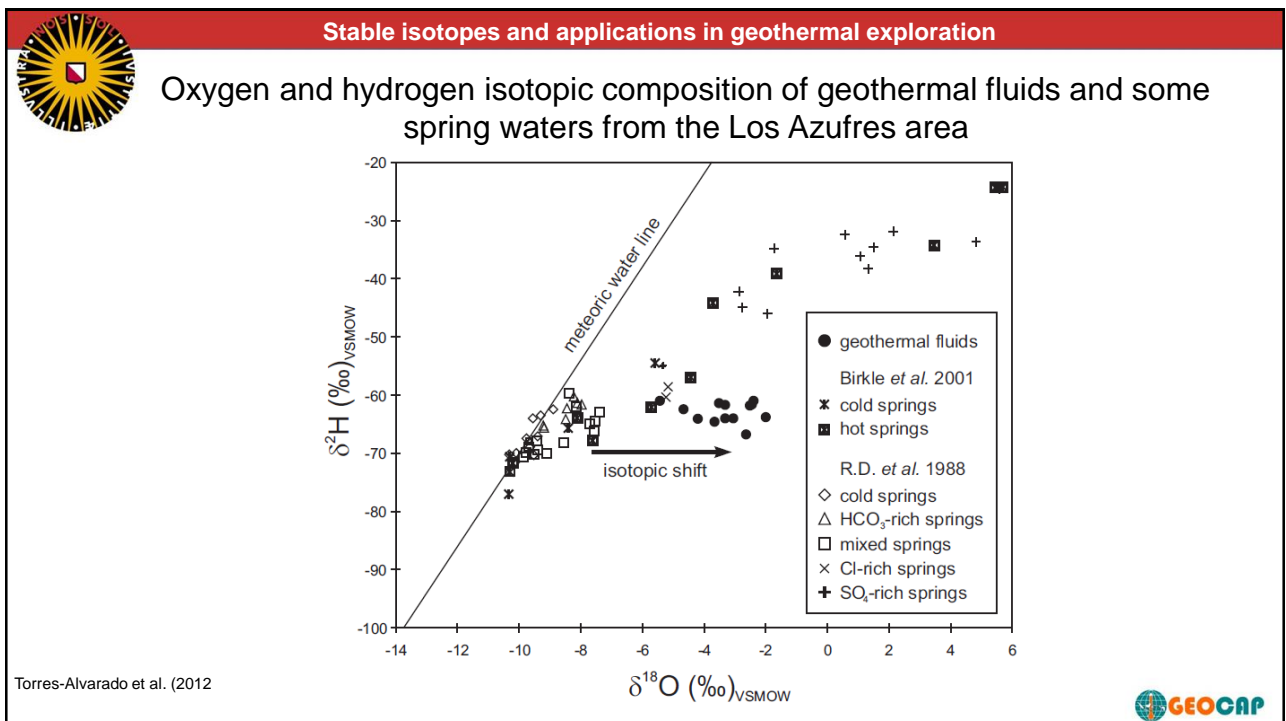
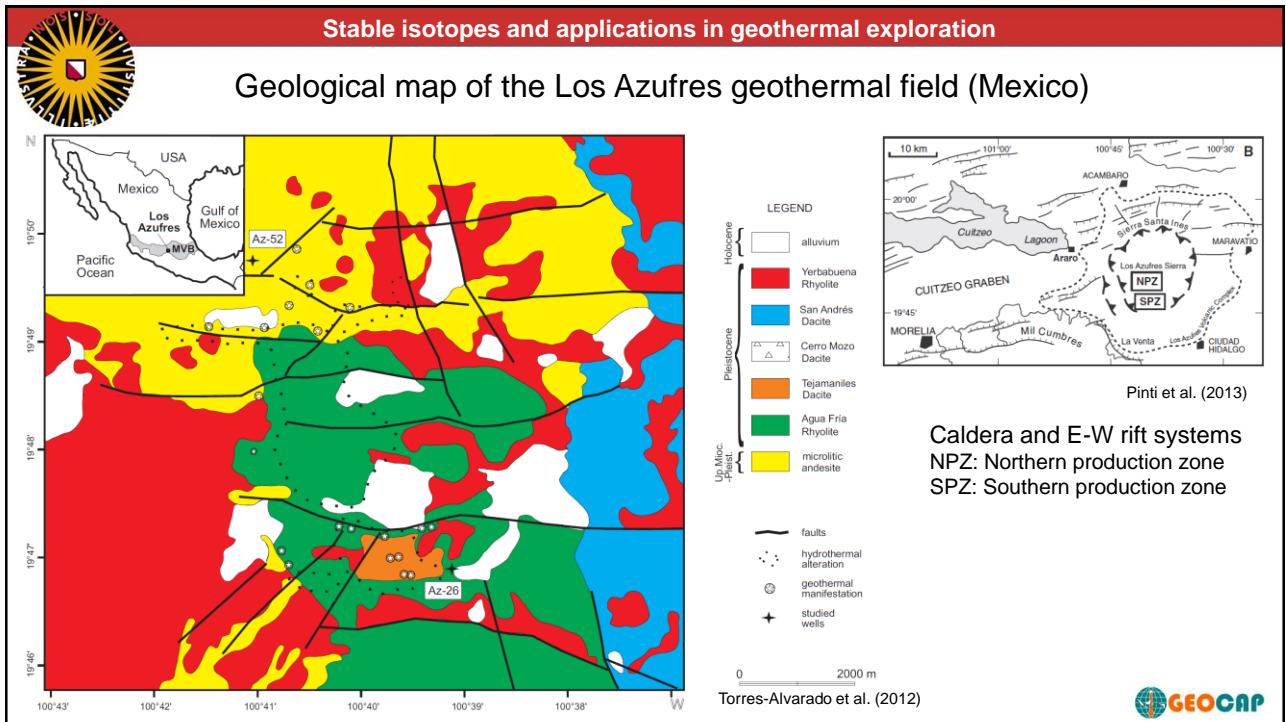


Fault-hosted hot springs and most of the volcano-hosted hot springs plot close to the Local Meteoric Water Line (LMWL), indicating meteoric water as the source of the hydrothermal fluids

stable isotope enrichments through

- Evaporation
- Combination of magmatic gas input and evaporation
- Andesitic water input

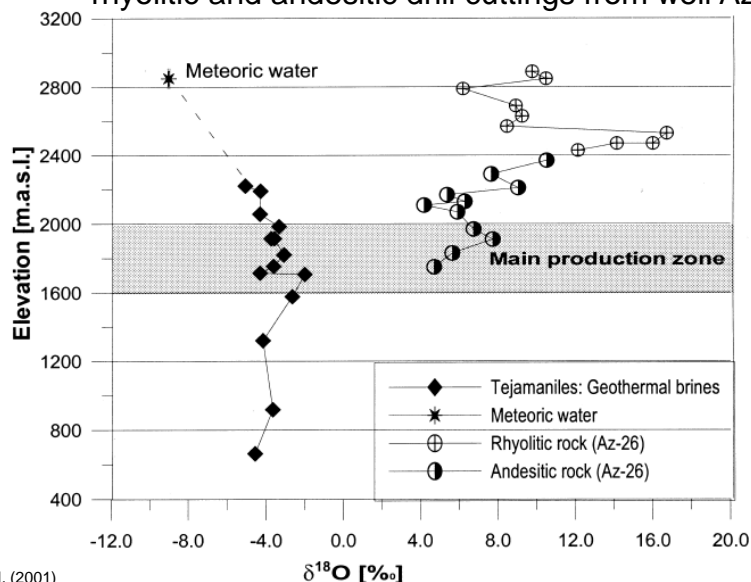
- fault-hosted
- ▲ volcano-hosted
- cold spring





### Stable isotopes and applications in geothermal exploration

Vertical distribution of  $\delta^{18}\text{O}$  values for early production geothermal brines and rhyolitic and andesitic drill cuttings from well Az-26.

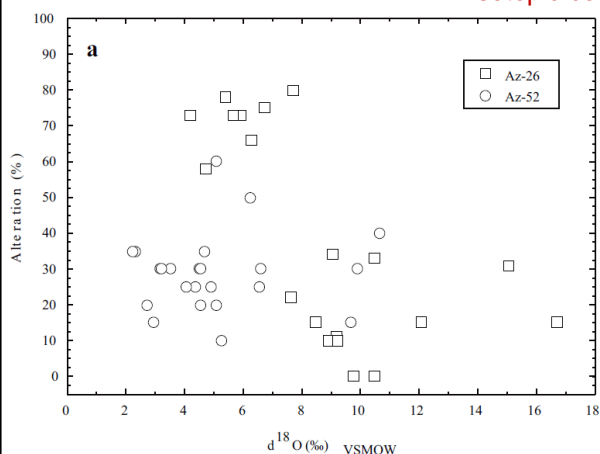


Birkle et al. (2001)

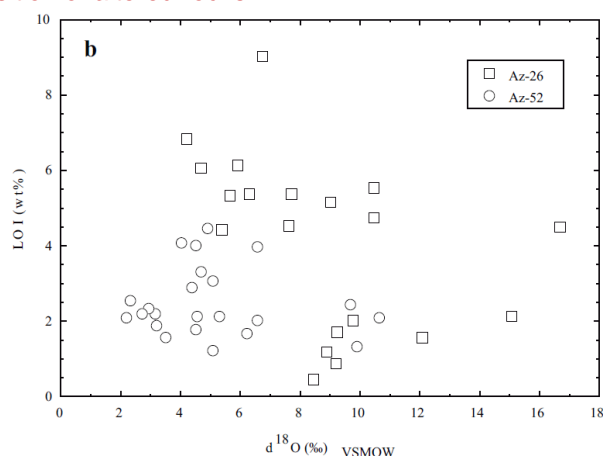


### Stable isotopes and applications in geothermal exploration

Lack of correlation between  $\delta^{18}\text{O}$  values and the amount of alteration or LOI:  
hydrothermal alteration of the rocks does not completely account for the final oxygen isotopic composition of altered rocks



amount of alteration minerals (%) vs.  $\delta^{18}\text{O}$  values of whole rock samples



loss on ignition (LOI, wt%) vs.  $\delta^{18}\text{O}$  values of whole rock samples

Torres-Alvarado et al. (2012)







### Stable isotopes and applications in geothermal exploration

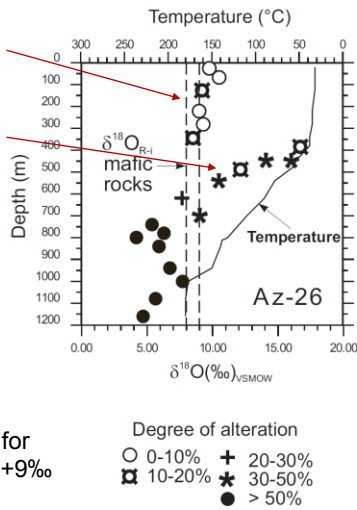
$\delta^{18}\text{O}$  values of whole rock samples vs depth, in-situ temperatures and degree of alteration for the wells Az-26 and Az-52

unaltered primary composition of the felsic caprock

increasing hydrothermal alteration

increasing hydrothermal alteration

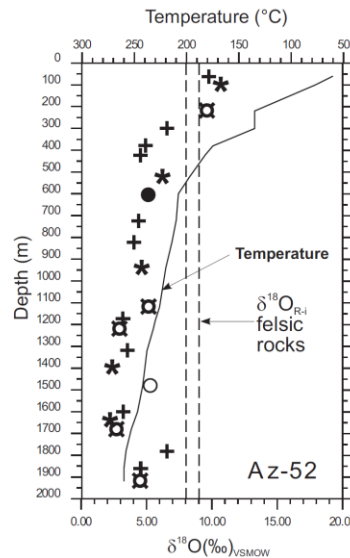
initial  $\delta^{18}\text{O} \approx +8\text{‰}$  for mafic rocks and  $\approx +9\text{‰}$  for felsic rocks



Degree of alteration

○ 0-10%    + 20-30%  
□ 10-20%    \* 30-50%  
● > 50%

Torres-Alvarado et al. (2012)



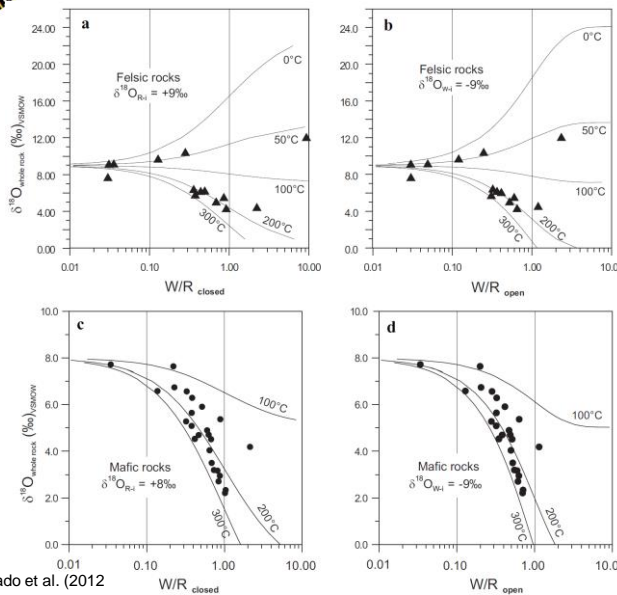
In lower temperature regions (up to  $\approx 90^\circ\text{C}$  or  $\approx 600\text{m}$  depth for Az-26, and  $\approx 300\text{m}$  depth for Az-52) isotope exchange between rock and thermal fluids causes a shift to heavier  $\delta^{18}\text{O}$ .

At higher temperatures the isotope exchange produces lighter  $\delta^{18}\text{O}$  values for the rock phase



### Stable isotopes and applications in geothermal exploration

Water/rock ratios from whole rock  $\delta^{18}\text{O}$  values: two temperature regimes



water-rock oxygen isotope interaction can be described by exchange between meteoric fluid and rocks at in-situ temperatures

$$W/R_{\text{closed}} = (\delta^{18}\text{O}_{\text{R-f}} - \delta^{18}\text{O}_{\text{R-i}}) / (\delta^{18}\text{O}_{\text{W-i}} - \delta^{18}\text{O}_{\text{R-f}})$$

$$W/R_{\text{open}} = \ln [ (\delta^{18}\text{O}_{\text{W-i}} + \Delta - \delta^{18}\text{O}_{\text{R-i}}) / (\delta^{18}\text{O}_{\text{W-i}} - \delta^{18}\text{O}_{\text{R-f}} + \Delta) ]$$

W: water

R: rock

f: final ratio

i: initial ratio

$\Delta$ : water-rock isotope fractionation for individual in-situ temperatures, assumed to be close to that of plagioclase-water

local meteoric water:  $\delta^{18}\text{O}_{\text{W-i}} = -9\text{‰}$

felsic rocks  $\delta^{18}\text{O}_{\text{R-i}} = +9\text{‰}$

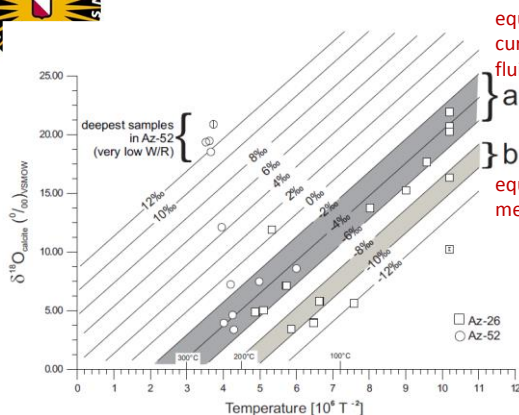
mafic rocks  $\delta^{18}\text{O}_{\text{R-i}} = +8\text{‰}$

Torres-Alvarado et al. (2012)



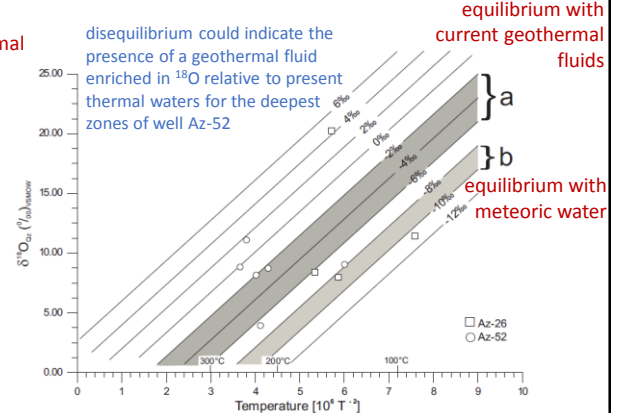


## Stable isotopes and applications in geothermal exploration



$\delta^{18}\text{O}$  values of analyzed **calcite separates** vs in-situ temperatures. The grey bars represent areas of isotopic equilibrium between calcite and present geothermal fluids (a:  $\delta^{18}\text{O} \approx -2$  to  $-6\text{‰}$ ) and meteoric water (b:  $\delta^{18}\text{O} \approx -8$  to  $-10\text{‰}$ ), considering the calcite-water fractionation factors from O'Neil et al. (1969)

Torres-Alvarado et al. (2012)



$\delta^{18}\text{O}$  values of analyzed **quartz separates** vs in-situ temperatures. The grey bars reflect areas of isotopic equilibrium between quartz and current geothermal fluids (a:  $\delta^{18}\text{O} \approx -2$  to  $-6\text{‰}$ ) and meteoric water (b:  $\delta^{18}\text{O} \approx -8$  to  $-10\text{‰}$ ), assuming the quartz-water fractionation factors of Clayton et al. (1972)



## Stable isotopes and applications in geothermal exploration

### Sources

- Birkle, P. and others, 2001. The origin of reservoir fluids in the geothermal field of Los Azufres, Mexico — isotopical and hydrological indications. *Applied Geochemistry*, 16: 1595–1610
- Pinti, D.L. and others, 2013. Evolution of the geothermal fluids at Los Azufres, Mexico, as traced by noble gas isotopes,  $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ,  $\delta^{13}\text{C}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ . *Journal of Volcanology and Geothermal Research*, 249: 1–11
- Purnomo, B.J. and Pichler, T., 2014. Geothermal systems on the island of Java, Indonesia. *Journal of Volcanology and Geothermal Research*. 285: 47–59
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- Varekamp, J.C. and Kreulen, R., 2000. The stable isotope geochemistry of volcanic lakes, with examples from Indonesia. *Journal of Volcanology and Geothermal Research*, 97: 309–327
- White, W.M. *Geochemistry*, Chapter 9: Stable Isotope Geochemistry, pp. 361–420



## **08 Sampling Techniques**

Pri Utami & Agung Harijoko  
(Universitas Gadjah Mada)





## **08. FLUID SAMPLING TECHNIQUES (PART-1)**



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Adapted from geothermal lecture handouts by Pri Utami at the Postgraduate Study Program, Geological Engineering UGM and Geothermal Institute, The University of Auckland.



### **Fluid Sampling Techniques | Pri Utami**

#### **Coverage**

##### **Part-1**

- 8.1. General sampling objectives
- 8.2. Potential hazards in thermal areas
- 8.3. Health and safety: policy and equipments
- 8.4. Design of sampling program
- 8.5. Water sampling parameters and equipments
- 8.6. Pre-sampling check
- 8.7. Manifestation feature survey
- 8.8. Guideline for feature description



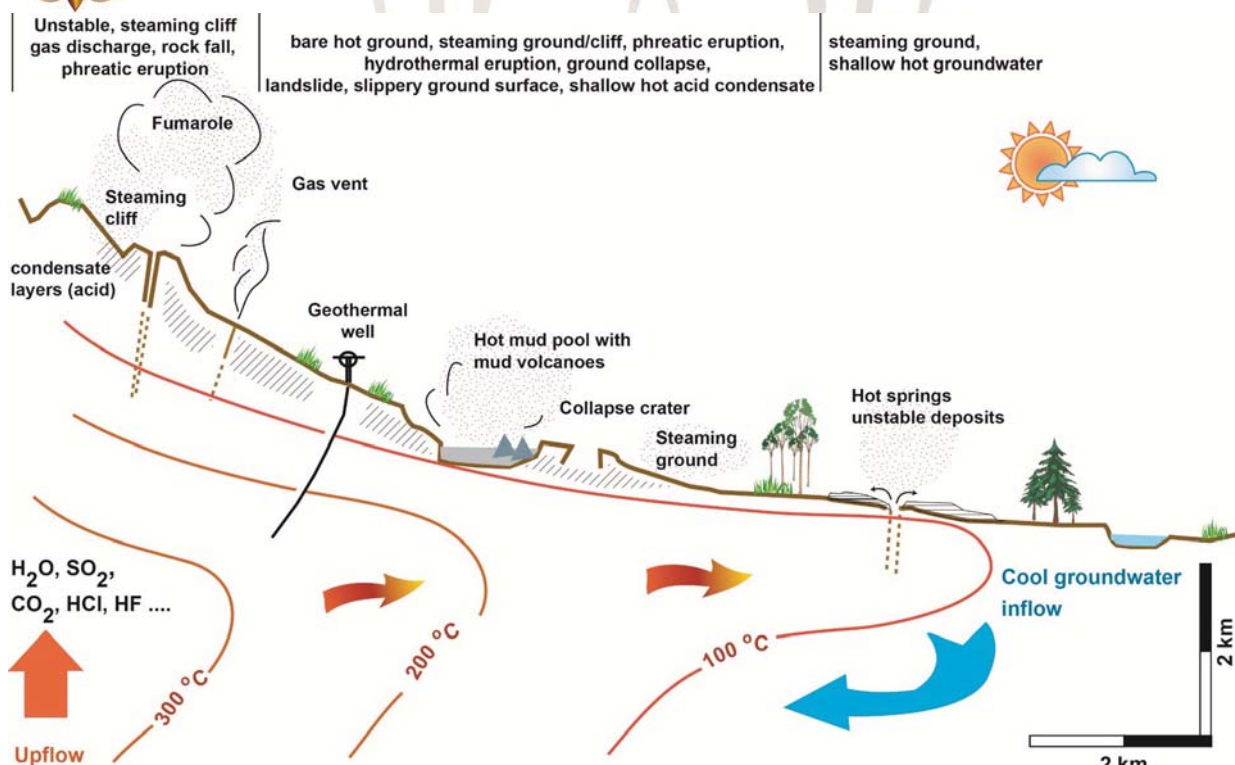
## 8.1 General sampling objectives

To characterise geothermal fluids by obtaining samples representative of the subsurface conditions.

- Large features
- Flowing features
- Hot features
- Obtain samples representing a variety of features



## 8.2. Potential Hazards in Thermal Areas



(Utami, 2011)





## Examples of dangerous sites in thermal manifestation area in New Zealand

Site with collapse crater



Unstable craters with hot springs



Hot spring with silica overhang



## Potential Hazards in Thermal Areas

- Fumarolic gas poisoning (short term and long term)
- Burns from fumaroles
- Gas ponding in low areas (e.g.,  $H_2S$ ,  $CO_2$ ) that may be present in dangerous concentration
- Burns from hot water and mud in streams and in crater lakes
- Hot unstable ground
- Steam clouds
- Ballistics
- Blast
- Collapse of crater rims
- Ejection of hot water





- Amadee Hot Springs, California: Land subsidence
  - Beowawe, Nevada: Cessation of geyser discharge
  - Brady Hot Springs, Nevada: Cessation of hot-spring discharge and onset of boiling and steam upflow from shallow aquifers
  - Coso Hot Springs, California: Increased activity of steam heated features
  - Dixie Valley, Nevada: Increased activity of steam-heated features and subsidence
  - Long Valley caldera, California: Increased steam discharge in the well field, decreased thermal-water discharge at sites downstream from the well field, and subsidence
  - Steamboat Springs, Nevada: Cessation of geyser discharge
- (From Sorey, 2000)



### 8.3 Important points in Health & Safety Policy

- Assess site for safe working areas and access
- Obtain permission to access the site
- Make communication plans with the company / institution base
- Use appropriate and servicable communication devices
- Personal equipments used must be suitable for the environment
- Staff with first aid training must be included in the field party



## 8.4 Health and Safety Equipment

- First aid kit + First aiders
- Burns kit
- Water
- Rope
- Communication devices
- Health and safety plan
- Gas masks / breathing apparatus
- Gloves
- Sampling pole
- Overalls
- Protective eyewear
- Gas monitor
- Hard hat
- At least one other person
- Employer / client H&S considerations



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- ✓ Assess site for safe working areas and access
- ✓ Record site details in the notebook
- Date and time
- Sampling team
- Site name
- Site description (location, feature characteristics (e.g. temperature, flow rate etc), surroundings (e.g., topography, deposits, include sketch maps))
- GPS location, GPS elevation
- Obtain photos and note in book
- Weather
- Samples to be collected + sample numbers + method of collection





**Train your staff for both  
sampling techniques and hazard  
& safety awareness !!!**



## 8.5. Design of the Sampling Program

- Mapping and characterising thermal manifestation aim to provide detailed information of a geothermal systems to support research, resource information, field management and protection.
- Definition of the objective of each type of project must be clear
- Project must be well planned and implemented.

**Three levels of mapping and characterisation of geothermal manifestations:**

### Level-1: Coarse

Major or apparently significant features are located, mapped and described.

Suitable for regional-scale exploration/prospect inventory

### Level-2: Detailed

Attempt to map and describe ALL surface features. Additional data (fluid chemistry, flow rates and heat flows are added.

Suitable for detailed exploration survey.

### Level-3: Comprehensive

Extension of level-2

Additional data (geophysical, biological, ecological) to be obtained.

Suitable for project with very specific purpose.





- Project objectives
  - Scientific objectives
  - Budget constraints (money and time)
  - Logistical constraints
- Verifiable
  - Site documentation
    - Location + metadata
    - Methods + metadata
  - Scientifically acceptable sampling methodology
  - Scientifically acceptable water analyses methodology
  - Quality control samples
    - Repeats
    - Duplicates
    - Spiked samples
    - Blanks
    - Laboratory duplicates
    - Parameters which will enable an ion balance



- Include end members if possible
  - Groundwater
  - Thermal features
  - Streams for CI balances
  - Other significant water bodies ?



## 8.6. Water Sampling Parameters

Water sampling – what parameters am I sampling for ?

### Rubber seal

Bicarbonate (total)  
pH  
Analysis temperature  
HCO<sub>3</sub>/Date Analysed  
Chloride

### Filtered

Sulphate  
Bromide  
Fluoride

### H<sub>2</sub>S

Sulphide (total as H<sub>2</sub>S)

### Filtered and Acidified

Ammonia (total as NH<sub>3</sub>)  
Aluminium  
Arsenic\*<sup>1</sup>  
Boron  
Calcium  
Cesium  
Iron  
Lithium  
Magnesium  
Potassium  
Rubidium  
Sodium  
Silica (as SiO<sub>2</sub>)

### Isotopes

Oxygen 18  
Deuterium

\*1 May require filtered and NaOH for strong acid-sulphate conditions to minimise the formation of arsenic sulphides.



## 8.7. Water Sampling Equipment

- Health and safety equipment
- Beaker
- Sampling pole + bottle
- Appropriate bottles
- Filtering equipment (syringes, 0.45 micron filters)
- Preservatives (concentrated HCl, Zinc Acetate, NaOH) + droppers
- Safety glasses, gloves
- Rubbish bag
- Marker pens, pencils, waterproof notebook
- Calibrated pH/Conductivity/temperature meter
- Appropriate buffer solutions



<http://www.gns.cri.nz>





### Water sampling equipment (cont'd)

- pH paper (acid and alkaline ranges)
- Calibration solutions for the meter
- Distilled water
- GPS, map
- Camera
- Watch with a stopwatch
- V-notch for stream / spring flows
- Spare batteries for meters
- A copy of the meter manuals

Check equipments and chemicals prior to going into the field !!



Rubber seal glass bottles for raw sample

Plastic bottles for filtered and acidified sample

Plastic bottles for filtered sample

11 ml Glass bijou bottles with air – tight lid for isotopes

47 mm plastic filter holder



Plastic bottles for raw sample

Plastic bottles for raw sample pre-spiked with 1 ml of 8 N NaOH

47 mm filters (0.45 microns)

Small disposable filter unit (45 microns)

60 ml Syringe

1:1 nitric acid

pipette





Gas monitor



## 8.8. Pre-sampling Checks

- Conduct equipment pre-checks prior to going into the field:
  - Confirm personnel
  - Confirm logistical arrangements
  - Confirm equipment
    - Check and calibrate meters
    - Check the age of the preservatives (expired ?)
    - Check the age of the calibration solutions (expired?)
    - Check the age of the disposable filters (expired ?)
    - Is the GPS on the correct data ?
    - Check gas meter
    - Check with laboratory for sampling/sending instructions



## 8.9. Manifestation Feature Survey

- Feature identity number
- Name of geothermal field
- Field code
- Coordinates
- Map sheet, datum, elevation
- Feature type
- Description
- Sketch map
- Photograph
- Additional comments
- Feature use
- Feature threats
- Access information



### THERMAL MANIFESTATION OBSERVATION FORM

(Bay of Plenty Regional Council Guideline 2012 – used with permission)

Feature ID		Historic ID		Feature Name																																									
Geothermal Field		Historic / Local Name																																											
Field Code		Survey																																											
Coordinates (Northing / latitude)				Error Estimate																																									
Coordinates (Easting / Longitude)				Elevation																																									
GPS WP No.		Relationship to Feature (outlet, centre, etc)																																											
Map Sheet		Map Datum		Elevation Datum																																									
Feature Type		Date / Time		Observer(s)																																									
Description																																													
<i>Sketch Map: show dimensions, North, photo point (P), sample (S), temperature (T), coordinate location (C) and relationship to nearby features</i>																																													
<table border="1"><tr><td>Size</td><td></td></tr><tr><td>Color</td><td></td></tr><tr><td>Clarity</td><td></td></tr><tr><td>Ebullition</td><td></td></tr><tr><td>Odor Gas</td><td></td></tr><tr><td>Temperature</td><td></td></tr><tr><td>Water Level</td><td></td></tr><tr><td>Flow Rate</td><td></td></tr><tr><td>Wind Speed</td><td></td></tr><tr><td>Air Temperature</td><td></td></tr><tr><td>Camera</td><td></td></tr><tr><td>Image Number</td><td></td></tr><tr><td>Water Sample</td><td>Yes <input type="checkbox"/> No <input type="checkbox"/></td></tr><tr><td>Details</td><td></td></tr><tr><td>Gas Sample</td><td>Yes <input type="checkbox"/> No <input type="checkbox"/></td></tr><tr><td>Details</td><td></td></tr><tr><td>Isotope Sample</td><td>Yes <input type="checkbox"/> No <input type="checkbox"/></td></tr><tr><td>Details</td><td></td></tr><tr><td>Biological Sample</td><td>Yes <input type="checkbox"/> No <input type="checkbox"/></td></tr><tr><td>Details</td><td></td></tr></table>						Size		Color		Clarity		Ebullition		Odor Gas		Temperature		Water Level		Flow Rate		Wind Speed		Air Temperature		Camera		Image Number		Water Sample	Yes <input type="checkbox"/> No <input type="checkbox"/>	Details		Gas Sample	Yes <input type="checkbox"/> No <input type="checkbox"/>	Details		Isotope Sample	Yes <input type="checkbox"/> No <input type="checkbox"/>	Details		Biological Sample	Yes <input type="checkbox"/> No <input type="checkbox"/>	Details	
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#### OFFICE USE ONLY

Reference		Date Entered		Entered By	
Photographs Downloaded	Yes <input type="checkbox"/> No <input type="checkbox"/>	Where			



## 8.10. Guideline for Feature Description

Color, water clarity or turbidity: indicators of the gross pool chemistry

- Alkali chloride water is very clear
- Mixed water will tend to be less clear and grow algae
- Acid features may be muddy fluids

Description of color and turbidity tend to be subjective, but grouping the observation introduces consistency.

Ebullience: reflects the amount of gas or steam in the discharge

- Sometimes a lot of gas can give misleading appearance of boiling !
- Note the locations of gas or steam upwelling on the sketch, as they may reflect multiple vents in the pool.

Odor: note the predominant odor of gases like  $H_2S$ .

- The presence of some gases can be detected by handheld monitors
- The true quantity can only be obtained with more sophisticated equipment.



**Temperature:** the location of temperature measurement is very important.

- Is the temperature uniform over the entire feature ?
- Is the point we measure the hottest in the location ?
- Or is it the overflow temperature ?

- ➡ The safest method is to use the thermocouples attached to a long probe.
- ➡ Infra-red guns and cameras tend to be affected by steam.

**Water level:** needs to be referenced to some stable permanent feature (easily identified and physically long-lived bench mark).

**Overflow rates:** individual or collective flow from a group of features

**Flow:** sum of average flow speed and channel cross-section. Can be done by timing a small float along a measured section of an outflow,

$$\text{Flow} = \{(\text{Width} \times \text{Depth} \times \text{Length}) / (\text{Time}/1000)\} \times 0.7$$

W, D, L in cm, T in second, 0.7 is the channel bed roughness factor





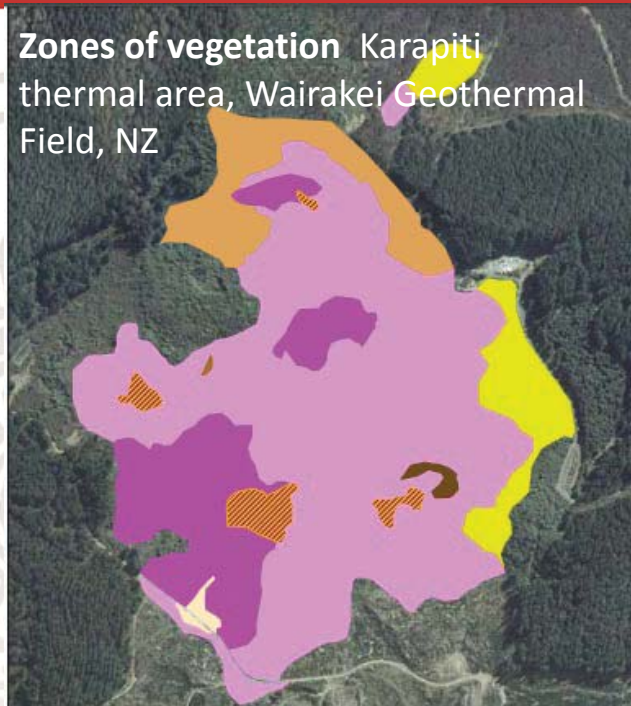
### Ground nature:

- Diffuse discharge (steaming ground, warm ground), strong discharge (fumarole)
- Vegetation (can be a guide to ecosystem)
- Altered ground
- Mineral deposits (silica sinter or travertine) and their micro-structures

### Wind speed and air temperature:

Needed when a heat flow study is being conducted.

**Zones of vegetation** Karapiti thermal area, Wairakei Geothermal Field, NZ



#### Legend

- Campylopus capillaceous mossfield
- Cheilantes sieberi-buffalo grass fernland
- Bare ground (human induced bare ground amongst geothermal habitat)
- Mingimingi-kanuka-manuka-karamu/bracken scrub
- Nonvegetated raw-soilfield
- Prostrate kanuka scrub
- Prostrate kanuka scrubland
- Whauwhaupaku scrub

[www.waikatoregion.govt.nz](http://www.waikatoregion.govt.nz)



### Wind speed and air temperature:

Needed when a heat flow study is being conducted.

### Ground nature:

- Diffuse discharge (steaming ground, warm ground), strong discharge (fumarole)
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- Altered ground
- Mineral deposits (silica sinter or travertine) and their micro-structures

## **08. FLUID SAMPLING TECHNIQUES (PART-2)**



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### **Fluid Sampling Techniques | Agung Harijoko**

## **Part-2**

- 8.11. Sampling methodology
- 8.12. Assess possible sources of contamination
- 8.13. Analytical methods
- 8.14. Gas sampling
- 8.15. Condensate sampling
- 8.16. Typical laboratory report for gases
- 8.17. Quality control checks
- 8.18. Summary of field sampling
- 8.19. Monitoring geothermal manifestations
- 8.20. Designing a thermal manifestation monitoring project





## 8.11. Sampling Methodology

- Assess site safety
- Prepare water sample site
- Label all bottles
- Put on safety equipment

### Collect sample

- Preferably from up-flow zone without disturbing sediment
- Rinse water collection vessel 3 times (bottle on pole and then beaker). Minimise potential contamination.
- Collect raw samples first

- Rubber seal



- Rinse 3 times, then fill to the top
- Close the clamp
- Turn bottle upside down to check that there is no air in the sample

- Bijou



- Rinse 3 times
- Fill to top and cap
- Minimize air content in the sample



Adapted from UGM-GNS NZAID Geothermal Course



- 100ml raw + preservative

- Rinse 3 times
- Fill most of the way
- If pH > 9 then add 4 drops Zn Acetate (6M liquid)
- If pH < 9 then add caustic soda (a few drops of 240 mg/l NaOH) until pH > 9, then add Zn Acetate as above.

### Filtered samples

- 100ml Filtered

- Rinse syringe 3 times
- Connect syringe to the filter and filter 5-10ml Open bottle and rinse 3 times with the filtered wa Fill bottle with filtered water

- 100ml Filtered and acidified

- As for 100ml filtered
- When bottle is almost full add conc. acid until pH < 2

- Secure samples
- Tidy site and check notebook
- Send samples to the laboratory as soon as practically possible
  - Chain of custody



Adapted from UGM-GNS NZAID Geothermal Course







## 8.12. Assess Possible Sources of Contamination

- Dirty equipment
- Rain (dilution and washing contaminants into samples)
- Airborne particles
- Sweat
- Soil/vegetation
- Preservatives
- Local sources



## 8.13. Analytical Methods

PARAMETER	METHOD USED	DETECTION LIMIT
Aluminium	ICP-OES APHA 3120-B 21st Edition 2005	0.15 mg/L
Ammonia (total as NH <sub>3</sub> )	Ion Selective Electrode APHA 4500-NH <sub>3</sub> D 21st Edition 2005	0.1 mg/L
Arsenic	ICP-OES APHA 3120-B 21st Edition 2005	0.015 mg/L
Bicarbonate (total)	HCO <sub>3</sub> Titration Method ASTM Standards D513-82 Vol.11.01 of 1988	20 mg/L
Boron	ICP-OES APHA 3120-B 21st Edition 2005	0.3 mg/L
Bromide	Ion Chromatography APHA 4110-B 21st Edition 2005	0.04 mg/L
Calcium	ICP-OES APHA 3120-B 21st Edition 2005	0.05 mg/L
Cesium	Flame Emission Spectrometry APHA 3500-Cs 21st Edition 2005	0.02 mg/L
Chloride (Groundwater method)	Ion Chromatography APHA 4110-B 21st Edition 2005	0.04 mg/L
Chloride (Geothermal method)	Potentiometric Method APHA 4500-Cl D 21st Edition 2005	20 mg/L
Fluoride	Ion Chromatography APHA 4110-B 21st Edition 2005	0.005 mg/L
Iron	ICP-OES APHA 3120-B 21st Edition 2005	0.08 mg/L
Lithium	ICP-OES APHA 3120-B 21st Edition 2005	0.01 mg/L
Magnesium	ICP-OES APHA 3120-B 21st Edition 2005	0.01 mg/L
pH	Electrometric Method APHA 4500-H+ B 21st Edition 2005	1
Potassium Groundwater method	ICP-OES APHA 3120-B 21st Edition 2005	0.11 mg/L
Rubidium	Flame Emission Spectrometry APHA 3500-Rb 21st Edition 2005	0.01 mg/L
Silica (as SiO <sub>2</sub> )	ICP-OES APHA 3120-B 21st Edition 2005	0.6 mg/L
Sodium – 818.326 nm (Geothermal method)	ICP-OES APHA 3120-B 21st Edition 2005	1.5 mg/L
Sodium – 818.326 nm (Groundwater method)	ICP-OES APHA 3120-B 21st Edition 2005	0.25 mg/L
Sulphide (total as H <sub>2</sub> S)	Methylene Blue Method APHA 4500-S <sub>2</sub> D 21st Edition 2005	0.01 mg/L
Sulphate	Ion Chromatography APHA 4110-B 21st Edition 2005	0.03 mg/L

Adapted from  
UGM-GNS NZAID  
Geothermal Course



## 8.14. Gas Sampling

- Natural feature gas sampling techniques (He, H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, Ar, H<sub>2</sub>S, CO<sub>2</sub>, NH<sub>3</sub>)
  - Pre-field preparation
    - Gases
    - Condensate
  - Sampling
  - Handling



Adapted from UGM-GNS NZAID Geothermal Course



## Bottle

- Rotoflo bottle – single neck



15.06.2010

Adapted from UGM-GNS NZAID Geothermal Course





## Sample bottle preparation

- Pour approx 50ml of 8M NaOH into the bottle
- *Apply vacuum to rotoflo*
  - Attach bottle to vacuum pump, neck up
  - Turn on vacuum pump, open bottle
  - Apply vacuum for 3 mins (-1 atm)
  - Close bottle. Turn off pump. Turn bottle upside down to ensure no leaks.
  - If no leaks, weigh bottle and record bottle number.
- Secure bottle



Adapted from UGM-GNS NZAID Geothermal Course



## Gas sampling - general

- **Sampling**
  - Secure tube/funnel into gas discharge
  - Want sample tubing above horizontal position
  - Less tubing sticking out as possible
  - Minimise amount of silicon tubing
  - Let all tubing warm up
  - Check flow through tubing using water



Adapted from UGM-GNS NZAID Geothermal Course





## Gas sampling – collecting the sample

- Purge neck of bottle for about 30 sec before connecting – watch for condensate.
  - Single arm rotoflo. Hold bottle in upside down position to ensure condensate dribbles out.
  - Double arm: connect spare tubing + clip to 1 arm, connect sample tubing to other arm. Open clip – flow through will purge. Can monitor flow by putting spare flow into water jug. Close clip prior to sampling and opening rotoflo.
- Connect tubing to bottle
- Turn bottle upside down/on a slant when sampling
- Slowly open bottle valve



Adapted from UGM-GNS NZAID Geothermal Course



## Gas sampling – collecting the sample

- Cool gas with water or ice (depending on water recycling system)
- Monitor bubbling. Shut bottle when bubbling gets slow
- Give bottle a shake + cool in water jug. Reopen valve a little to get more gas sample if possible. Repeat 3 times.
- Secure bottle
  - Check rotoflo valve when sample has cooled
- Note bottle number in notebook
- Collect duplicate samples
- Send to lab
  - Hazardous samples



Adapted from UGM-GNS NZAID Geothermal Course



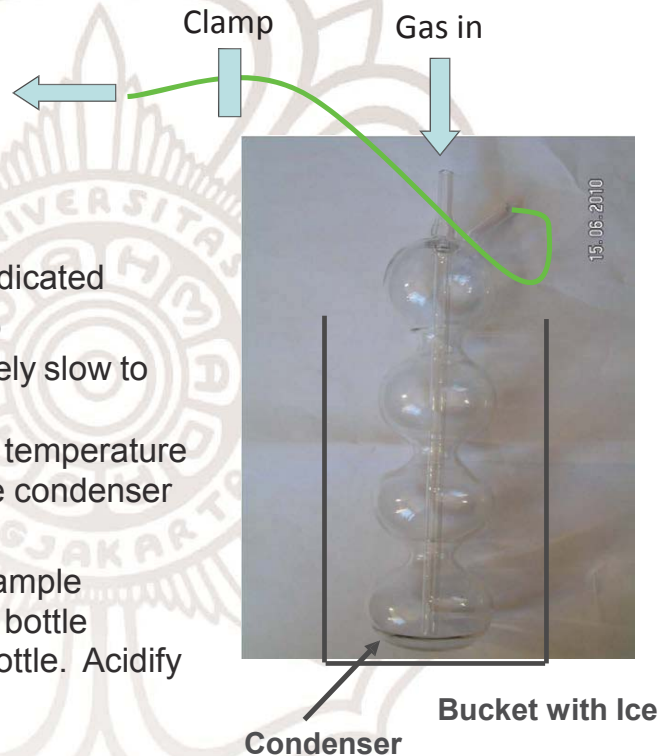
## 8.15. Condensate Sampling

### Purpose :

- $O^{18}$  and  $H^2$
- Alternative for  $NH_3$

### Method

1. Connect up system as indicated
2. Regulate flow with clamp
  - Flow should be relatively slow to enable condensation.
  - Adjust flow so that the temperature is warm to touch at the condenser outlet.
3. Collect approx 50ml of sample
  - Approx 20ml into a Bijou bottle
  - Approx 30ml into a PE bottle. Acidify until pH <2



Adapted from UGM-GNS NZAID Geothermal Course



## 8.16. Typical Laboratory Report for Gases



WAIRAKEI ANALYTICAL LABORATORY  
Private Bag 2005, Taupo  
Phone: (07) 374 8211  
Fax: (07) 374 8199  
e-mail: wlabmanager@gns.cri.nz

To:  
Client

### ANALYTICAL REPORT: Fumarole

	Laboratory Ref. No	2901610
	Collection Date	10/1/2000
	Site ID	Fumarole
	Field ID	1
Carbon Dioxide	mmoles/100 moles H2O	2129
Ammonia in steam	mmoles/100 moles H2O	0.23
Argon	mmoles/100 moles H2O	0.12
Helium	mmoles/100 moles H2O	0.006
Hydrogen	mmoles/100 moles H2O	5.0
Hydrogen sulphide	mmoles/100 moles H2O	65
Methane	mmoles/100 moles H2O	78
Nitrogen	mmoles/100 moles H2O	33
Oxygen	mmoles/100 moles H2O	<0.001

Analyst Comments: The results pertain to samples as received. This document shall not be reproduced, except in full.

Report Date: 5/05/2009  
Report No: WAL090415001  
Page: 2 of 2  
NTC Number: Sample

Bruce Mountain Ph.D.  
Geochemist



This laboratory is accredited by International Accreditation New Zealand.  
The tests reported herein have been performed in accordance with its terms  
of accreditation, with the exception of the tests marked with a \*

Gas Analysis

Gas Chromatography -- Journal of International Assoc. of Volcanology & Chemistry.  
Vol  
39 No. 4 -- Giggenbach W.F. (1975)

Adapted from UGM-GNS NZAID Geothermal Course







### 8.17. Quality Control Checks

- Check field QC samples (Duplicates etc)
- Do the data look realistic ?
- Compare the results to historical data
- Ion balance on water samples
  - Use chemical modelling software code to calculate



### 8.18. Summary of Field Sampling

1. Sampling in geothermal areas can be hazardous.
2. Sampling programmes need to be correctly designed to maximise scientific and economic objectives.
3. Appropriate data needs to be collected with the water/gas samples.
4. A range of sampling methods may be required and will depend on the parameters required.
5. Multiple methods of data quality control should be used to ensure data is as accurate as possible.
6. Quality geochemical data is needed for defensible interpretations that can be relied upon.



Adapted from UGM-GNS NZAID Geothermal Course





## 8.19. Monitoring Geothermal Manifestations

There is an increasing awareness about the possible changes or damages of natural thermal environments and chemical contamination of soil, water, and air due to the extraction of geothermal energy.

Collection of a pre-development baseline of physical, chemical, and biological data for thermal manifestations (and geothermal environment in general) is essential for:

1. Impact assessment associated with geothermal development.
2. Identification of specific impacts which may or may not be directly attributable to geothermal development.

(Webster, 1995)

**A good baseline data set can therefore provide some measure of protection against false accusation of damages.**



## 8.20. Designing a Thermal Manifestation Monitoring Project

- Collecting thermal manifestation data to assess changes with time.
- Features selected for monitoring must be representative.
- Data collection can be done by regular field visits or by logging feature parameters on data loggers. Sampling time intervals must be representing the activity of the features.
- Thermal feature monitoring must not only be done on producing geothermal field, but also on geothermal tourism destinations, and on the area that may be subject to volcanic unrest.



## THERMAL MANIFESTATION OBSERVATION FORM (RE-SURVEY)

(Bay of Plenty Regional Council Guideline 2012 – used with permission)

Survey		Date / Time		Observer(s)	
Feature ID		Feature Name			
Description					
<p>Sketch Map: show dimensions, North, photo point (P), sample (S), temperature (T), coordinate location (C) and relationship to nearby features</p>					
				Size	
				Color	
				Clarity	
				Ebullition	
				Odor Gas	
				Temperature	
				Water Level	
				Flow Rate	
				Wind Speed	
				Air Temperature	
				Camera	
				Image Number	
				Water Sample	Yes <input type="checkbox"/> No <input type="checkbox"/>
				Details	
				Gas Sample	Yes <input type="checkbox"/> No <input type="checkbox"/>
				Details	
				Isotope Sample	Yes <input type="checkbox"/> No <input type="checkbox"/>
				Details	
				Biological Sample	Yes <input type="checkbox"/> No <input type="checkbox"/>
				Details	
Additional Comments					

## **09 Environmental Impact of Geothermal Activity and Production**

Manfred van Bergen  
(Utrecht University)



**GEOCHEMISTRY FOR GEOTHERMAL DEVELOPMENT**  
**UGM – UU – Geocap Capacity Building Program**  
**21 - 25 August, 2017**



**09. ENVIRONMENTAL IMPACT OF  
 GEOTHERMAL ACTIVITY AND PRODUCTION**

Manfred van Bergen  
 Utrecht University



**Environmental Impact of geothermal activity and production**

**Potential environmental impacts from geothermal development**

Gaseous emissions

Water pollution

Solids emissions

Noise pollution

Land use

Land subsidence

Induced seismicity

Induced landslides

Water use

Disturbance of natural hydrothermal manifestations

Disturbance of wildlife habitat, vegetation, and scenic vistas

Catastrophic events

Thermal pollution





## Environmental Impact of geothermal activity and production



## Environmental Impact of geothermal activity and production

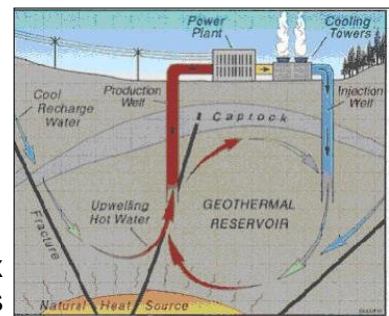
Most adverse environmental effect of geothermal energy utilization is chemical pollution



photo: E. Layman

From gaseous components in steam discharged into the atmosphere

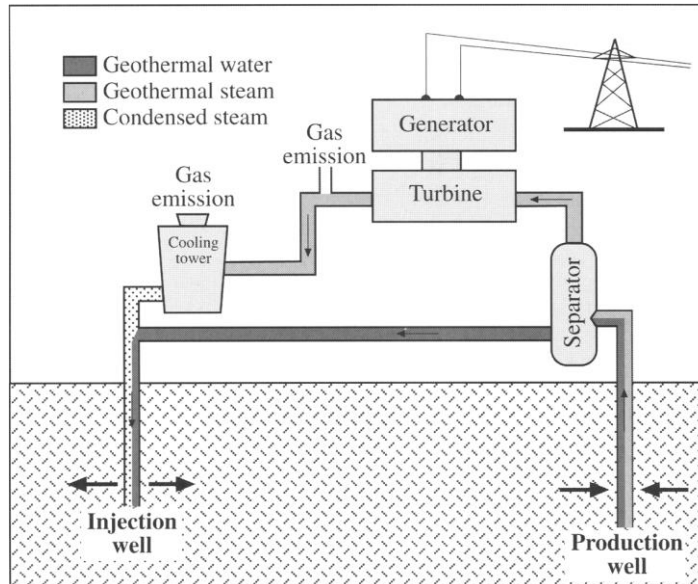
From aqueous components in spent water that may mix with surface- and groundwaters





## Environmental Impact of geothermal activity and production

Schematic layout of a classic geothermal power plant



(Arnórsson, 2004)

The main escape routes for steam are from the cooling tower and gas ejectors, which are located just downstream from the turbine



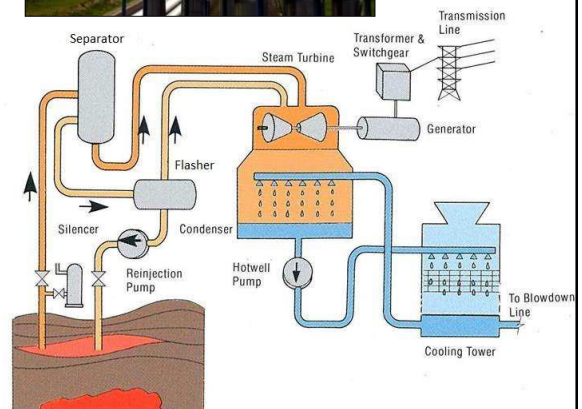
## Environmental Impact of geothermal activity and production



Poisonous chemical components in geothermal steam escape into the atmosphere from electric power plants via ejector exhausts, cooling towers, silencers, and drains and traps

These compounds include  $\text{H}_2\text{S}$ , B, Hg, As and Rn

Not directly poisonous but environmentally harmful:  $\text{CO}_2$  and  $\text{CH}_4$







## Environmental Impact of geothermal activity and production

### Chemical composition of geothermal fluids

- Dissolved solids content of geothermal water ranges from a few hundred mg/L (ppm) to as much as 30% by weight
- The total gas content of geothermal steam is typically between 0.2 and 1 vol% but can be as high as 20% by volume

*The concentrations of dissolved solids and gases in geothermal fluids are determined by:*

- their sources of supply to the fluid
- the formation of hydrothermal minerals, which remove dissolved components from the fluid

*The sources of dissolved solids and gases include:*

- the rock through which the fluid percolates
- magma
- dissolved matter in the recharging water

(Arnórsson, 2004)



## Environmental Impact of geothermal activity and production

### Compositions of separated well waters from wet steam wells

Location <sup>†</sup>	Rock type	Aquifer temperature (°C)	pH/°C <sup>‡</sup>	SiO <sub>2</sub>	B	Na	K	Ca	Mg	CO <sub>2</sub>	SO <sub>4</sub>	H <sub>2</sub> S	Cl	F	Total dissolved solids
Cerro Prieto 5, Mexico	Sediments	289		790	14.5	6950	1670	395	0.45	31.0	5.0	5.0	12900	1.90	22748
Krafla 15, Iceland	Basalt	265	8.99/19	797	2.0	206	38.3	1.60	0.0049	43.6	198.9	82.8	24.5	1.58	1300
Krafla 20, Iceland	Basalt	280	7.46/20	815	1.7	214	43.7	0.94	0.006	207.8	38.8	53.4	114.3	1.29	1371
Ngawha 9, New Zealand	Sediments	228	7.70/20	559	1250	1193	107	3.50	0.12	167.0	25.0	1.0	1700.0	1.20	4953
Námafjall 12, Iceland	Basalt	250	7.63/26	447	4.9	111.8	16.8	0.40	0.0024	13.2	14.4	110.0	41.5	0.47	646
Nisyros 2, Greece	?	279	4.47/19	718	55	23754	3224	8594	52.5	637	24.6	1.2	56007	1.76	92865
Ohaaki 28, New Zealand	Andesite	274	8.12/20	784	52	910	155	1.3	0.07	191	30.0	—	1414	6.1	3483
Olkaria 25, Kenya	Basalt-trachyte	260	9.15/25	641	5.5	522	94	1.1	0.11	150	28.0	2.12	671	70.0	2135
Reykjanes 8, Iceland	Basalt	248	6.38/20	631	8.7	11150	1720	1705	1.44	63.1	29.3	2.2	22835	0.21	38124
Salton Sea 1, California	Sediments <sup>  </sup>	300	5.2/20	400	390	50400	17500	28000	233	7100	5.4	16	155000	15.0	256784
Tongonan 202, Philippines	Andesite	312	7.08/25	1034	235	6750	1710	211	0.08	67.1	19.0	10.0	12390	—	22395
Wairakei 24, New Zealand	Rhyolite	248	7.70/15	557	26.2	1256	200	26.7	0.02	64.1	34.2	—	2183	6.90	4334
Zunil D-1, Guatemala	Granodiorite	296	8.13/25	896	36.2	866	230	3.73	0.22	29	25.0	2.9	1506	4.63	35880
Geysir, Iceland	Basalt + rhyolite	87	9.41/25	534	1.05	238	22.6	0.77	0.0038	143.3	96.3	2.98	124.3	8.85	1123
Landmannalaugar, Iceland	Rhyolite	96	9.08/26	190	7.69	382	13.6	14.4	0.0087	9.5	16.3	5.59	602.6	10.6	1243
Laugaból, S-Iceland	Basalt	98	9.56/23	279	0.58	120	5.74	1.40	0.0014	38.4	74.0	4.56	40.4	1.98	549
Varmahlid, I Iceland <sup>‡</sup>	Basalt	89	9.47/24	123	0.47	75.1	1.90	1.72	0.0020	31.7	50.7	2.8	27.4	2.20	304
Yellowstone, Wyoming, USA	Rhyolite	93	8.61/120	243	3.98	331	9.45	1.00	0.001	20.7	1.09	324	31.60	965	

(Arnórsson, 2004)



## Environmental Impact of geothermal activity and production

### Gas concentrations in steam from geothermal wells

Location	Sampling pressure (bars)	CO <sub>2</sub>	H <sub>2</sub> S	H <sub>2</sub>	CH <sub>4</sub>	N <sub>2</sub>	O <sub>2</sub>	Ar	Vol% of gas in steam
Cerro Prieto, Mexico	0.0	195.2	18.9	11.5	12.8	1.49	0	0.035	0.432
Krafla 15, Iceland	11.7	250.0	37.5	21.2	0.044	1.88	0.034	0.034	0.560
Nagwha 9, New Zealand	0.0	160.3	1.87	0.5	4.84	0.59	0.003	0.004	0.303
Námafjall 12, Iceland	28.4	142.0	51.4	89.5	0.782	2.47	0.05	0.050	0.516
Nisyros 2, Greece	18.0	306.6	5.27	0.22	1.48	0.28	—	0.030	0.565
Ohaaki 28, New Zealand	0.0	744.4	11.56	1.36	10.92	6.45	0		1.396
Olkaria 25, Kenya	0.0	78.3	5.61	4.33	0.17	2.44	0.006		0.164
Reykjanes 8, Iceland	10.0	103.7	3.13	0.22	0.11	0.65	0		0.194
Tongonan 202, Philippines	0.0	96.9	3.61						0.181
Wairakei 24, New Zealand	0.0	31.1	0.47	0.07	0.03	0.22	0		0.057
Zuni D-1, Guatemala	0.0	157.9	5.78	0.25	0.12	1.51	0		0.298

(Arnórsson, 2004)



## Environmental Impact of geothermal activity and production

### Airborne pollutants - Carbon dioxide (CO<sub>2</sub>)

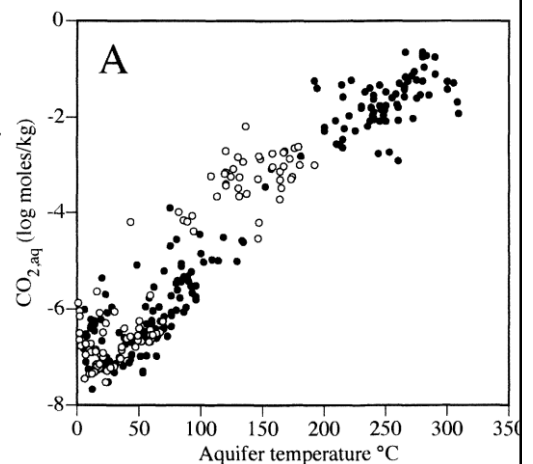
CO<sub>2</sub> concentrations in >100° geothermal reservoir waters are generally controlled by equilibrium with various mineral buffers

Aqueous CO<sub>2</sub> concentrations increase with increasing T

In the range of about 230-300° the mineral buffer in systems hosted by basaltic to silicic volcanics is **clinozoisite + prehnite + quartz + calcite**

The concentration of CO<sub>2</sub> in steam discharged from wet-steam wells is higher than that of the parent fluid, frequently between 50 and 300 mmoles/kg but values as high as 1000 mmoles/kg are not uncommon

(Arnórsson, 2004)



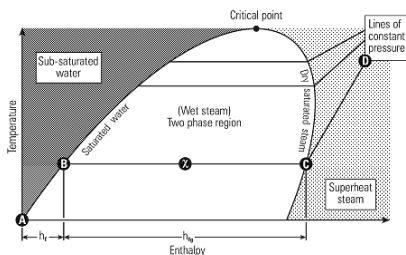


## Environmental Impact of geothermal activity and production

### Airborne pollutants - Carbon dioxide ( $\text{CO}_2$ )

*The concentrations of  $\text{CO}_2$  in steam from wet-steam wells depend on:*

- the  $\text{CO}_2$  concentration in the parent geothermal water
- the steam fraction, which has formed by depressurization boiling
- the reservoir steam fraction (if present)
- the boiling processes that produce the steam



## Environmental Impact of geothermal activity and production

### Airborne pollutants - Carbon dioxide ( $\text{CO}_2$ )

- **The concentration of  $\text{CO}_2$  in steam of well discharges may change with exploitation decline** as a consequence of recharge of cooler water into producing aquifers coupled with insufficient supply of  $\text{CO}_2$  from other sources (magma, the reservoir rock) for maintaining equilibrium with a specific mineral buffer
- **Boiling in producing aquifers**, enhanced by exploitation-induced pressure drawdown, **and separation of water and steam during lateral flow in the aquifer**, with only the water flowing into producing wells, **may also lead to a decrease in the  $\text{CO}_2$  of well discharges**. Such a decrease is accompanied by an increase in the quantity of  $\text{CO}_2$  emitted from fumaroles and/or the formation of a steam cap over the liquid-dominated reservoir
- **Emission of  $\text{CO}_2$  from a geothermal reservoir can be very much enhanced by exploitation** relative to the initial natural emission, at least during the early years of exploitation, when steam caps develop in response to production. The enhanced  $\text{CO}_2$  emission may occur through fumaroles, but also through wells, which produce from the steam cap

(Arnórsson, 2004)







## Environmental Impact of geothermal activity and production

### Airborne pollutants – Methane (CH<sub>4</sub>)

- Concentrations of CH<sub>4</sub> in geothermal fluids are variable
- Sometimes CH<sub>4</sub> aquifer fluid concentration is controlled by attainment of equilibrium for the (slow) reaction  $\text{CH}_4 + 2\text{H}_2\text{O} = \text{CO}_2 + 4\text{H}_2$
- When equilibrium is not attained, the aquifer fluid concentrations of CH<sub>4</sub> are probably governed by the supply of CH<sub>4</sub> to the fluid
- Methane concentrations in geothermal fluids tend to be highest in systems hosted by marine sediments
- The concentrations of CH<sub>4</sub> in geothermal steam are affected by the same parameters as for CO<sub>2</sub>
- Methane is, on a molal basis, 21 times more effective in absorbing infrared radiation than CO<sub>2</sub>

(Arnórsson, 2004)



## Environmental Impact of geothermal activity and production

### Airborne pollutants – Hydrogen sulfide (H<sub>2</sub>S)

- Concentrations of H<sub>2</sub>S in aquifer waters of undisturbed geothermal systems are considered to be controlled by specific mineral buffers
- In high-T waters (230-300°) of low salt content, which have a relatively high pH and are highly reducing:  
pyrite + pyrrhotite + epidote + prehnite
- In waters of higher salinity, which are less reducing than waters of low salt content, the mineral buffer may consist of  
pyrite + magnetite + epidote + prehnite



(Arnórsson, 2004)

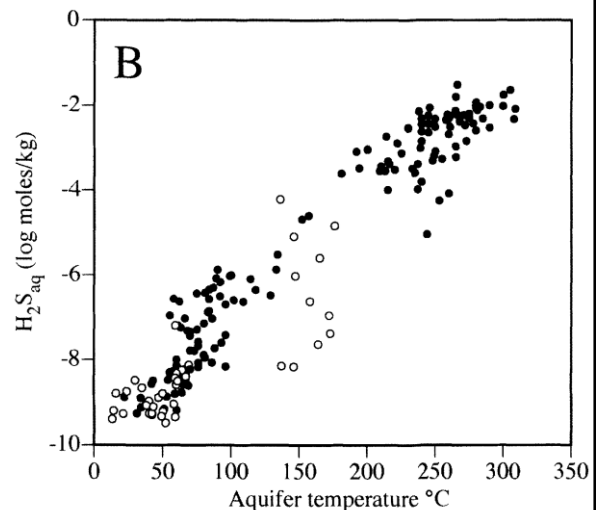




## Environmental Impact of geothermal activity and production

### Airborne pollutants – Hydrogen sulfide ( $H_2S$ )

- $H_2S$  concentrations in geothermal aquifer waters vary with T
- The scatter of the data points at each T (at least when  $T > 200^\circ$ ) may be due to operation of different mineral buffers or variation in the composition of one or more of the minerals constituting these buffers, in particular the epidote



(Arnórsson, 2004)



## Environmental Impact of geothermal activity and production

### Airborne pollutants – Hydrogen sulfide ( $H_2S$ )



- $H_2S$  in steam discharged from wet-steam wells of high-T geothermal systems typically lie in the range of 2-20 mmol/kg, but they may be as high as 50 mmol/kg
- In a particular area,  $H_2S$  in steam discharged from fumaroles is generally lower than in steam from wells
- $H_2S$  in the atmosphere has negative effects on vegetation
- a risk for public health ( $>0.3$  ppm  $H_2S$  in the air) depend on weather conditions and distance from the powerplant
- The  $H_2S$  in the steam may be removed/reduced either upstream or downstream from the turbine
- methods include (1) scrubbing with alkali, (2) use of steam re-boilers, and (3) compression and use of chlorine- and bromine-stabilized biological oxidizing agents as a catalyst to oxidize  $H_2S$  to  $H_2SO_4$

(Arnórsson, 2004)





## Environmental Impact of geothermal activity and production

### Airborne pollutants – arsenic (As), boron (B) and mercury (Hg)

- As, B, and Hg are typically enriched in geothermal fluids, as compared to surface- and groundwaters
- Hg is quite fugitive and partitions significantly into the steam phase at low T
- Owing to the high concentrations of As, B, and Hg in geothermal fluids, hot spring and fumarole discharges contaminate stream and river waters, accumulate in vegetation and fish
- Elevated concentrations of As, B, and Hg have been reported around geothermal power plants, both in the atmosphere and in vegetation



(Arnórsson, 2004)

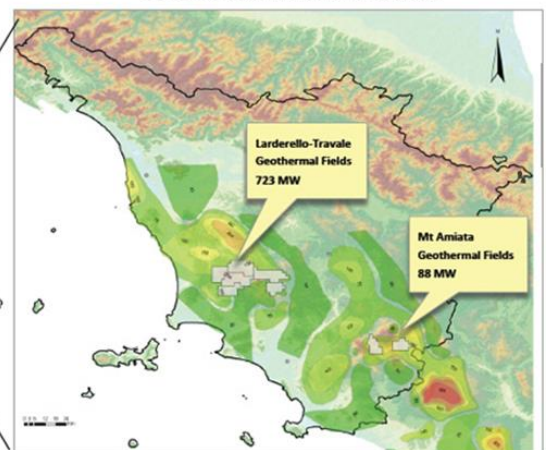


## Environmental Impact of geothermal activity and production – Monte Amiata, Italy

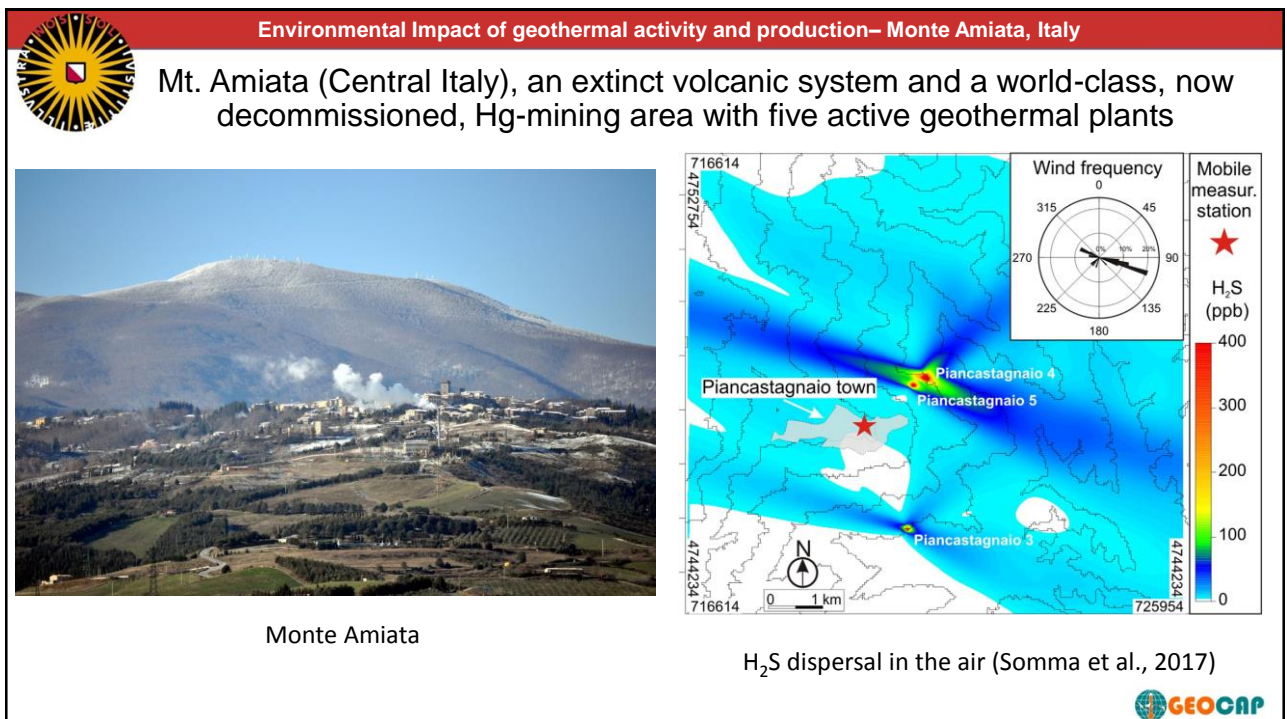
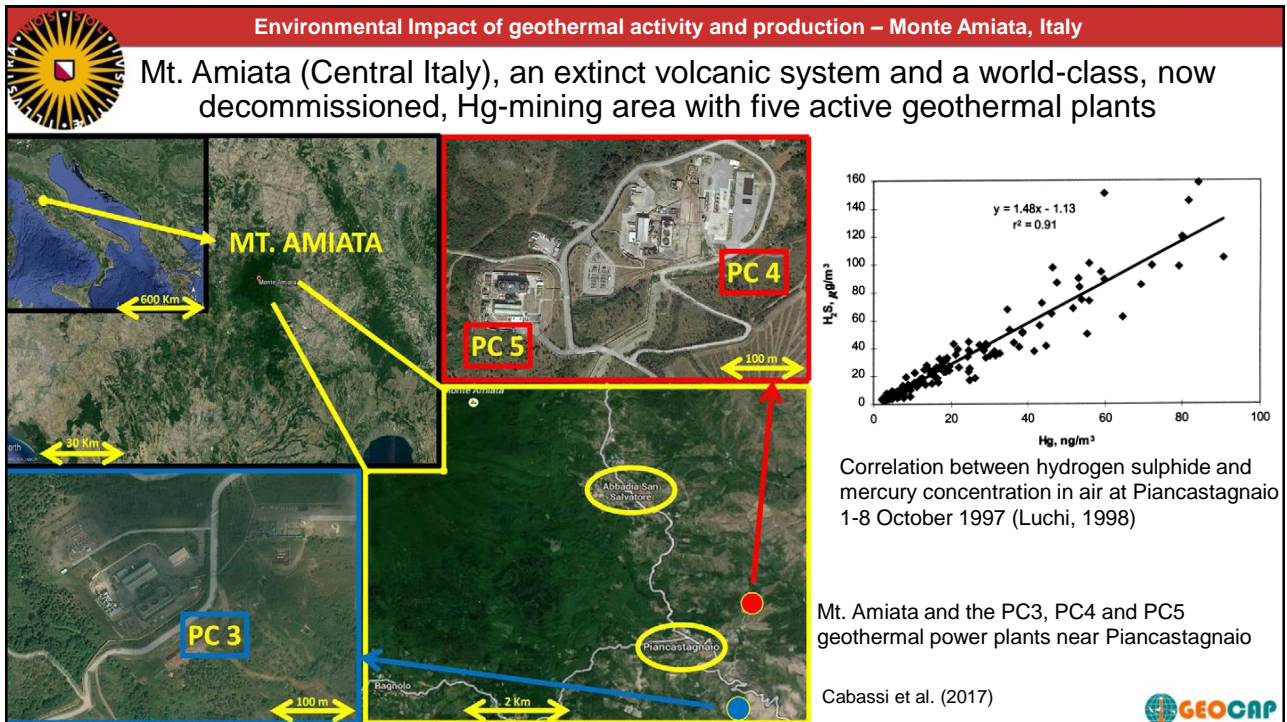
Mt. Amiata (Central Italy), an extinct volcanic system and a world-class, now decommissioned, Hg-mining area with five active geothermal plants

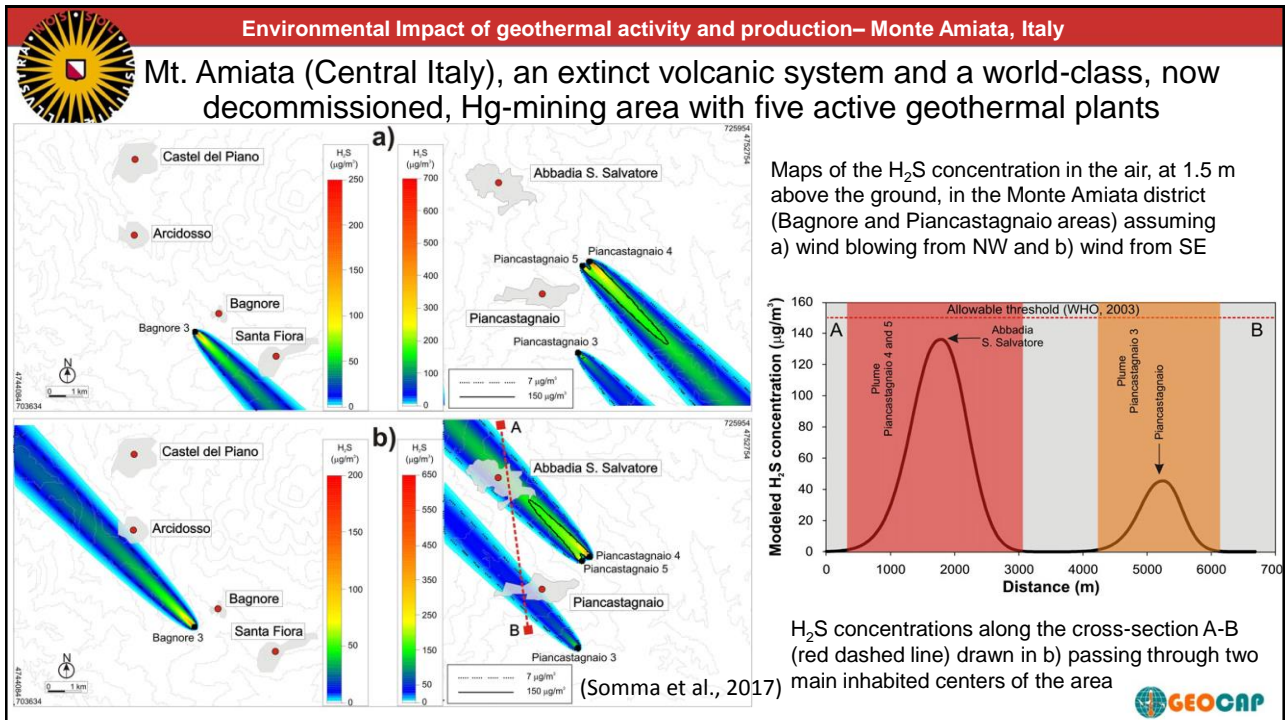


Geothermal areas in Tuscany in January 2010









**Environmental Impact of geothermal activity and production**

Waterborne pollutants – As, B and  $\text{H}_2\text{S}$

- Other elements that may be present in harmful concentrations include Al, F, ammonia ( $\text{NH}_3$ ), and various heavy metals
- Geothermal fluids may exhibit a very high salt content
- High concentrations of heavy metals are associated with high-T brines
- High B and As concentrations are found in many geothermal systems associated with andesitic volcanism
- Boron-rich geothermal waters are known to form upon reaction with marine sediments
- The source of the B is the illite of the marine sediments
- Waters of geothermal systems hosted by basaltic rock are low in B and As, and heavy metals, but relatively high in both  $\text{H}_2\text{S}$  and Al

(Arnórsson, 2004)

GEOCAP



## Environmental Impact of geothermal activity and production

### Waterborne pollutants - Boron and arsenic

- Geothermal waters of high-T systems in andesitic and silicic volcanics at converging plate boundaries:
  - As normally 1-10 ppm, but up to 50 ppm
  - B typically 10-50 ppm, but up to 1000 ppm
- high-T fluids hosted in basaltic rocks on the diverging plate boundary in Iceland are much lower in As and B
- The concentrations of As and B in geothermal fluids are positively related to their concentrations in the enclosing rocks. their primary minerals are the source of these elements

(Arnórsson, 2004)



## Environmental Impact of geothermal activity and production

### Waterborne pollutants – Boron is bad for crops

- High concentrations of B in soil water may be harmful for certain crops. The most sensitive crops can tolerate no more than 0.5-1.0 ppm B
- Boron concentrations in geothermal waters are not expected to exceed acceptable limits for stock watering and aquatic life
- Surface disposal of well water rich in B creates an environmental problem
- Possible solutions (1) injection of the waste water back into the geothermal reservoir, (2) removal of the B from the water using ion-exchange

(Arnórsson, 2004)



Boron (B) toxicity inhibits the formation of starch from sugars and affects the formation of B-carbohydrate complexes

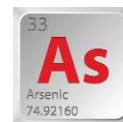




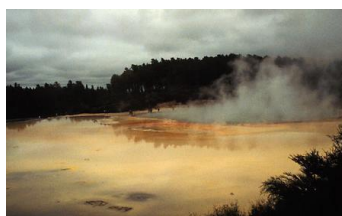


## Environmental Impact of geothermal activity and production

### Waterborne pollutants – Poisonous As



- Arsenic is one of the most carcinogenic and toxic substances in surface- and groundwaters
- The maximum allowable As concentration in drinking water is 0.05 ppm, and 0.01 ppm for aquaculture
- Concentrations in geothermal waters may be as high as 50 ppm
- $\text{As}^{3+}$  is harmful, whereas  $\text{As}^{5+}$  is not. In geothermal waters, As is largely  $3+$ , but upon contact with the air, it is relatively rapidly oxidized to  $\text{As}^{5+}$  (Arnórsson, 2004)



Champagne Pool in the Waiotapu geothermal area. Precipitation of arsenic sulphides rich in trace metals (Leeds Univ.)



## Environmental Impact of geothermal activity and production

### Waterborne pollutants – Hydrogen sulphide

#### *Total sulphide-S concentrations (as $\text{H}_2\text{S}$ )*

- <5 ppm in boiled, relatively saline high-T waters (>1000 ppm Cl)
- 100 ppm in high-T waters of low salt content hosted by basaltic rocks
- < 2 ppm in low-T waters
- the  $\text{H}_2\text{S}$  species is poisonous, not total sulphide-S

#### *pH determines the fraction of $\text{H}_2\text{S}$ in total sulphide-S:*

- at pH = 7,  $\text{H}_2\text{S}$  accounts for about 50% of the total sulphide-S
- In dilute high-T waters, which build up a high pH (>9) by boiling, practically all the sulphide-S is present as  $\text{HS}^-$

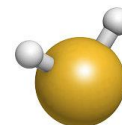
(Arnórsson, 2004)



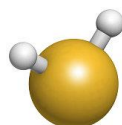


## Environmental Impact of geothermal activity and production

### Waterborne pollutants – Hydrogen sulphide



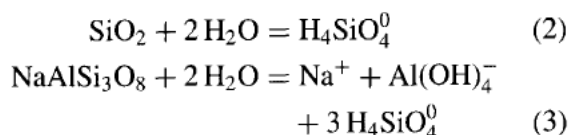
- If high-pH, sulphide-rich geothermal water mixes with surface or groundwater so that the pH of the mixed water is significantly lowered, the H<sub>2</sub>S concentration of the mixed water may exceed 1 ppm depending on the dilution effect
- Such concentrations (or even lower) are toxic to many types of fish within a period of 24 hours
- Hence, H<sub>2</sub>S-bearing water from geothermal power plants, whether separated water or condensate, may have harmful effects on aquatic life and water quality if disposed of on the surface, where it can seep into the soil and mix with surface- and shallow groundwater (Arnórsson, 2004)



## Environmental Impact of geothermal activity and production

### Waterborne pollutants – Aluminium

- In geothermal waters, which have equilibrated with low-albite (NaAlSi<sub>3</sub>O<sub>8</sub>) and quartz (SiO<sub>2</sub>) or chalcedony, Al concentrations decrease at any specific temperature with increasing Na concentrations, that is, increasing water salinity
- Geothermal reservoir waters generally closely approach equilibrium with low-albite when T is above about 100°. Equilibrium with chalcedony is attained for waters with temperatures below 180° but with quartz at higher temperatures



- With increasing T, at a particular salinity (Na concentration), Al aqueous concentrations increase because low-albite solubility increases much more with rising temperature than quartz solubility
- High-T waters with low salinity and low Na (<200ppm) may contain as much as 2-3 ppm Al. By EU standards, recommended Al concentration in domestic waters is 0.05 ppm, and the permissible limit is 0.2 ppm. For aquaculture it is less. Thus, the Al content of high-T geothermal waters may far exceed the permissible limit (Arnórsson, 2004)
- Low-T waters of low salt content may also exceed the permissible limit, if pH > 9





## Environmental Impact of geothermal activity and production

### Waterborne pollutants – Fluoride



- Fluoride concentrations in geothermal waters hosted by silicic volcanics are controlled by fluorite solubility.
- In geothermal waters in basalt, ion-exchange equilibria involving OH<sup>-</sup> and F<sup>-</sup> and an OH-bearing silicate mineral probably control the aqueous activity of F
- Fluoride concentrations of 10-20ppm are common in waters in silicic volcanics
- F concentrations in geothermal waters typically lie in the range of 0.5 to 2 ppm depending on T and salt content of the water
- Aqueous F concentrations in silicic rock environments far exceed the permissible limits for water for domestic use of 1.5 ppm by EU standards
- Adverse effects of F-bearing water include damage on dental enamel (dental fluorosis). It may also cause skeletal damage in humans or cattle

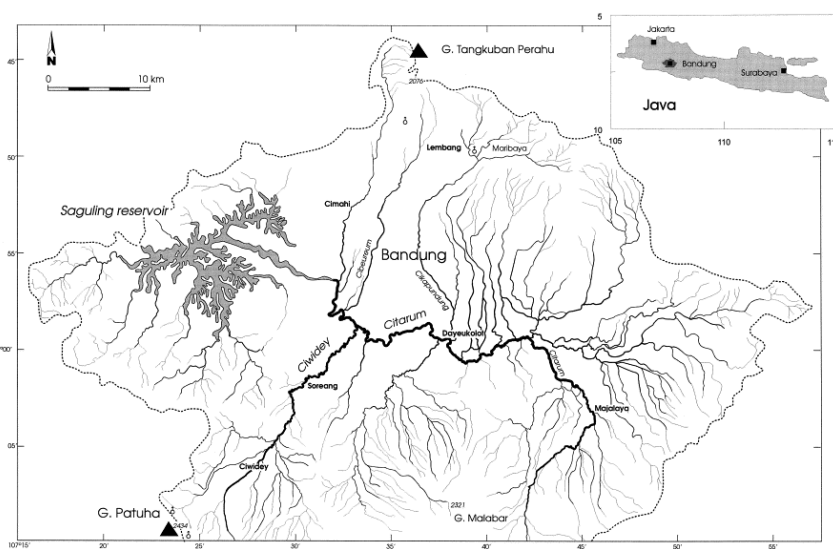
(Arnórsson, 2004)



## Environmental Impact of geothermal activity and production: Patuha - Ciwidey

### Upper Citarum River basin: anthropogenic and natural (hydrothermal) sources of pollution

Ciwidey River and several northern tributaries are influenced by natural contaminants originating at the Patuha and Tangkuban Perahu volcanoes and associated hydrothermal areas



The quality of the Citarum River water is affected by effluent from industrial and domestic sources which contributes to pollution of the Saguling reservoir

(Sriwana et al., 1998)







## Environmental Impact of geothermal activity and production: Patuha - Ciwidey

### Patuha area: acid, power and pollution

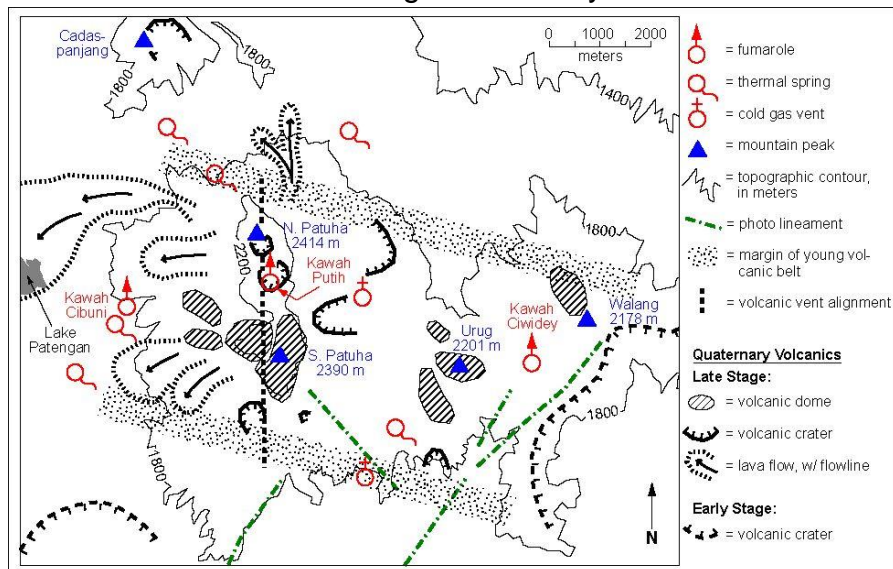


GEOCAP



## Environmental Impact of geothermal activity and production: Patuha - Ciwidey

### Patuha geothermal system



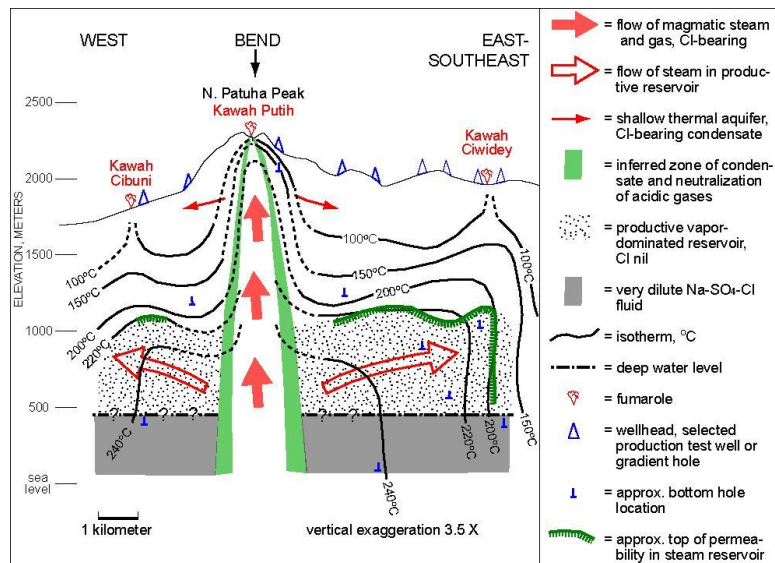
(Layman and Soemarinda, 2003)

GEOCAP



## Environmental Impact of geothermal activity and production: Patuha - Ciwidey

### Patuha geothermal system



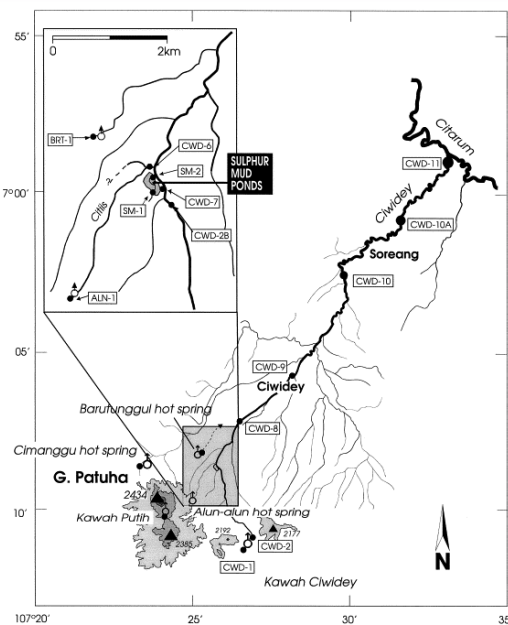
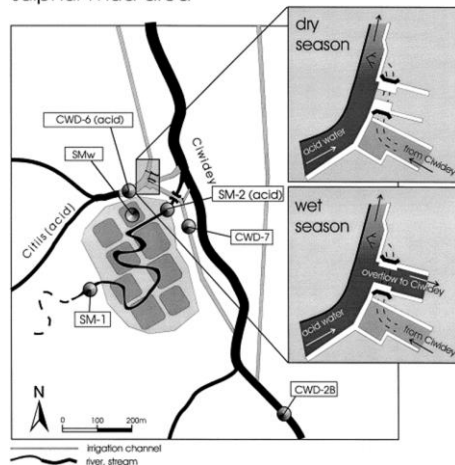
(Layman and Soemarinda, 2003)



## Environmental Impact of geothermal activity and production: Patuha - Ciwidey

### Polluting sources: natural acid streamwater and ancient sulphur mud disposal site

sulphur mud area



(Sriwana et al., 1998)





## Environmental Impact of geothermal activity and production: Patuha - Ciwidey

### Variation of pH and concentr. of dissolved elements along the Ciwidey River

Ciwidey River is contaminated by potentially harmful elements originating from sources that have been enriched by natural processes within the Patuha volcanic system

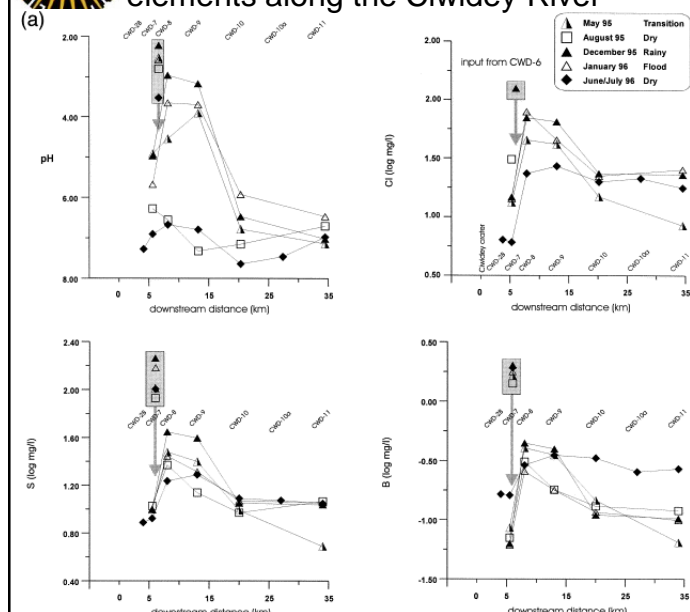
Discharges from two acid streams cause decreases of pH and increases of dissolved major elements and trace metals

One of the streams originates at a flank spring which may have a subsurface connection with highly acid sulphur and chlorine-rich water produced in an active crater lake near the summit of the volcano

The other stream is acidified by interaction with man-made deposits of sulphur-rich lake sediments brought down from the crater during exploitation activities in the past

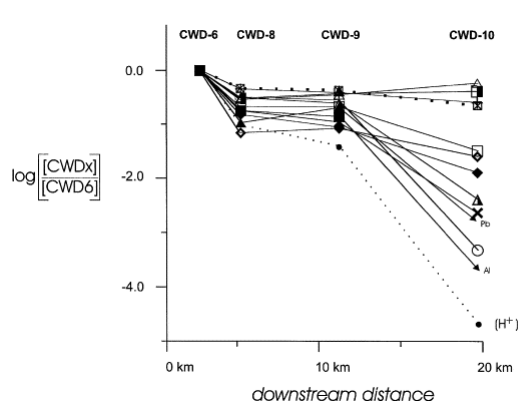
There is a strong seasonal influence on downstream discharge of pollutants

(Sriwana et al., 1998)



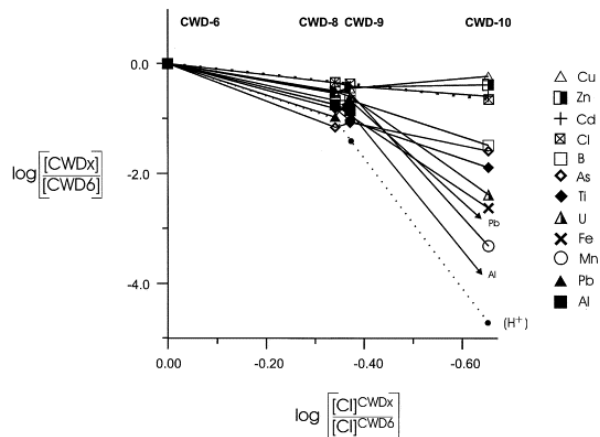
## Environmental Impact of geothermal activity and production: Patuha - Ciwidey

### Behaviour of dissolved elements along the Ciwidey River



Attenuation of chlorine (heavy dots) and trace metal concentrations

(Sriwana et al., 1998)



Attenuation through dilution and sorption onto solids







Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

Environmental impact from a volcanic lake

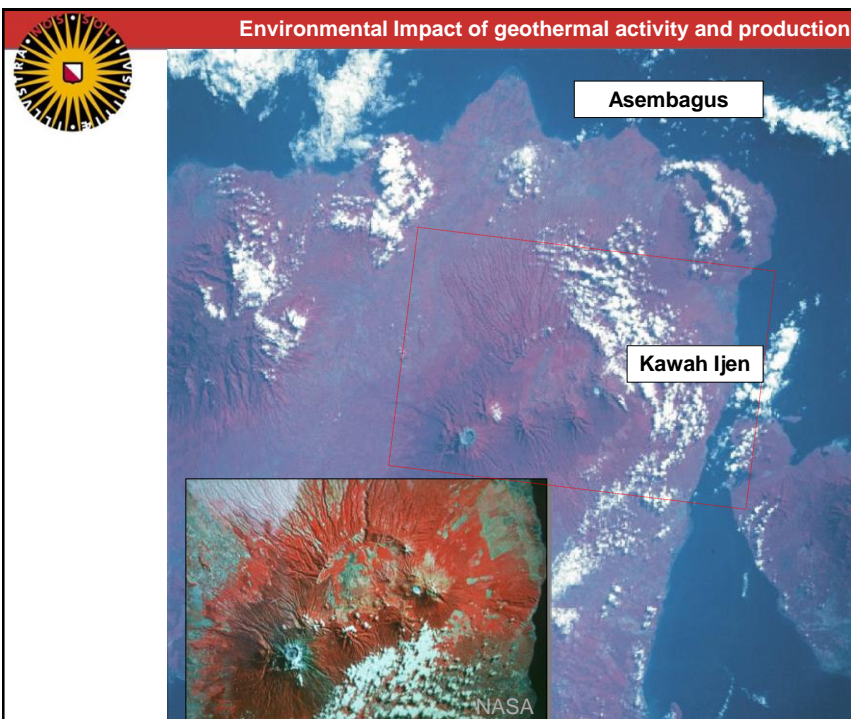




- Background
- Following the stream of chemicals
- Impact on agriculture
- Impact on health

GEOCAP

Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus



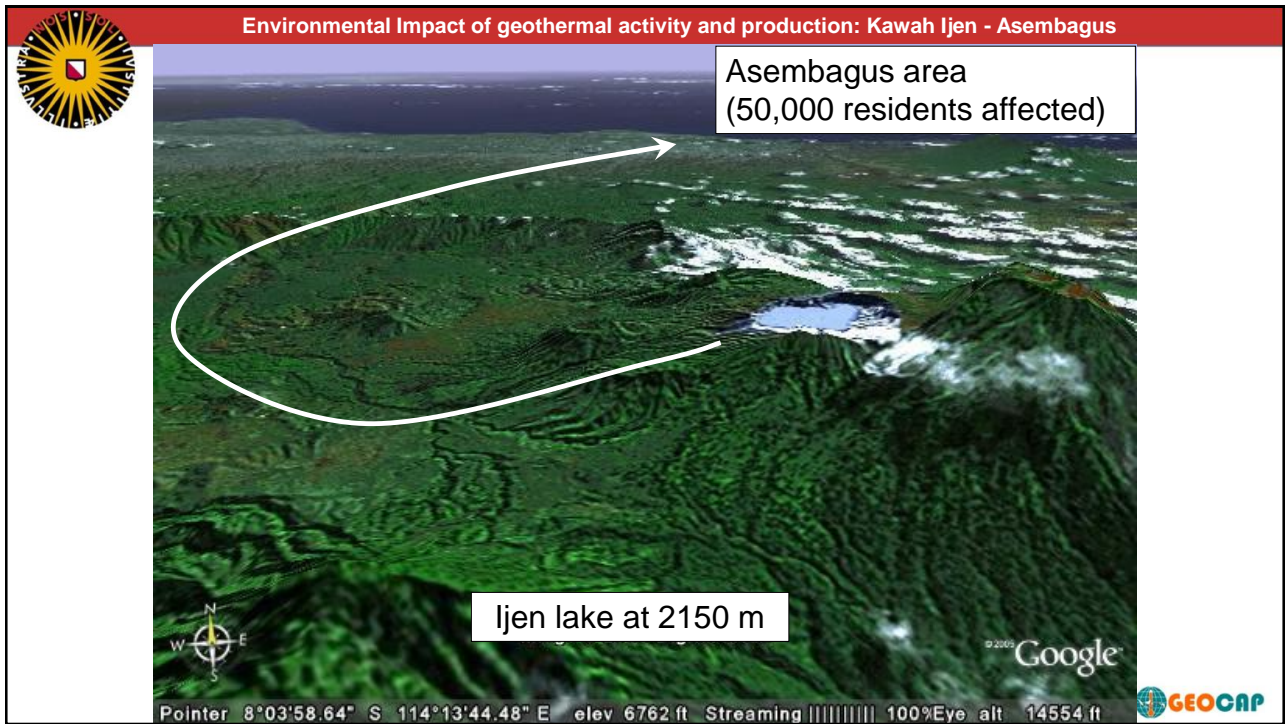
Asembagus coastal plain

Ijen caldera  
Diameter: ~16 km

NASA

GEOCAP







Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

Volcanic gas produces sulfur

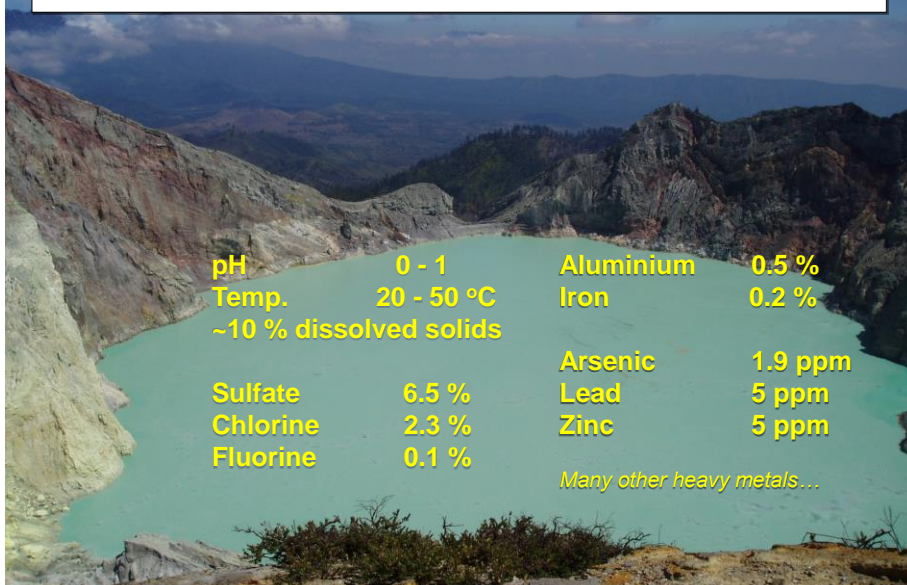
Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

Gas also enters  
at the bottom  
confirmed by echo  
sounding  
(Takano et al., 2000)  
and makes the  
lake acid



# Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

One of the chemically most extreme environments in the World !



pH 0 - 1  
Temp. 20 - 50 °C  
~10 % dissolved solids

Sulfate 6.5 %  
Chlorine 2.3 %  
Fluorine 0.1 %

Aluminium 0.5 %  
Iron 0.2 %

Arsenic 1.9 ppm  
Lead 5 ppm  
Zinc 5 ppm

*Many other heavy metals...*



# Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

Dam with sluice regulates water outflow



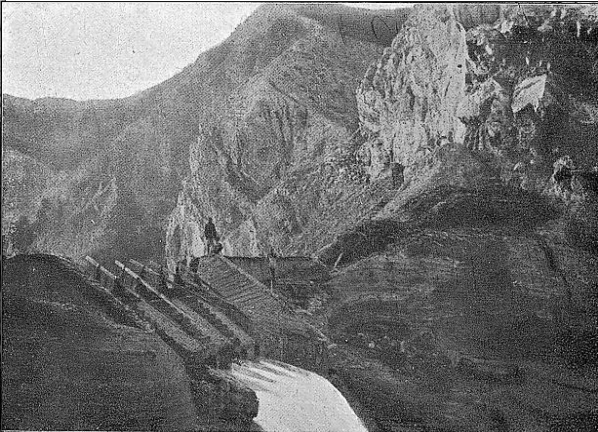
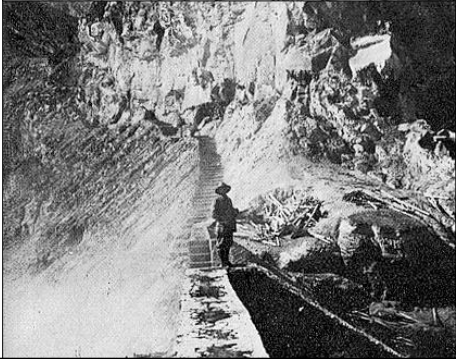




Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus



Opening the sluice  
19 March 1922



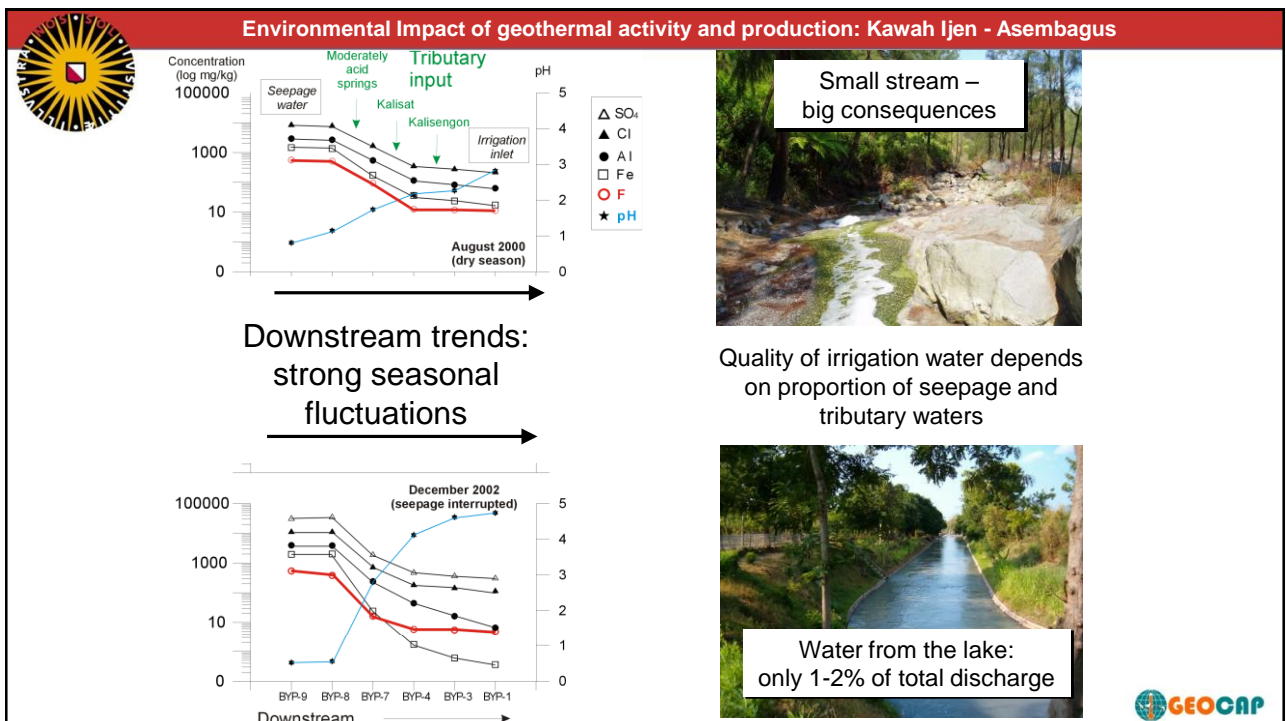
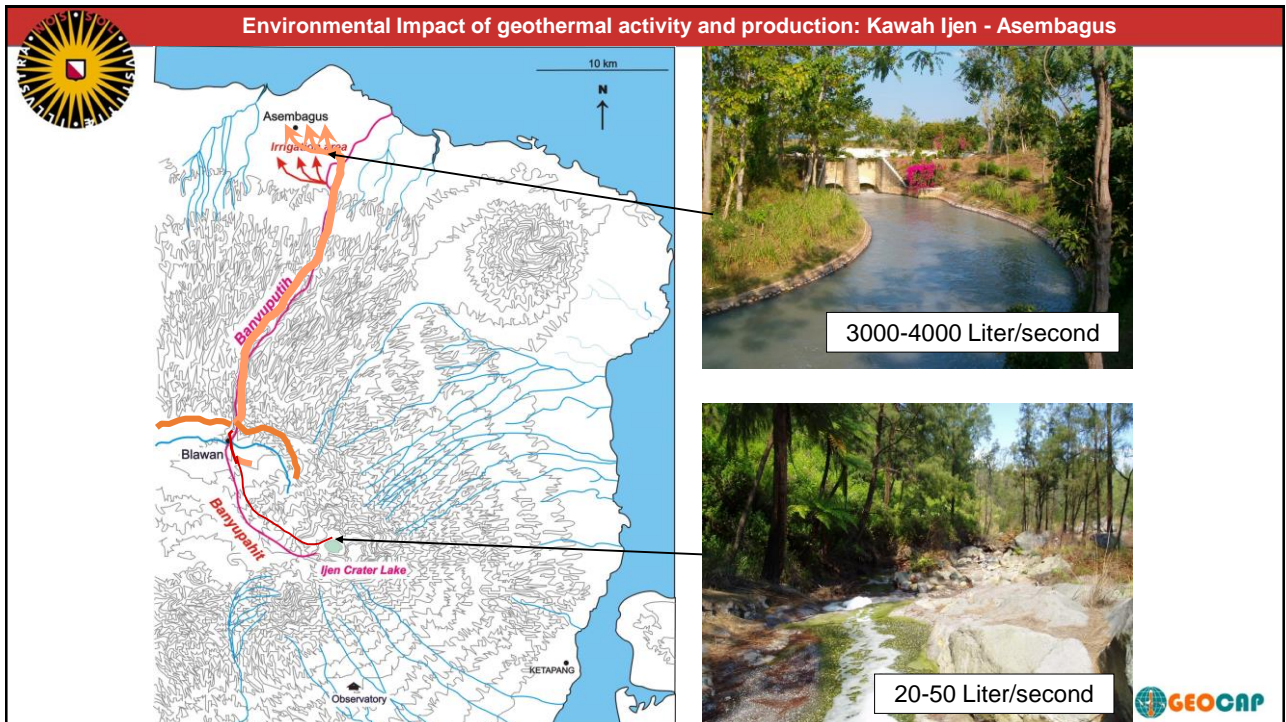
Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus



But the lake still loses water...







# Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

A continuous stream of harmful elements...

	ton/day
Sulfate	219
Chlorine	85
Aluminium	24
Fluorine	5
	kg/day
Zinc	26
Lead	11
Arsenic	7.3
Copper	6

# Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

Irrigation inlet - Lewung

All river water is used during the dry season  
3564 ha irrigation area





# Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

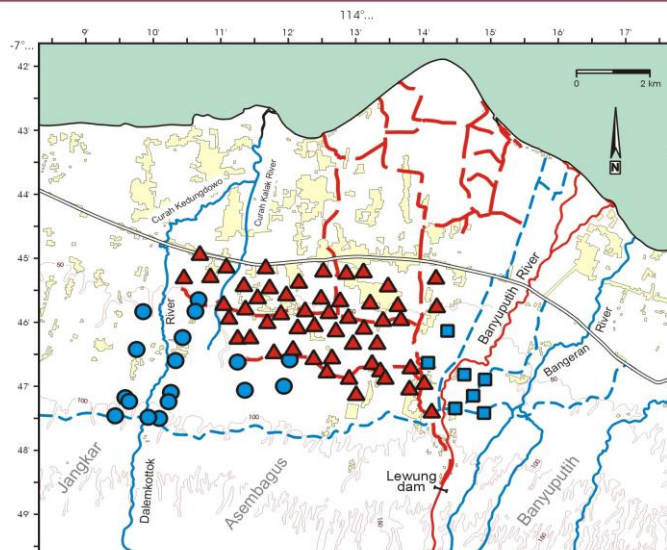
Quality guidelines for irrigation water are exceeded

	Banyuputih river (irrigation inlet)	Canadian guideline
Date	Juni-00	
pH	2.7	
Sulfate	732	100
Chloride	243	100
Fluoride	14.5	1
Aluminium	76	5
Boron	0.9	0.1
Iron	25.5	5
Manganese	1.2	0.2

Concentrations are  
2.5 – 15 times too high



# Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus



Sampling locations:

- ▲ acid
- neutral east
- neutral west
- acid river
- - - acid channel
- neutral river
- - - neutral channel
- village
- - - subdistrict boundary
- - - elevation contour (m)

Near the irrigation  
channels:

Top soils are very acid

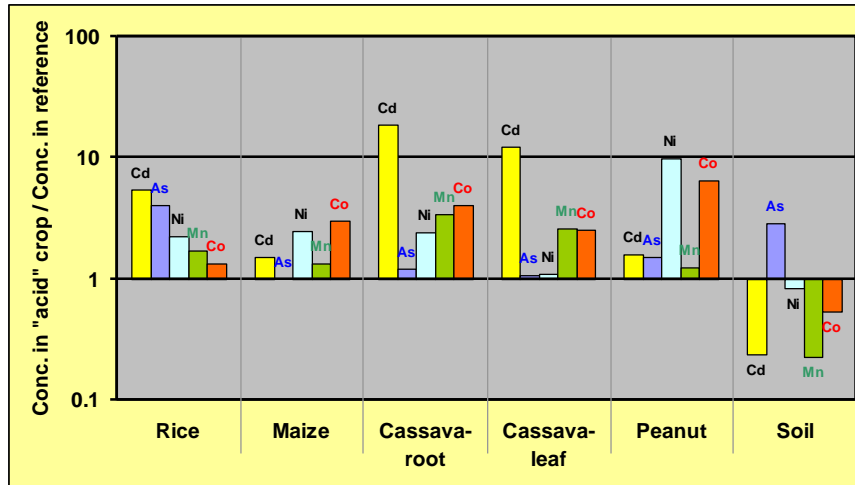






# Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

Higher metal concentrations in crops  
where irrigation water is acid



Heikens et al., 2005b



# Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

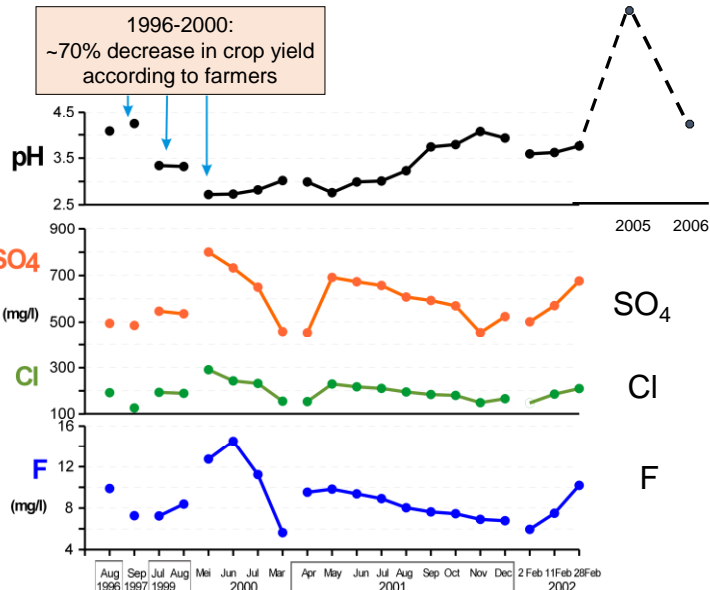
Sometimes crops don't grow when water is too acid...





# Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

Irrigation water quality is not constant !



## Possible explanations:

- Lake water more acid ~~XXXX~~
- More water from the lake ~~XXXX~~
- Less water from tributaries
- Change in rainfall



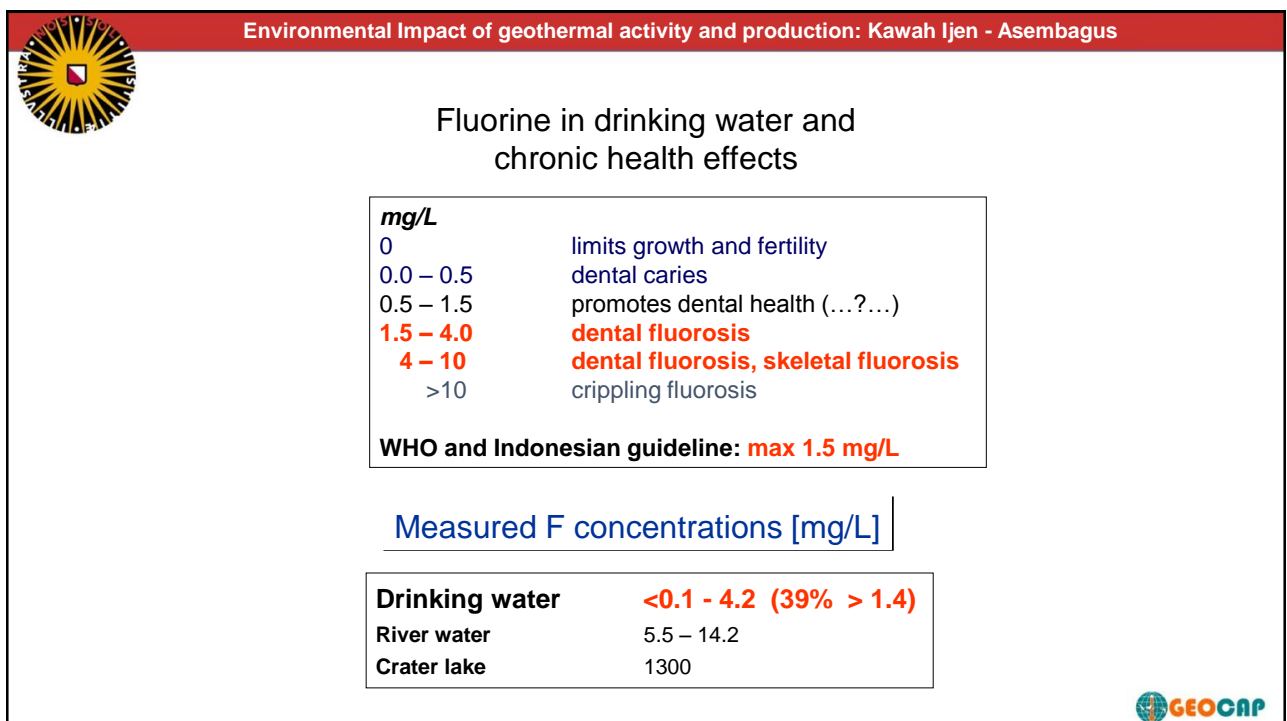
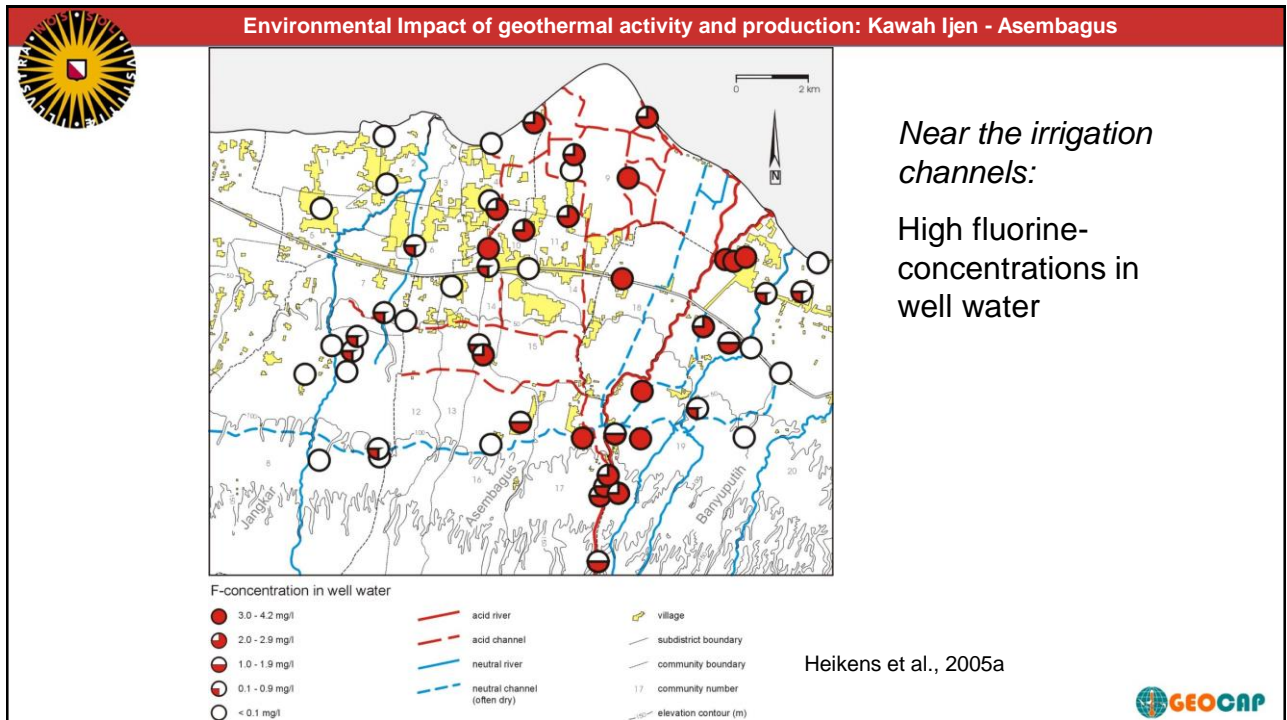
# Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

Inferior drinking water quality in irrigation area



WHO guidelines are exceeded for **fluorine**, boron, sulfate and chlorine in many wells

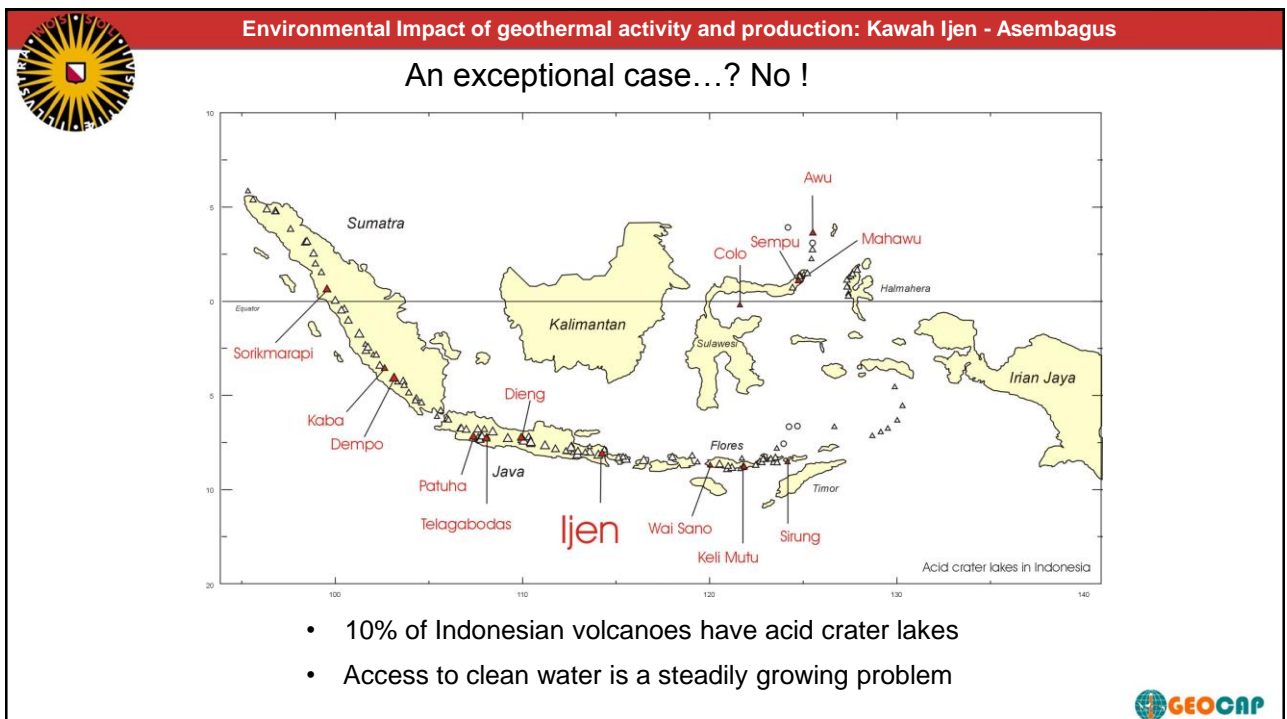
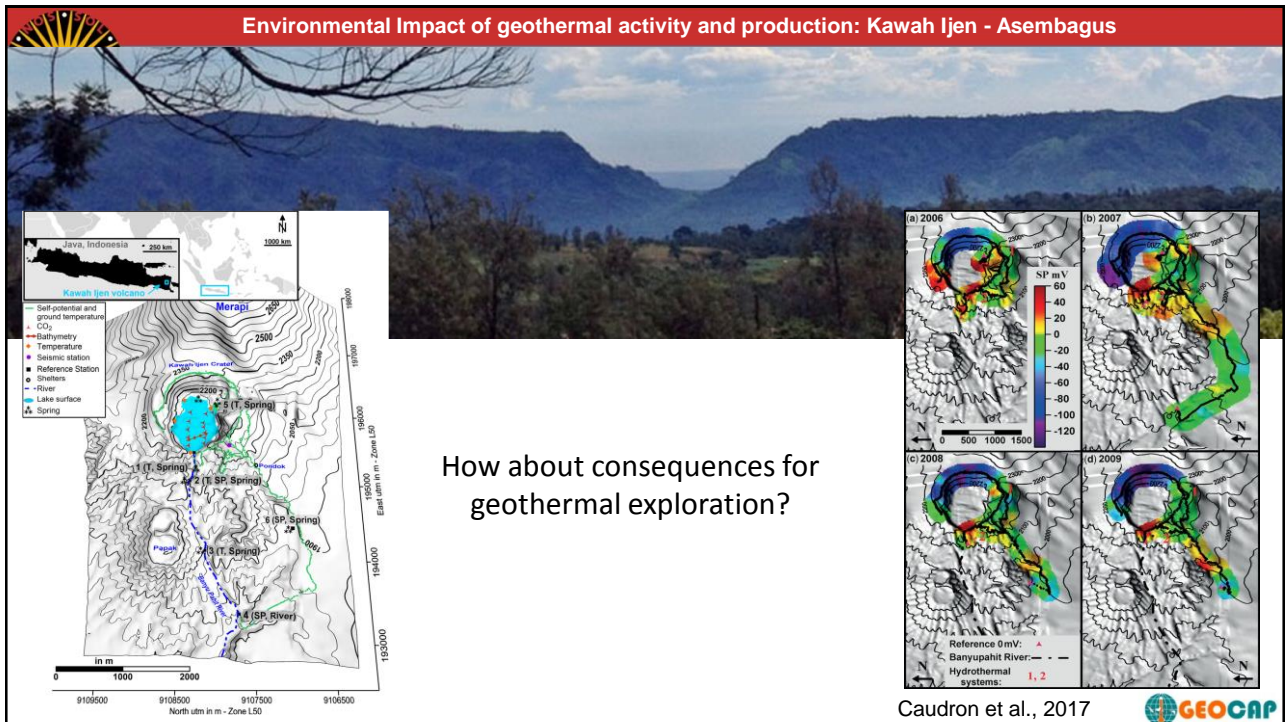






## A photograph of two young boys. The boy on the left is looking towards the camera with a slight smile, showing some yellowish-brown staining on his upper front teeth. The boy on the right is looking slightly away from the camera, also showing significant yellowish-brown staining on his upper front teeth. A hand is visible at the top, holding a small, round, brown object, possibly a piece of food or a small toy. The background is blurred, showing some green fabric. A white text box with a black border is at the bottom right, containing the text: "Dental fluorosis is widespread !".

[illegible]





## Environmental Impact of geothermal activity and production: Kawah Ijen - Asembagus

### Examples of solutions and actions

#### 1. Technical solutions

- Drinking water
- Irrigation water

#### 2. Monitoring program and early warning

- Water quality
- Lahar
- Lake activity

#### 3. Public awareness

#### 4. Permanent communication between stakeholders

- Water management
- Land use
- Environmental protection

#### 5. Further research needed



### Literature sources

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- Somma, R. and others, 2017. Modelling of hydrogen sulfide dispersion from the geothermal power plants of Tuscany (Italy), *Science of the Total Environment*, 583: 408–420
- Sriwana, T. and others, Volcanogenic pollution by acid water discharges along Ciwidey River, West Java Indonesia. *Journal of Geochemical Exploration*. 62: 161–182





## **10 Case Study: The Karaha-Telaga Bodas Geothermal Field**

Manfred van Bergen  
(Utrecht University)

**GEOCHEMISTRY FOR GEOTHERMAL DEVELOPMENT**  
**UGM – UU – Geocap Capacity Building Program**  
**21 - 25 August, 2017**



**10. CASE STUDY: THE KARAHA -TELAGA BODAS GEOTHERMAL FIELD**

Manfred van Bergen  
 Utrecht University



**Case study: The Karaha -Telaga Bodas geothermal field**



**Geothermal fields in West Java**

**Vapor-dominated geothermal systems:**

Kamojang  
 Darajat  
 Wayang Windu  
 Patuha

**Kahara-Telaga Bodas (KTB)**

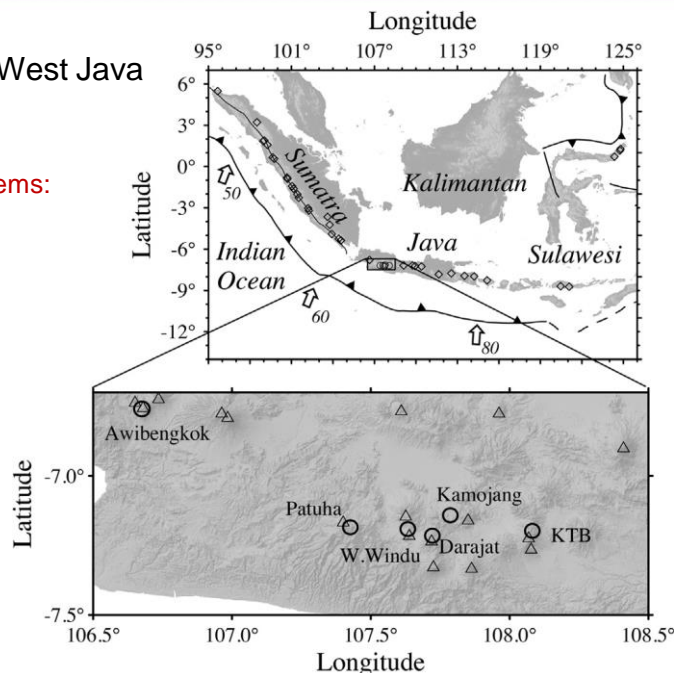
**Liquid-dominated system:**

Awibengkok

**Triangles:**

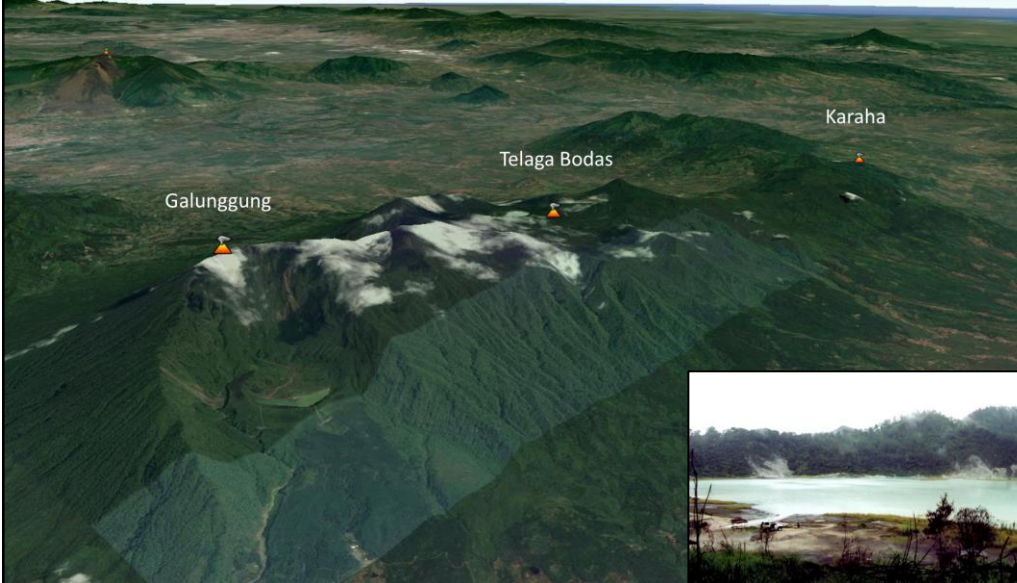
volcanoes with recent activity

Raharjo et al. (2016)



Case study: The Karaha -Telaga Bodas geothermal field

The Karaha–Telaga Bodas area




Galunggung

Telaga Bodas

Karaha

Large eruption of Galunggung in 1982  
More than 40,000 people evacuated.


Warm acid lake, fumaroles, mud pools and warm springs of Telaga Bodas



Case study: The Karaha -Telaga Bodas geothermal field

Contents

- Surface manifestations
- Well data: temperatures, stratigraphy, mineral distributions
- Fluid compositions – springs, lake, gas
- Resistivity imaging – liquid, vapor, clay
- Modeling mineral stabilities, water-rock interactions, liquid properties
- Rock alteration sequence
- Fluid inclusions
- Conceptual model for the evolution of the geothermal system







### Case study: The Karaha -Telaga Bodas geothermal field

#### Telaga Bodas surface manifestations



### Case study: The Karaha -Telaga Bodas geothermal field

#### Telaga Bodas surface manifestations





# Case study: The Karaha -Telaga Bodas geothermal field

## Karaha area surface manifestations



# Case study: The Karaha -Telaga Bodas geothermal field

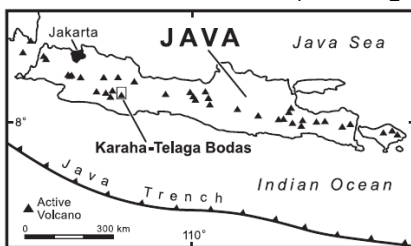
Distribution of volcanic features,  
thermal manifestations and  
geothermal wells

Kawah Galunggung is the main vent  
of Galunggung Volcano

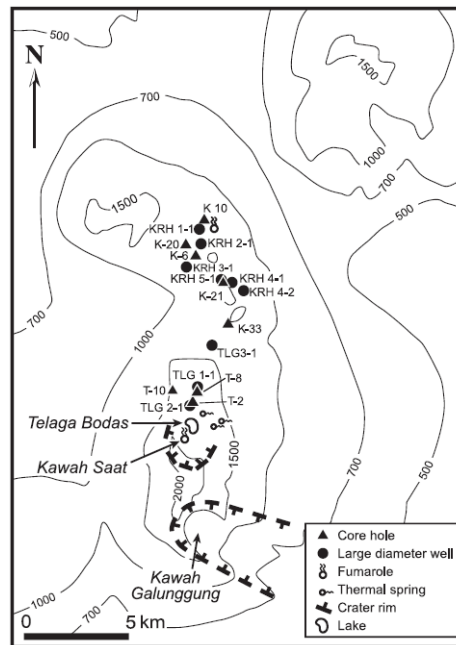
Telaga Bodas is an acid lake

Acid  $\text{Cl-SO}_4$  springs discharge down  
slope of Telaga Bodas

Springs at Kawah Karaha discharge  
acid  $\text{SO}_4$  or  $\text{CO}_2$ -rich waters



Moore et al. (2008)







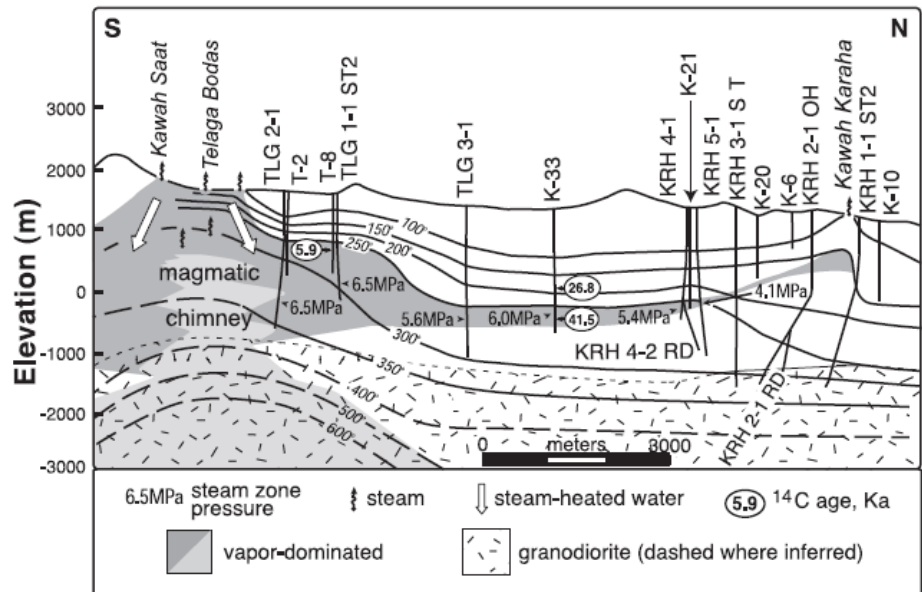
### Case study: The Karaha -Telaga Bodas geothermal field

Conceptual model of the geothermal system along the ridge axis

Geometry of the steam and liquid zones based on flow tests and downhole measured pressures

Temperatures are shown as solid lines where measured and dashed where inferred

Depth and geometry of the granodiorite in the south from hydrothermal minerals and gravity data



Moore et al. (2008)



### Case study: The Karaha -Telaga Bodas geothermal field

#### Principal well facts

Well*	Total Depth (m)	True Vertical Depth (m)	Elevation Kelly Bushing (m)+	Elevation Total Depth (m)	Maximum T(°C)
K-6	614	614	1332	718	126
K-10	1311	1311	1193	-118	146
K-20	1018	1018	1289	271	180
K-21	1654	1654	1416	-238	259
K-33	2018	2018	1383	-635	256
KRH 1-1 ST2	3041	2829	1267	-1562	316
KRH 2-1 OH	3064	2842	1342	-1500	272
KRH 2-1 RD	2763	2649	1342	-1307	304
KRH 3-1 ST	3077	2970	1409	-1561	334
KRH 4-1	1849	1812	1387	-425	263
KRH 4-2 RD	2418	2316	1387	-930	249
KRH 5-1	2444	2436	1410	-1026	279
T-2	1383	1383	1670	288	321
T-8	1326	1326	1630	304	288
T-10	1586	1586	1460	-127	263
TLG 1-1 ST2	1782	1742	1629	-113	288
TLG 2-1	2588	2282	1677	-605	353
TLG 3-1	2480	2478	1435	-1043	296

\*OH = original hole; RD = redrill; ST = side track. +Elevations are in meters with respect to sea level. The data were provided by Karaha Bodas Co. LLC.

Moore et al. (2008)







### Case study: The Karaha -Telaga Bodas geothermal field

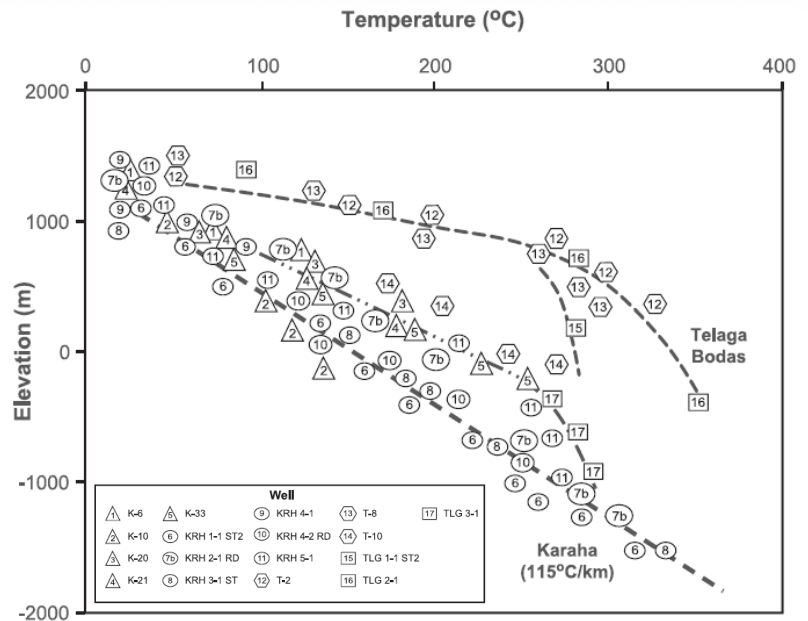
Composite graph of the temperature data with respect to elevation

The data define three trends:

**southern** (Telaga Bodas)

**intermediate** (largely central parts of Karaha –Telaga Bodas system)

**northern** (Karahah)

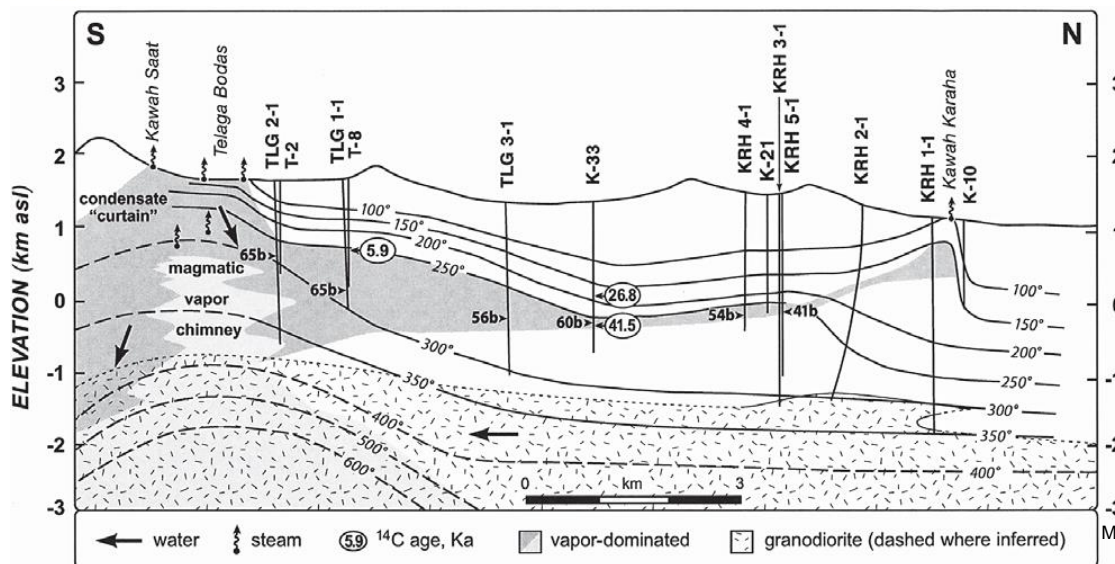


Moore et al. (2008)



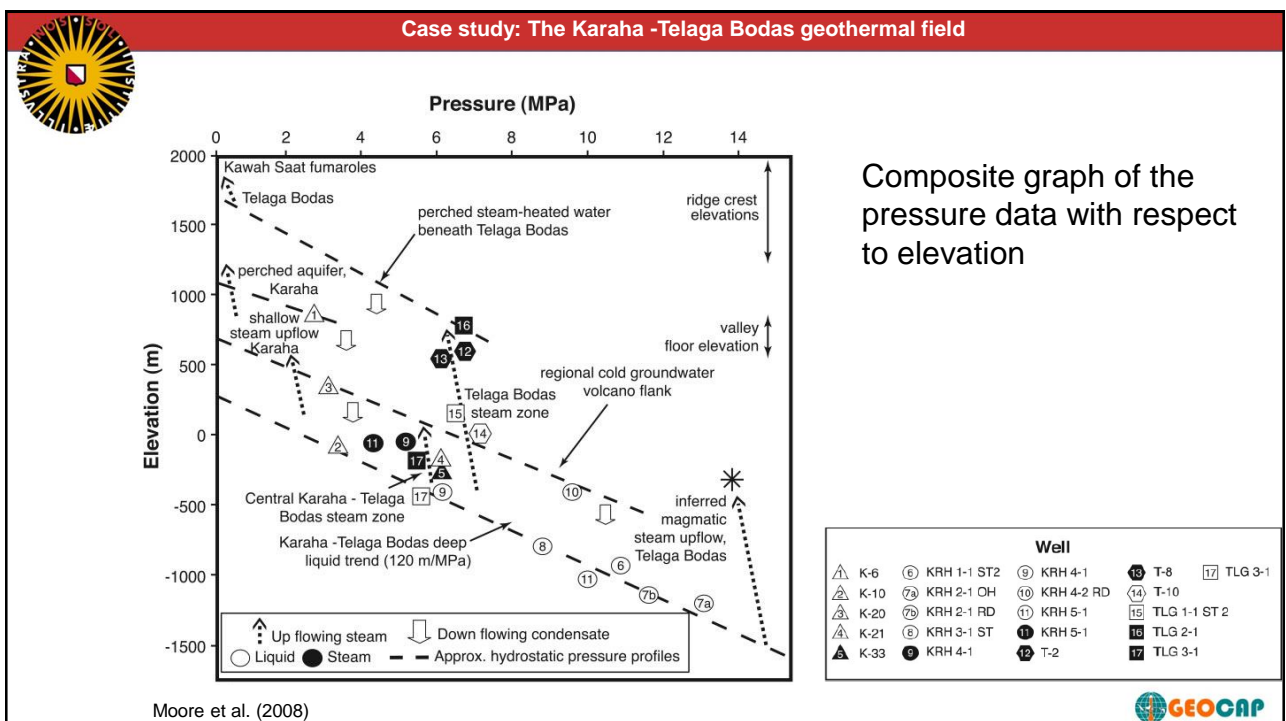
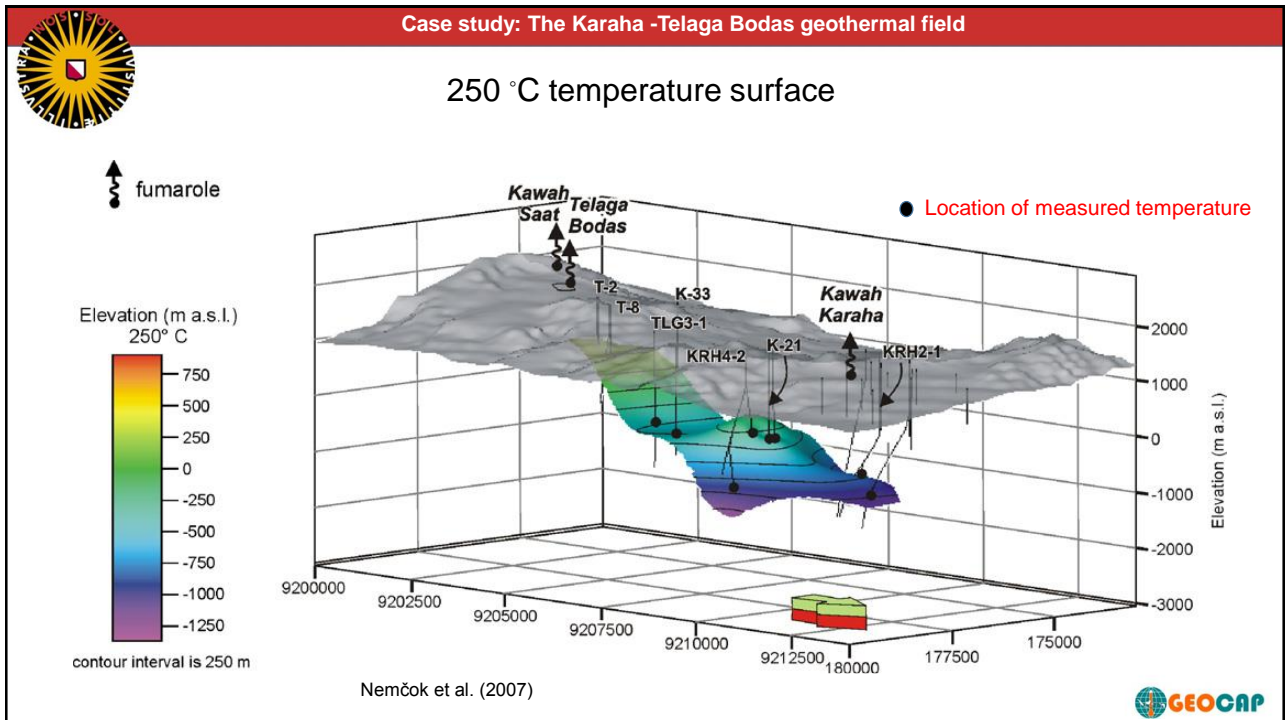
### Case study: The Karaha -Telaga Bodas geothermal field

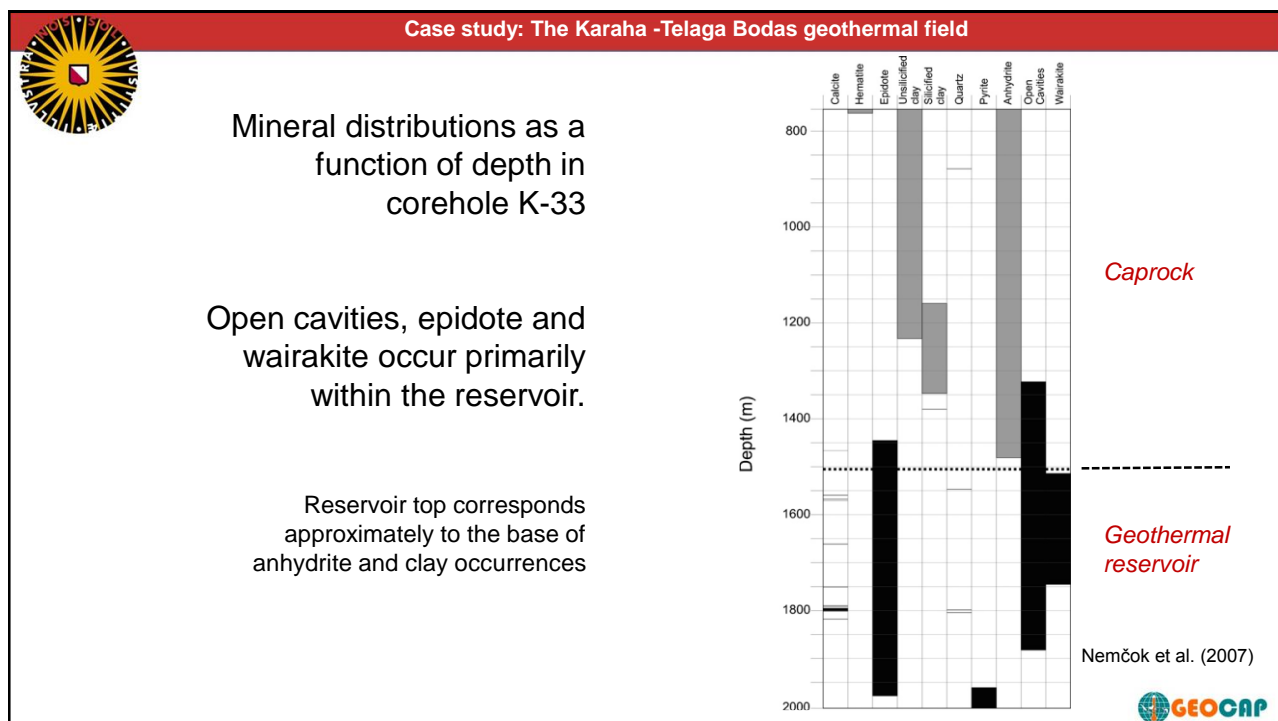
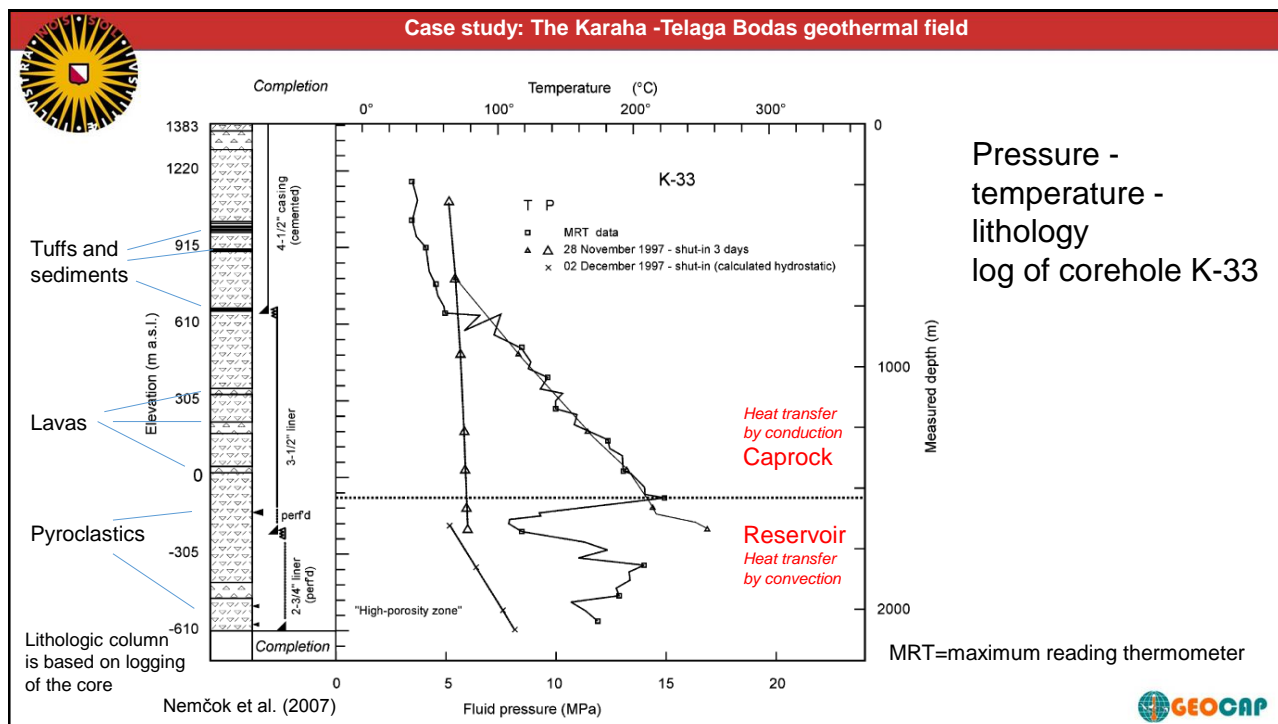
Cross-section with subsurface conditions and major hydrological features



Moore et al. (2004)









## Case study: The Karaha -Telaga Bodas geothermal field

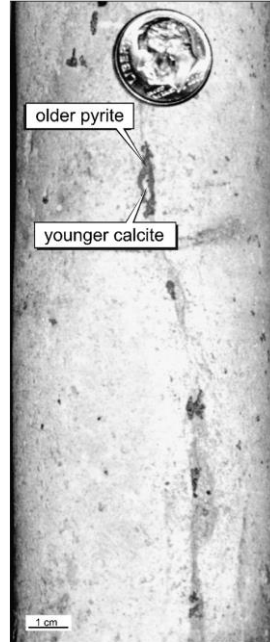


Vuggy fracture in  
corehole K-33 at  
1854m depth

The fracture (in the  
reservoir section of  
the well) is lined  
with quartz

Interior consists of  
interconnected  
irregular cavities

Host rock is an  
andesite lava flow



Small-scale normal  
fault in corehole K-  
33 at 2017m depth

Lined with pyrite

Later sealed by  
younger calcite that  
precipitated from  
downward-  
percolating  
condensate

Nemčok et al. (2007)



## Case study: The Karaha -Telaga Bodas geothermal field



Corehole K-33

Penetrative  
dissolution of  
feldspars and partial  
filling of the pore  
space by epidote

From 1751m depth



Dissolution of feldspars  
in a lava flow at 1870m  
depth

Dissolution increases  
porosity, which controls  
the strain-hardening  
behavior of the rock

During deformation, this  
results in shear bands  
characterized by  
decreased porosity

Nemčok et al. (2007)

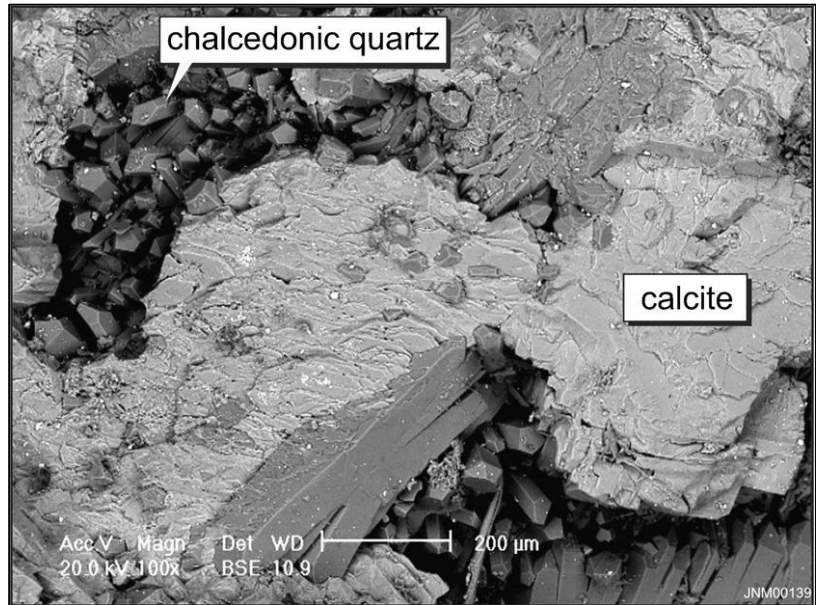




### Case study: The Karaha -Telaga Bodas geothermal field

Scanning electron microscope (SEM) back-scattered electron image of a vein from core hole T-2 at 794m depth

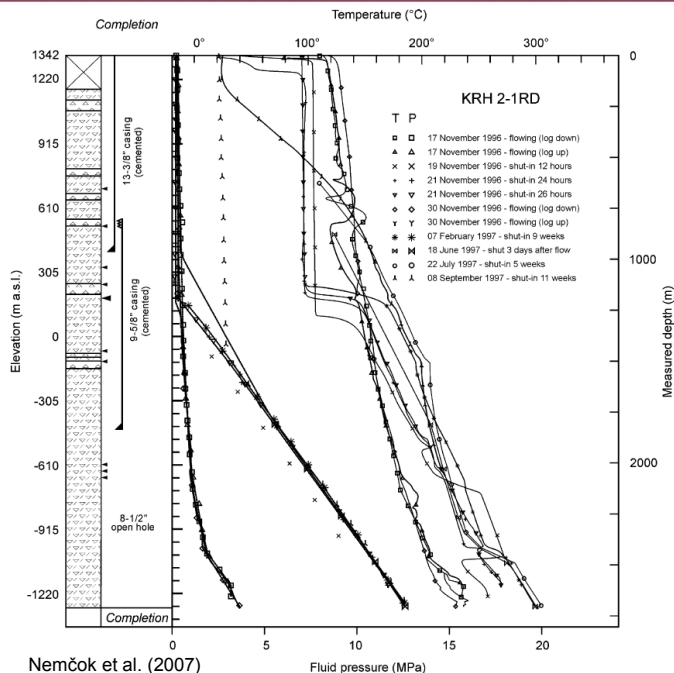
The vein is filled by **chalcedonic quartz**, which precipitated from upward-moving fluids, and **younger calcite**, which precipitated from downward-percolating condensate



Nemčok et al. (2007)



### Case study: The Karaha -Telaga Bodas geothermal field



Lithologic column is based on logging of cutting samples

Nemčok et al. (2007)

Pressure -  
temperature -  
lithology  
log of corehole  
KRH 2-1 RD

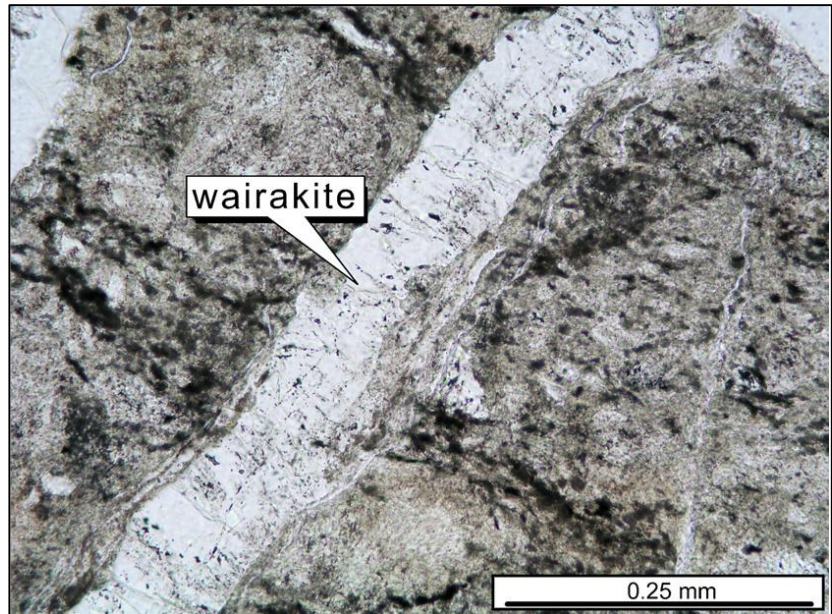




### Case study: The Karaha -Telaga Bodas geothermal field

Penetrative argillic alteration of a tuffaceous deposit cut by a vein of wairakite

sample (1996m depth) from the reservoir section of well KRH 2-1 RD (KE-13ST)



Nemčok et al. (2007)

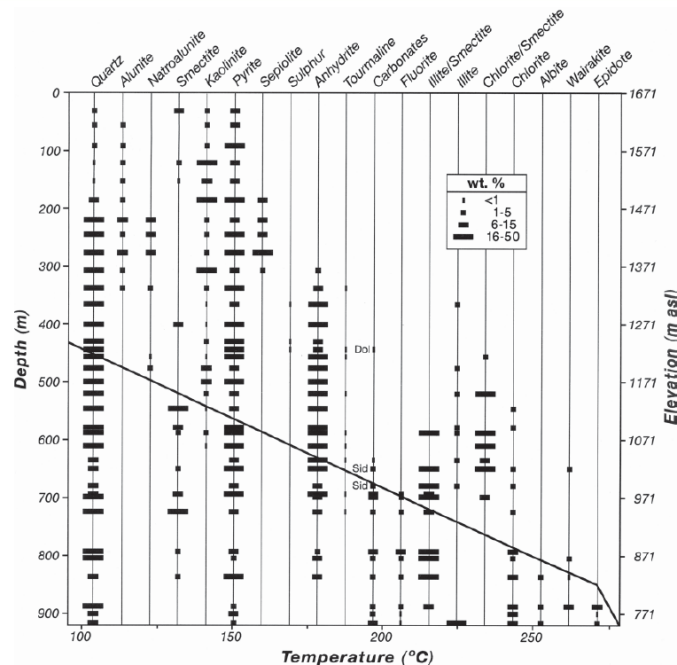


### Case study: The Karaha -Telaga Bodas geothermal field

Mineral distributions in the upper 900 m of core hole T-2

Solid line:  
downhole measured  
temperatures

The well recorded a maximum  
temperature of 321°C  
at its base (1383 m, 288 m asl)



Moore et al. (2004)

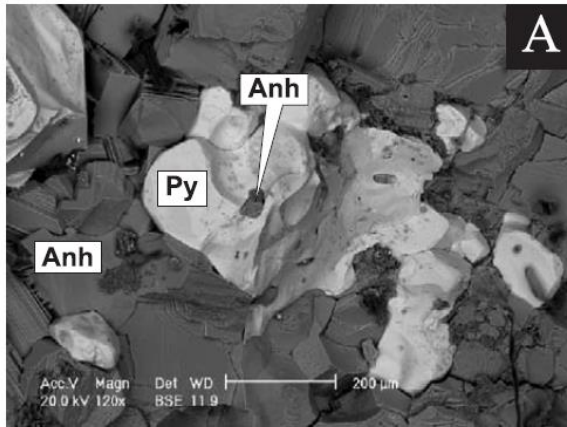




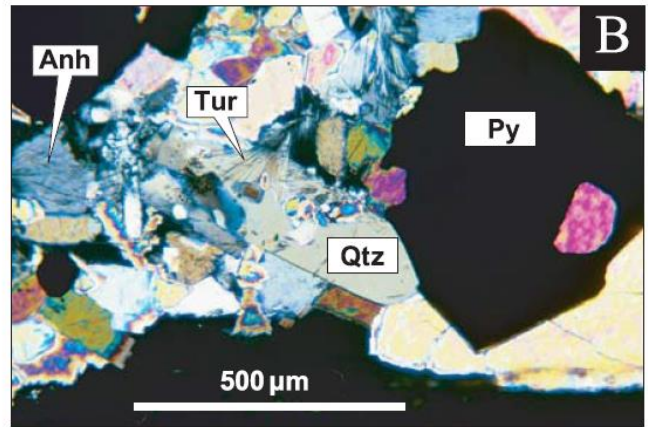


### Case study: The Karaha -Telaga Bodas geothermal field

#### Characteristic mineral textures from core hole T-2



SEM – back-scattered electron image of pyrite (py) replacing anhydrite (anh). Remnants of anhydrite are encapsulated in the pyrite.  
From a depth of 679 m



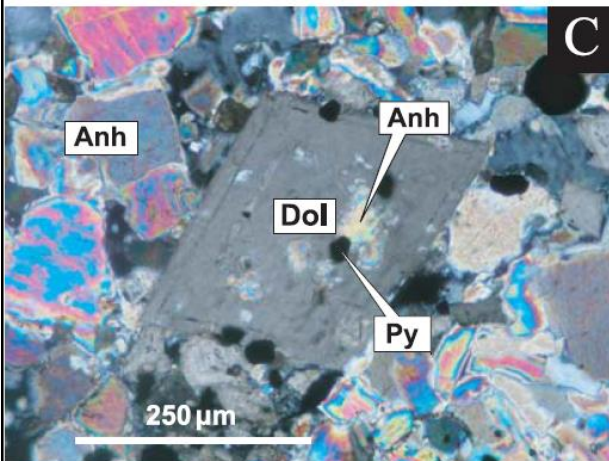
Fine-grained needles of tourmaline (tur) are encapsulated in anhydrite (anh) and quartz (qtz). The pyrite (py) encapsulates anhydrite and is coated by later anhydrite. From a depth of 634 m

Moore et al. (2004)

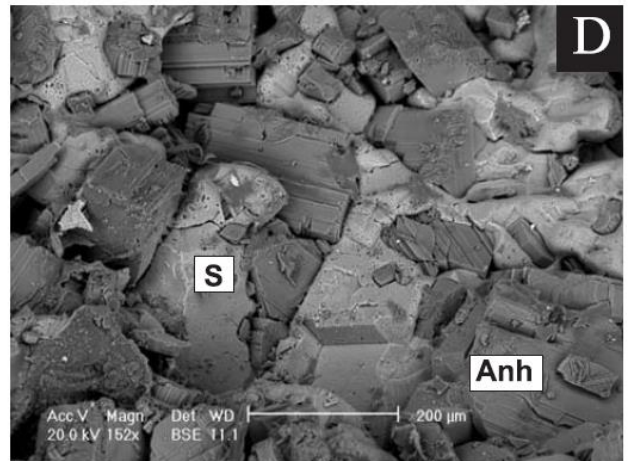


### Case study: The Karaha -Telaga Bodas geothermal field

#### Characteristic mineral textures from core hole T-2



Dolomite (dol) after anhydrite (anh) and pyrite (py). From a depth of 442 m



SEM – back-scattered electron image of native sulfur (S) after anhydrite (Anh). From a depth of 434 m

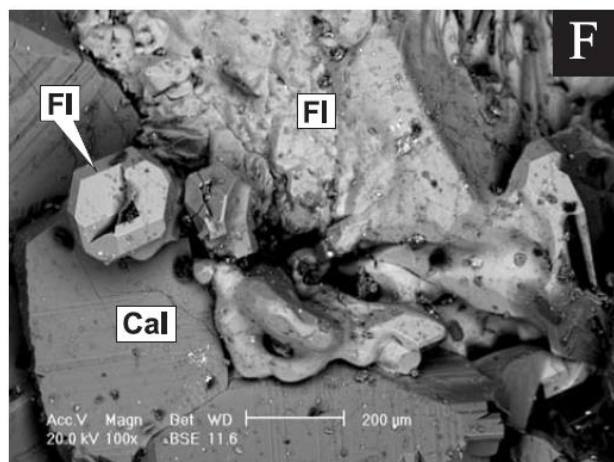
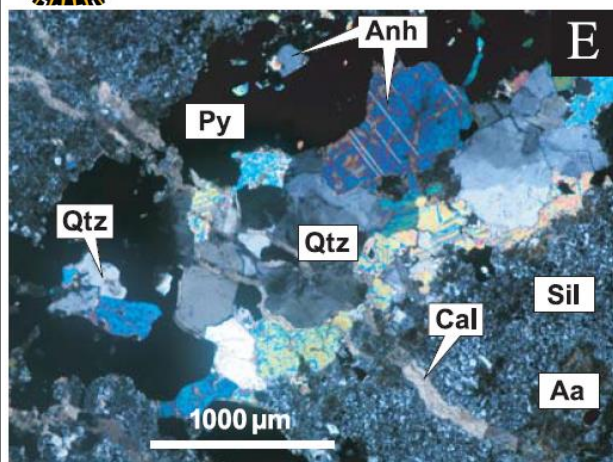
Moore et al. (2004)





### Case study: The Karaha -Telaga Bodas geothermal field

#### Characteristic mineral textures from core hole T-2



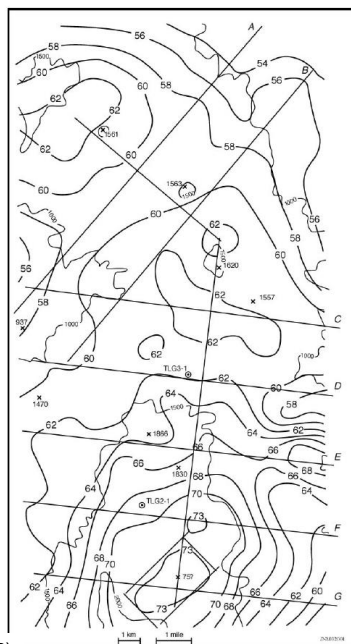
Altered and veined pyroclastic deposit displaying progressive effects of the **early liquid-dominated system** [pervasive argillic alteration (aa) and later silicification (sil)], **decompression** [quartz (qtz)], and **descending steam condensate** [anhydrite (anh), followed by pyrite (py) and then calcite (cal)]. From a depth of 694 m

SEM – back-scattered electron image of fluorite (fl) after calcite (cal). From a depth of 793 m

Moore et al. (2004)



### Case study: The Karaha -Telaga Bodas geothermal field



#### Densities of samples from core hole T-8

Depth of Sample (m)	Sample Lithology	Sample Density (gm/cc)
770.7	andesite lava flow	2.53
778.1	andesite lava flow	2.50
794.7	Tuff	2.57
802.2	Tuff	2.52
885.3	Tuff	2.59
904	Tuff	2.49
978.7	andesite lava flow	2.39
1042	Tuff	2.37
1095.5	Tuff	2.38
1132.3	Tuff	2.61
1174.4	andesite lava flow	2.45
1240.4	andesite lava flow	2.60
1306	Tuff	2.44
Average		2.50
Standard Deviation		0.08

Tripp et al. (2002)

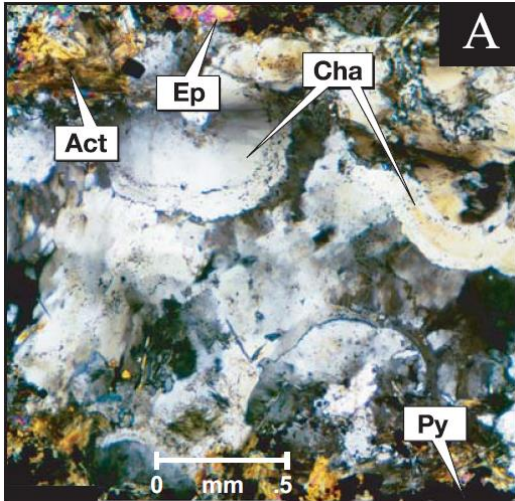
Bouguer gravity map



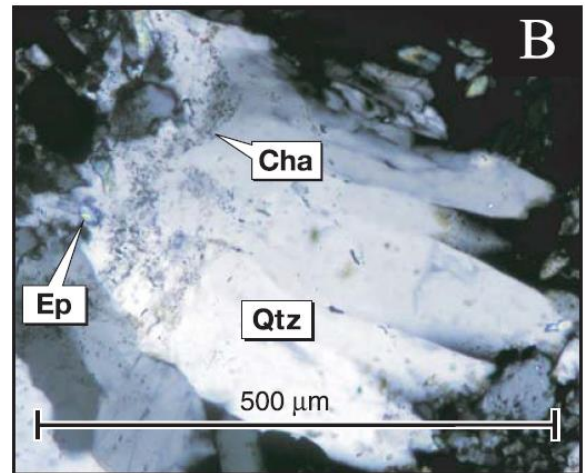


## Case study: The Karaha -Telaga Bodas geothermal field

Quartz veins displaying botryoidal textures indicating deposition as chalcedony or possibly amorphous silica



Vein cutting wallrocks with the high-T alteration assemblage epidote + actinolite + pyrite. From a depth of 1139 m in core hole T-8



Botryoidal textures are preserved in the cores of the crystals. From a depth of 1203 m in core hole T-8

Moore et al. (2004) GEOCAP

## Case study: The Karaha -Telaga Bodas geothermal field

SEM – back-scattered electron image of anhydrite coated with a Ti-rich precipitate.

**The anhydrite encapsulates crystals of epidote**

The sample is from a depth of 1045 m (586 m asl) in core hole T-8

**Anhydrite from this depth contains inclusions of halite saturated fluid**



Moore et al. (2004)

GEOCAP





### Case study: The Karaha -Telaga Bodas geothermal field

#### Compositions of representative reservoir and lake waters

Sample*	T (°C) <sup>+</sup>	Res Stm Frac (%) <sup>+</sup>	pH <sup>§</sup>	Na	K	Ca	Mg	B	SiO <sub>2</sub>	Cl	SO <sub>4</sub>	HCO <sub>3</sub>	nkc (°C) <sup>#</sup>	qtz (°C) <sup>##</sup>
K-33a	250	25	7.50	140	35.0	4.7	0.34	3.13	273	35.1	57.4	334	249	203
K-33b	250	25	7.30	133	33.8	3.9	0.75	2.97	331	37.8	84.4	304	251	219
KRH 2-1 RD	225	7	8.15	424	51.8	3.7	0.31	33.0	348	534	128	196	228	223
KRH 3-1 STb	265	15	8.33	497	95.5	2.6	0.02	43.4	541	826	58.5	64.8	268	267
KRH 4-1a	250	70	7.73	1313	201	24.8	0.04	106	391	2247	28.8	92.5	248	233
KRH 4-1b	250	74	7.80	1251	188	24.0	<0.01	103	365	2107	26.5	83.9	245	227
KRH 4-1c	250	67	7.73	1428	230	42.6	0.21	110	402	2450	21.9	72.8	247	236
KRH 5-1a	280	22	7.16	2983	832	675	0.92	102	110	6909	19.9	25.7	272	143
KRH 5-1b	280	34	7.01	2983	999	726	1.03	1.05	528	7014	13.8	30.8	285	264
KRH 5-1c	280	11	6.60	3547	1069	929	2.31	129	70	8033	3.6	<3.13	278	118
TLG 3-1a	220	85	7.28	770	112	46.7	0.01	165	502	1315	78.6	72.6	225	258
TLG 3-1b	220	88	7.11	671	101	77.5	0.02	189	148	1223	79.4	56.5	218	161
TLG 3-1c	220	88	7.01	769	120	143	0.03	144	186	1539	50.2	53.2	217	175
TLG 3-1d	220	87	7.00	794	132	190	0.02	303	424	1660	45.2	51.7	219	241
Telaga Bodas <sup>^</sup>			0.40	122	30.1	394	206	1.3	348	8850	30500			

Analytical values in mg/L. See Appendices 1 and 2 for sampling conditions, dates and weirbox compositions. \*Multiple samples are labeled alphabetically. <sup>+</sup>Temperature of the principal reservoir feed zone. <sup>+</sup>Calculated fraction of reservoir steam in the well discharge. <sup>§</sup>Laboratory pH. The pH of Telaga Bodas water was calculated from ion balance criteria (Moore and others, 2004a). <sup>#</sup>Temperatures calculated using the Na-K-Ca geothermometer (Fournier and Truesdell, 1973). <sup>##</sup>Temperatures calculated using the quartz geothermometer (Fournier and Potter, 1982). <sup>^</sup>Lake water. The sample contains 2320 mg/L Fe.

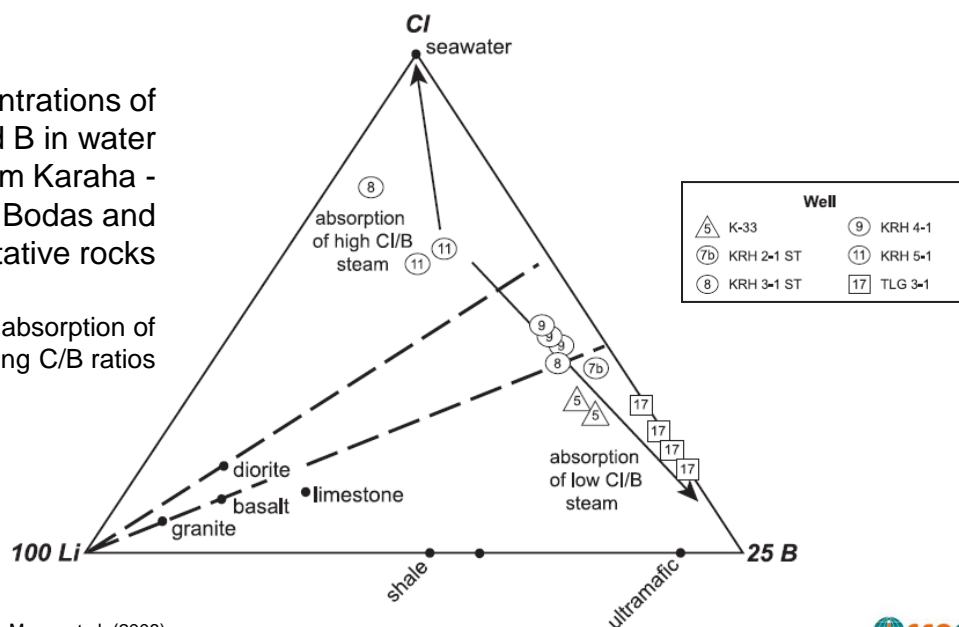
Moore et al. (2008)



### Case study: The Karaha -Telaga Bodas geothermal field

Relative concentrations of  
Li, Cl and B in water  
samples from Karaha -  
Telaga Bodas and  
representative rocks

Trend lines suggest absorption of  
steam with varying C/B ratios



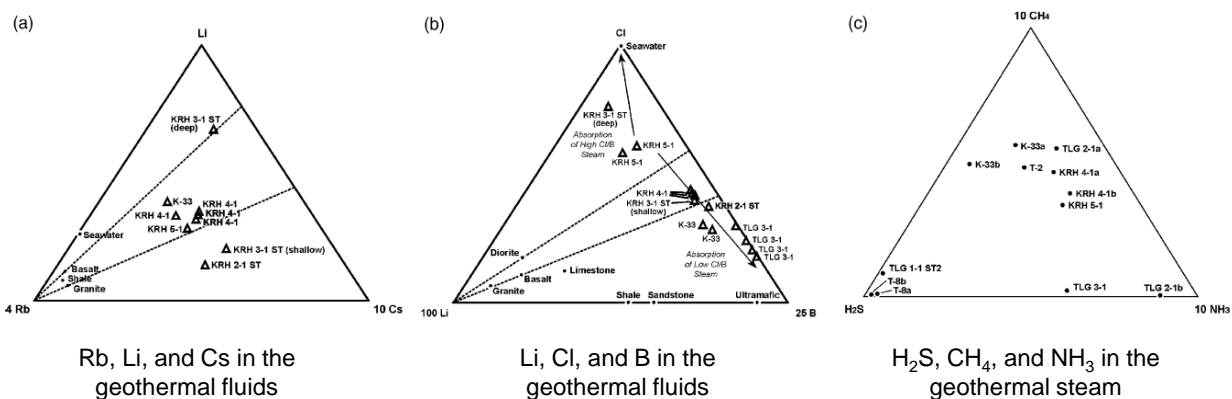
Moore et al. (2008)





### Case study: The Karaha -Telaga Bodas geothermal field

## Relative concentrations of minor components in geothermal fluids and steam



The data define three groups

Nemčok et al. (2007)



### Case study: The Karaha -Telaga Bodas geothermal field

## Gas compositions of geothermal fluids

Sample <sup>*</sup>	Date	Stm Press (MPa g) <sup>§</sup>	Stm Fract (%) <sup>‡</sup>	Air (%)	Total Gas (wt%)	Mole percent of dry gas						
						CO <sub>2</sub>	H <sub>2</sub> S	NH <sub>3</sub>	Ar	N <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub>
K-33a	12/1/97	0.44	40	4.57	20.0	95.8	2.64	0.190	0.0075	0.481	0.556	0.326
K-33b	12/1/97	0.44	40	0.56	28.7	96.1	3.11	0.051	0.0020	0.183	0.355	0.173
KRH 4-1a	9/13/97	1.36	72	2.05	4.5	93.8	3.60	0.607	0.0008	0.495	0.831	0.692
KRH 4-1b	9/13/97	1.36	72	0.02	4.5	93.1	4.02	0.897	0.0042	0.430	0.812	0.706
KRH 5-1a <sup>+</sup>	12/17/97	0.55	34	0.03	1.1	92.4	4.41	0.799	0.0149	1.043	0.641	0.578
T-2	10/18/97	1.31	92	0.18	7.8	97.0	1.87	0.161	0.0022	0.247	0.321	0.403
T-8,a	7/13/97	0.22	97	0.57	8.3	90.4	8.07	<0.027	0.0002	0.119	0.009	1.35
T-8,b <sup>++</sup>	7/26/97	0.54	95	0.00	8.2	91.8	10.0	0.019	0.0005	0.200	<0.007	2.63
TLG 1-1 <sup>+</sup>	12/1/97	1.31	94	0.06	3.6	80.8	10.4	0.017	0.0724	6.64	0.100	1.80
TLG 2-1a	2/18/98	0.93	95	0.21	21.5	96.9	1.07	0.220	0.0017	0.193	0.400	1.17
TLG 2-1b	2/18/98	0.93	95	1.69	29.6	97.8	0.51	0.412		0.919	<0.002	0.008
TLG 3-1a <sup>+</sup>	2/23/98	0.16	93	0.17	0.5	84.8	10.5	1.644	0.0255	2.27	0.060	0.745

<sup>\*</sup>Multiple samples are labeled alphabetically. <sup>+</sup>Aerated drilling fluid contamination. <sup>++</sup>Gases sum to 104.7%. <sup>§</sup>Steam pressure (MPa gauge). <sup>‡</sup>Steam fraction.

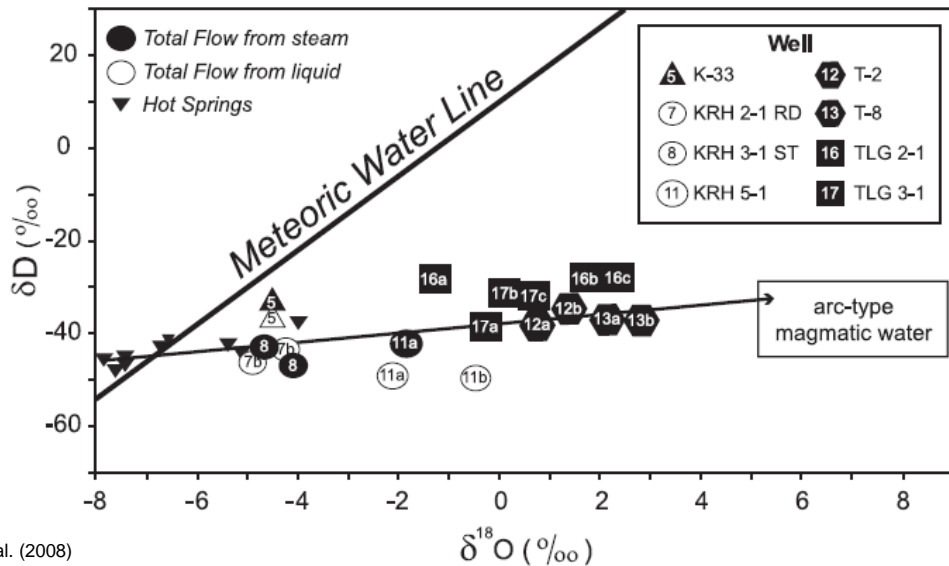
Moore et al. (2008)





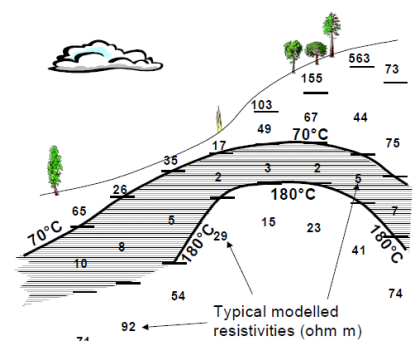
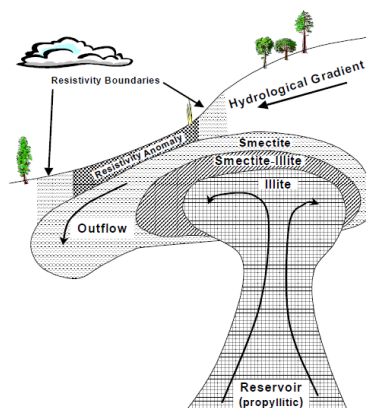
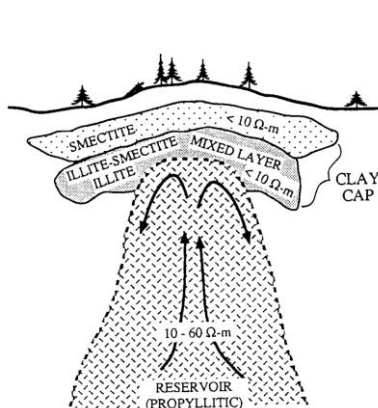
### Case study: The Karaha -Telaga Bodas geothermal field

#### Stable isotope compositions of spring and well samples



### Case study: The Karaha -Telaga Bodas geothermal field

#### Resistivity imaging from MT surveys to locate the geothermal reservoir



Layered resistivity models and likely temperatures above and below the conductive layer

Anderson et al. (2000)

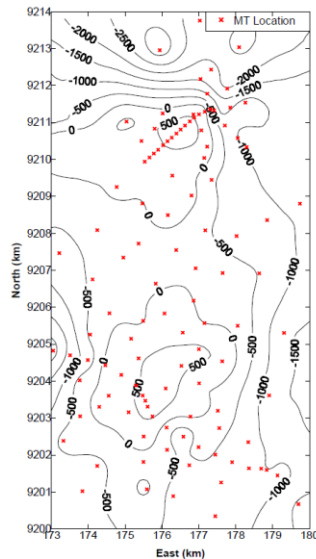




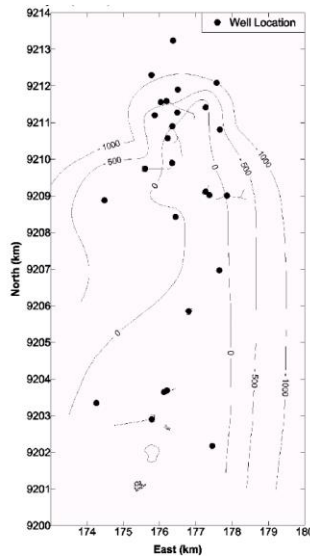


### Case study: The Karaha -Telaga Bodas geothermal field

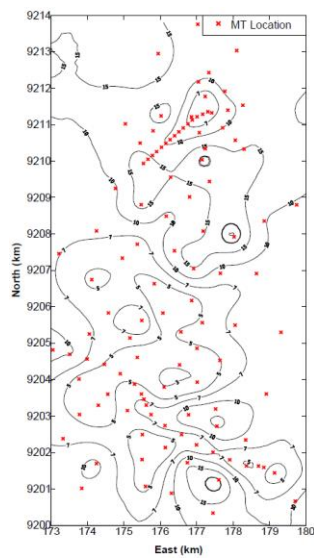
## Resistivity imaging from MT surveys to locate the geothermal reservoir



Elevation of base of conductive layer (m asl)  
Anderson et al. (2000)



Elevation of 180°C isotherm



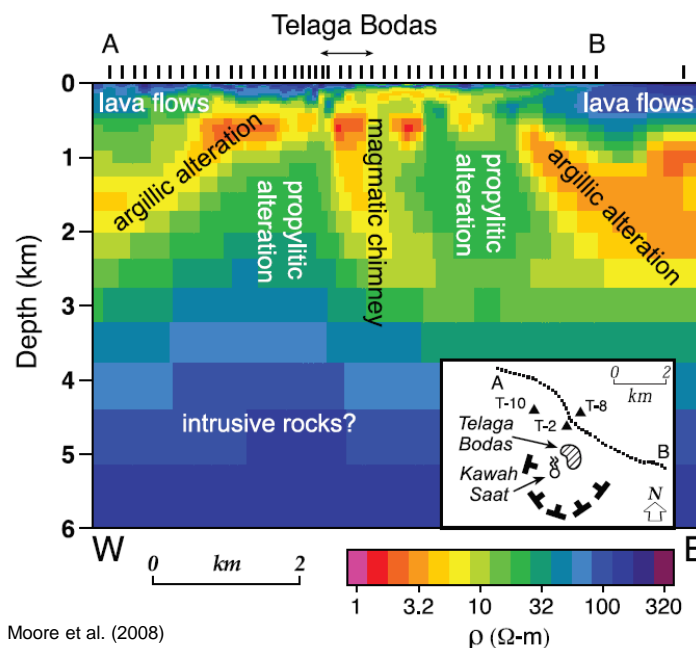
Apparent resistivity at 1 Hz



### Case study: The Karaha -Telaga Bodas geothermal field

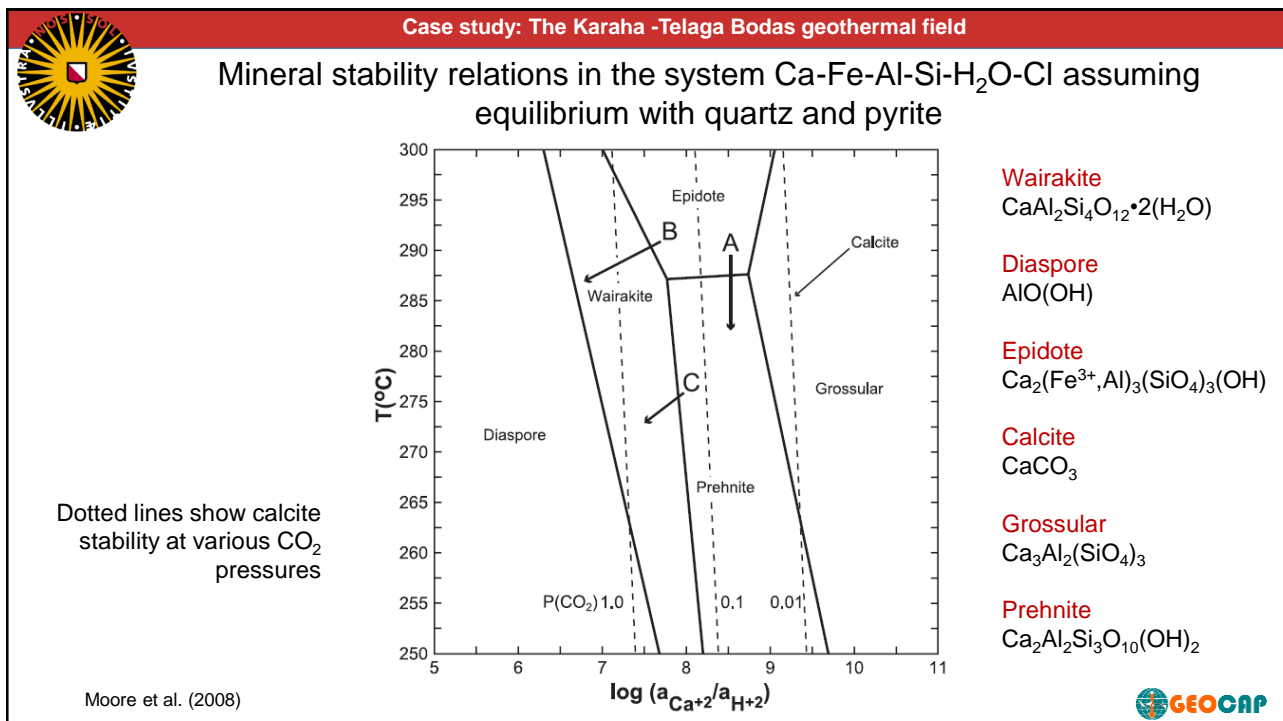
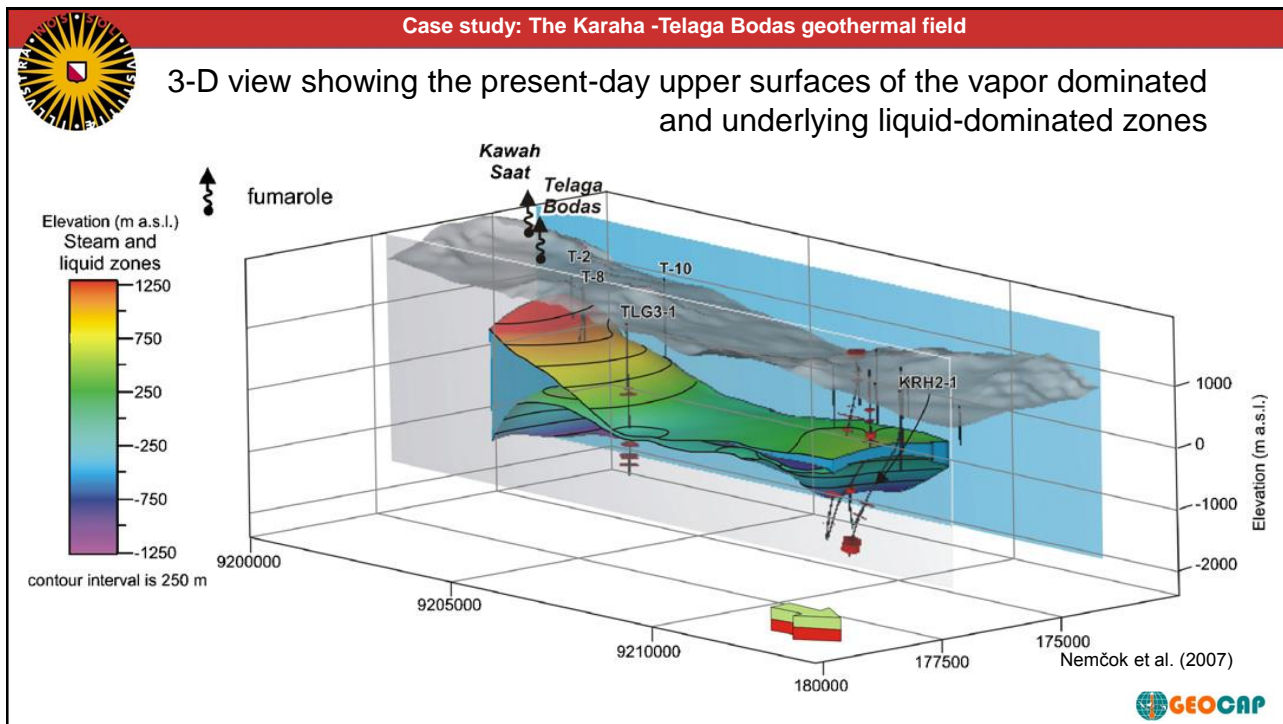
## Resistivity model

the magmatic chimney is vapor-dominated



Moore et al. (2008)

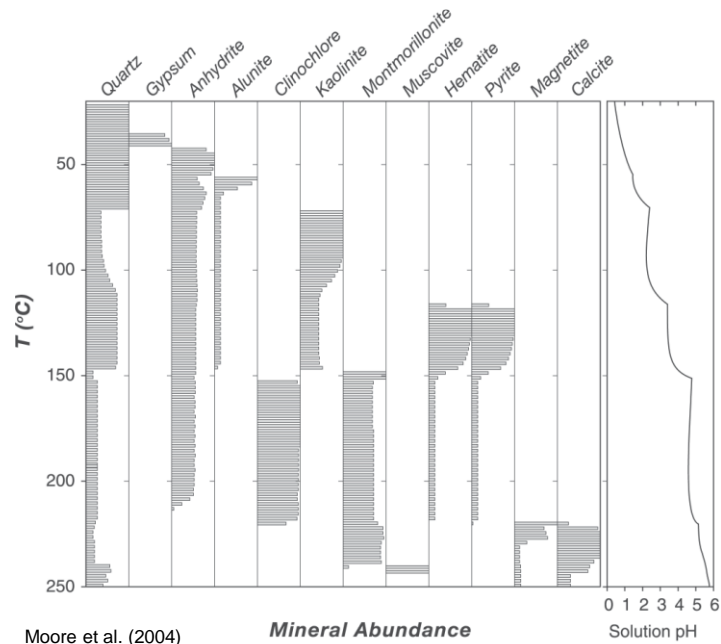






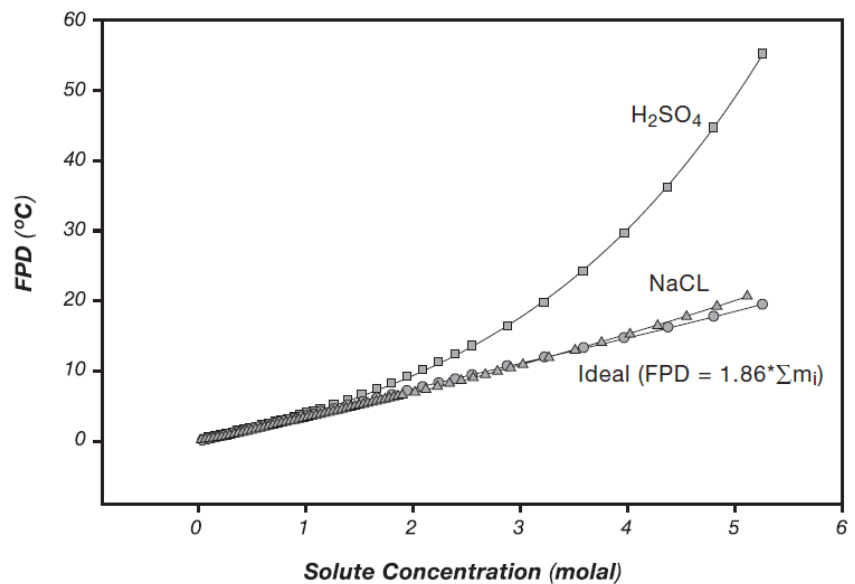
### Case study: The Karaha -Telaga Bodas geothermal field

Simulated assemblages of minerals resulting from the reaction of 1 kg of modified Telaga Bodas water with 200 g of andesite

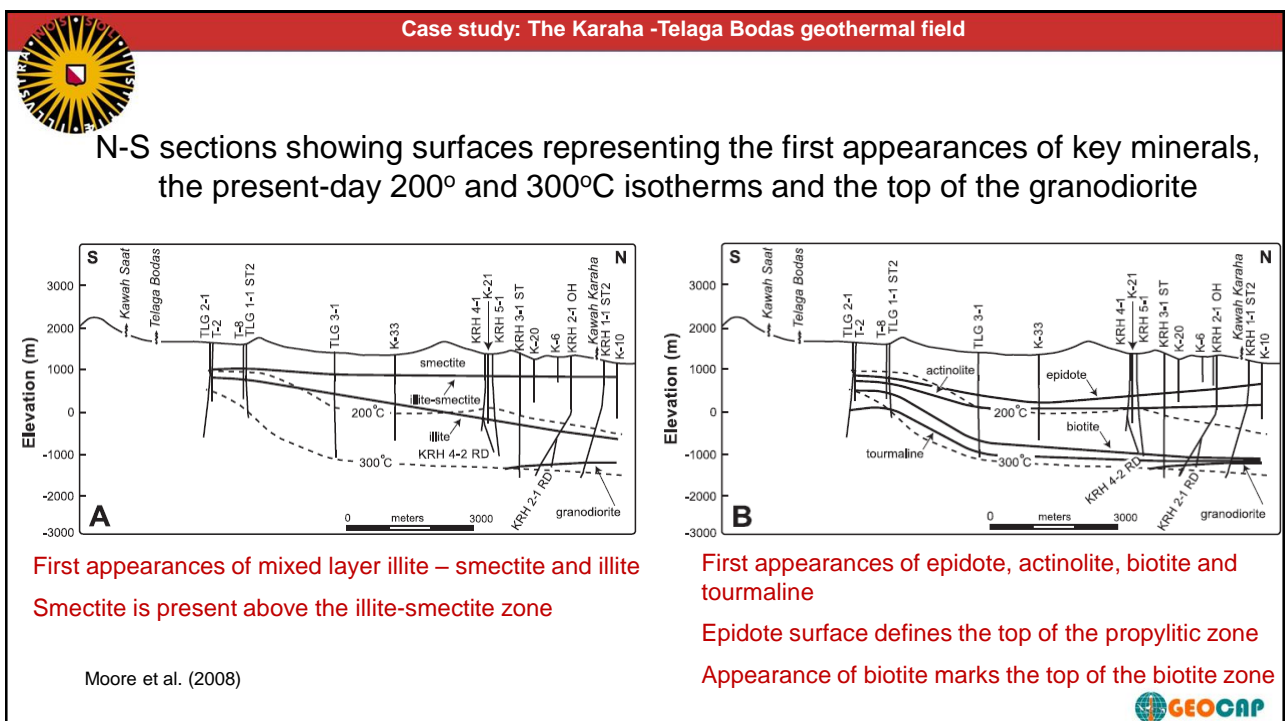
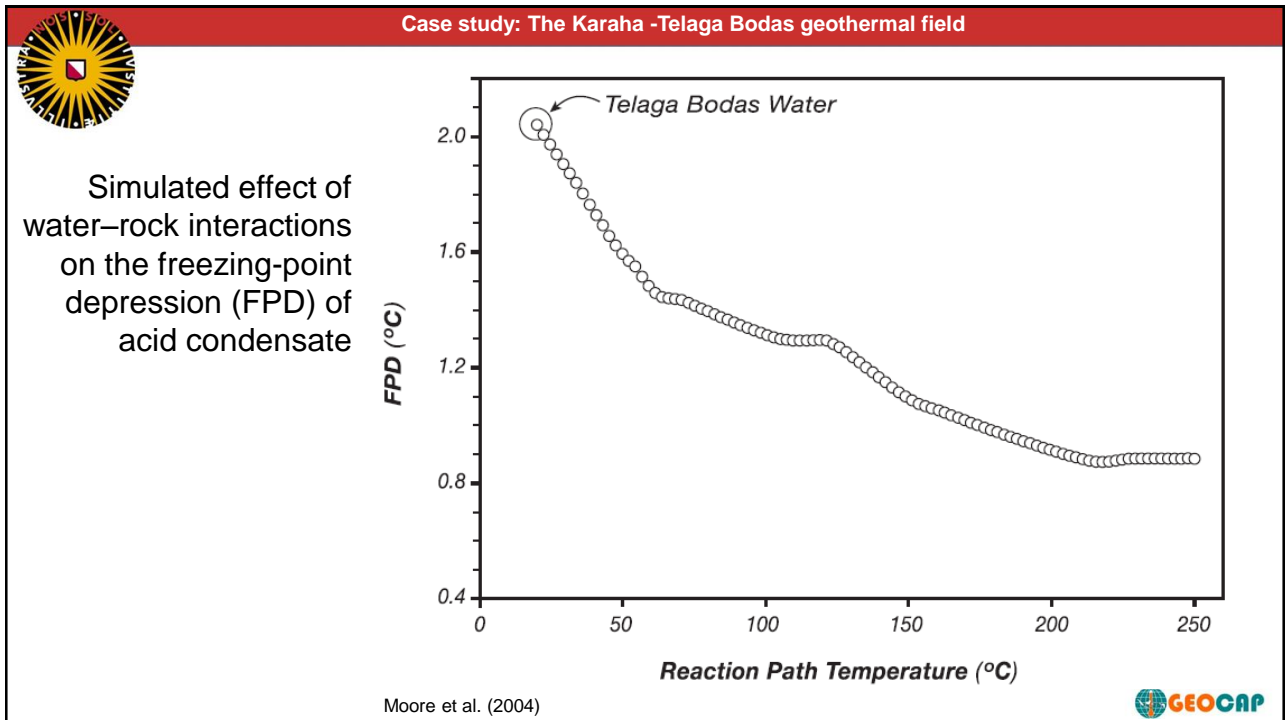


### Case study: The Karaha -Telaga Bodas geothermal field

Freezing-point depression (FPD) effects due to non-ideal behavior in NaCl and H<sub>2</sub>SO<sub>4</sub> solutions



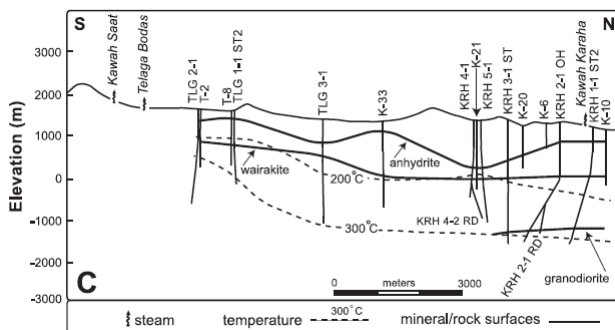






### Case study: The Karaha -Telaga Bodas geothermal field

N-S sections showing surfaces representing the first appearances of key minerals, the present-day 200° and 300°C isotherms and the top of the granodiorite



First appearances of anhydrite and wairakite

Moore et al. (2008)

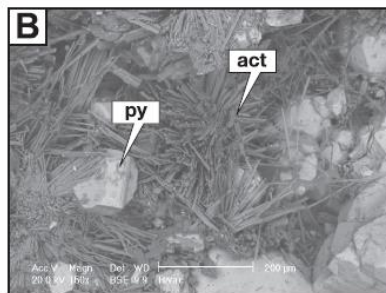
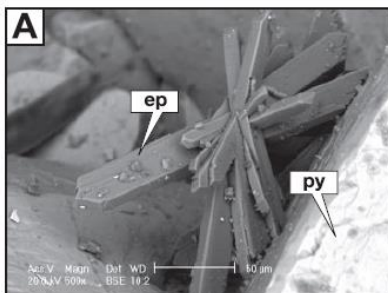


### Case study: The Karaha -Telaga Bodas geothermal field

Minerals and textures typical of propylitically altered rocks (assemblage 1)

SEM backscattered electron image of epidote and pyrite

From 691 m elevation in T-2

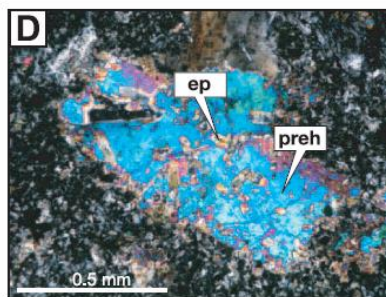
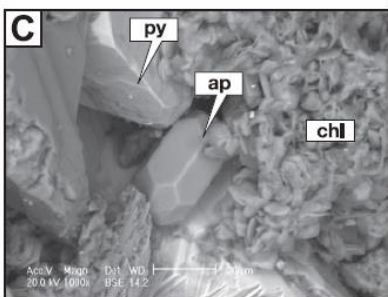


SEM backscattered electron image of intergrown actinolite and pyrite

From 586 m elevation in T-8

SEM backscattered electron image of apatite, pyrite and chlorite

From 783 m elevation in T-2



Photomicrograph of prehnite encapsulating numerous small crystals of epidote

From -369 m elevation in K-33

Moore et al. (2008)



**Case study: The Karaha -Telaga Bodas geothermal field**

**Textures of silica minerals representative of assemblage 2**

**A** Alternating layers of amorphous silica (black) and chalcedony (light Gray)  
*Calcite and a zeolite mineral were deposited after the silica polymorphs*  
 From 626 m elevation in K-21

**B** Chalcedony filling a vug lined with calcite  
 From 492 m elevation in T-8

**C** Chalcedony vein cutting wall rocks containing epidote actinolite pyrite  
 From 492 m elevation in T-8

**D** Quartz overgrowths on chalcedony  
*Botryoidal textures preserved at base of crystals*  
 Epidote grain encapsulated in chalcedony  
 From 428 m elevation in T-8

Moore et al. (2008)

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**Case study: The Karaha -Telaga Bodas geothermal field**

**Textures of silica minerals representative of assemblage 2**

**E** SEM back-scattered electron image of quartz  
 A few younger blocky calcite crystals fill spaces between the quartz crystals  
 From 878 m elevation in T-2

**F** SEM back-scattered electron image of quartz crystals  
 Arrow points to quartz crystal with curved "c" axis. The quartz crystals postdate actinolite needles  
 From 462 m elevation in T-8

Moore et al. (2008)

GEOCAP





### Case study: The Karaha -Telaga Bodas geothermal field

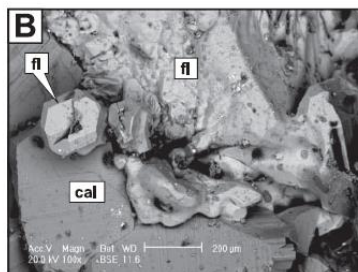
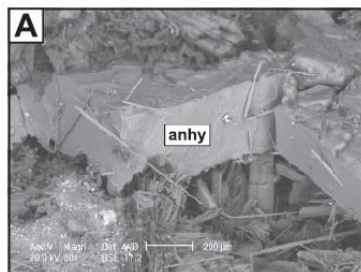
## Minerals and textural relationships typical of assemblage 3

SEM back-scattered electron image of anhydrite encapsulating crystals of epidote and needles of actinolite  
*Calcite and a zeolite mineral were deposited after the silica polymorphs*

From 629 m elevation in T-8

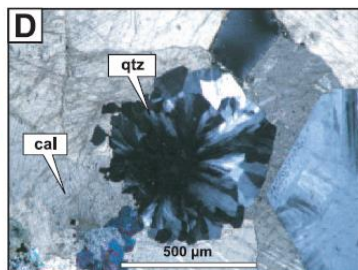
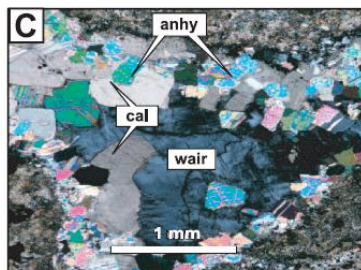
Chalcedony filling a vug lined with calcite

From 492 m elevation in T-8



SEM back-scattered electron image of fluorite deposited on calcite

From 878 m elevation in T-2



Quartz crystal formed during assemblage 2 encapsulated in assemblage 3 calcite

*Complex extinction pattern is typical of assemblage 2 quartz*

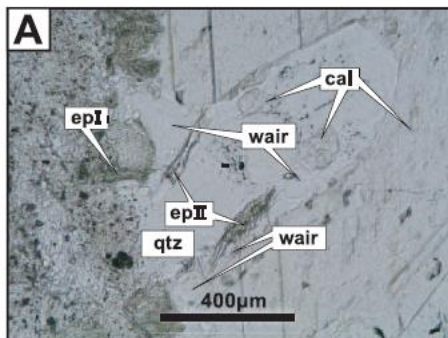
irregular edges of the quartz crystal reflect dissolution by steam condensate  
From 169 m elevation in K-33

Moore et al. (2008)



### Case study: The Karaha -Telaga Bodas geothermal field

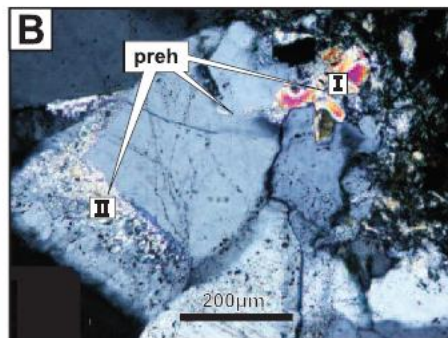
## Photomicrographs of transitional assemblages



Vein quartz (representing assemblage 2) is intergrown with epidote, wairakite and calcite  
*Wairakite and calcite are representative of assemblage 3.*

Earlier epidote (ep 1) representing assemblage 1 occurs in the wall rock. Growth of wairakite and calcite continued after quartz deposition, filling the vein interior

From -222 m elevation in K-21



Quartz (representing assemblage 2) with growth zones outlined by prehnite

*Prehnite, which formed late in the evolution of assemblage 1, was growing on the vein wall prior to quartz deposition*

An older crystal of epidote lies beneath the quartz crystal.

From 20 m elevation in K-33

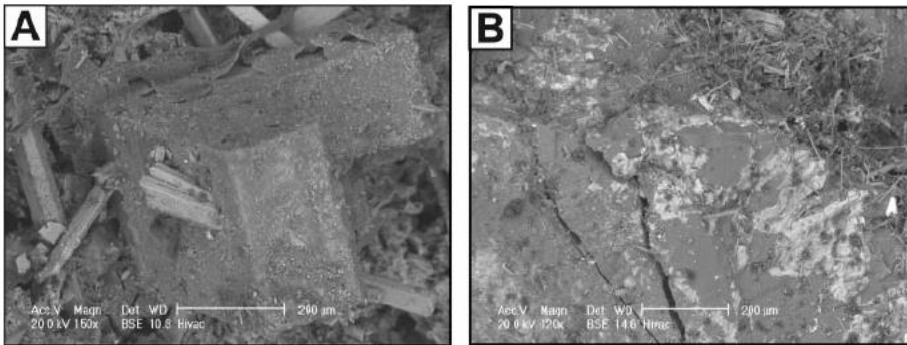
Moore et al. (2008)





### Case study: The Karaha -Telaga Bodas geothermal field

#### SEM backscattered electron images of scale deposits



Ti-rich precipitate coating anhydrite

The anhydrite encapsulates crystals of epidote

586 m elevation in T-8

White encrustations of FeCl<sub>x</sub> on quartz

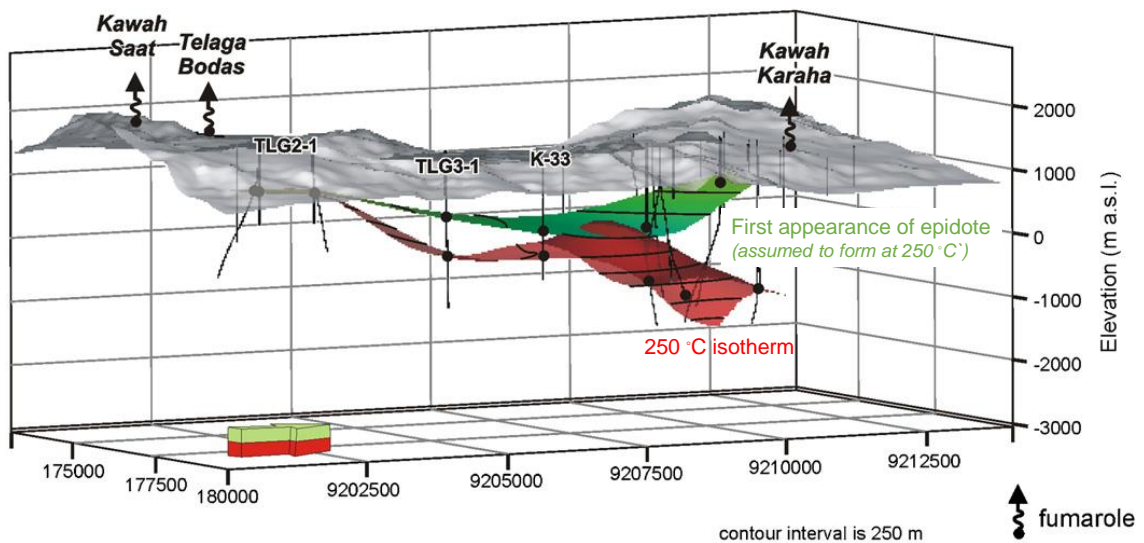
From 461 m elevation in T-8

Moore et al. (2008)



### Case study: The Karaha -Telaga Bodas geothermal field

#### Cooling since the formation of epidote



Nemčok et al. (2007)





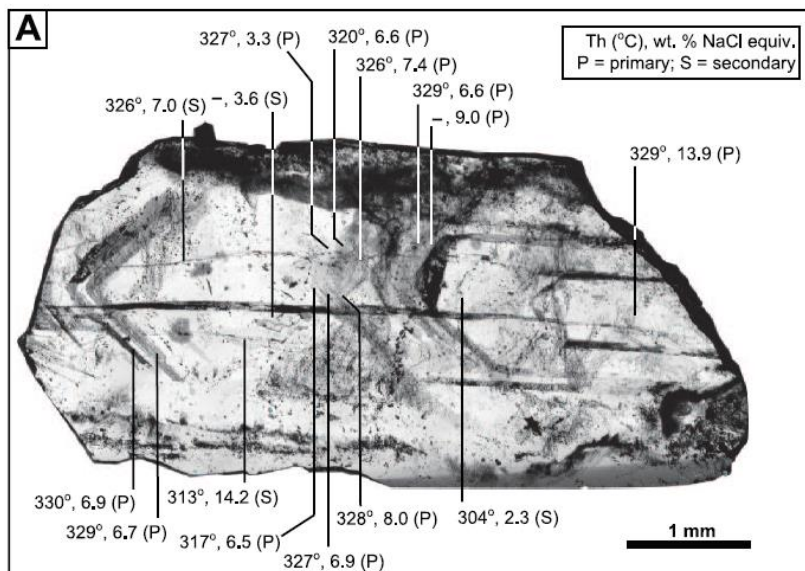
# Case study: The Karaha -Telaga Bodas geothermal field

## Examples of fluid inclusion types

**Quartz crystal with fluid inclusions trapped in growth zones (primary inclusions (p)) and healed fractures (secondary inclusions (s))**

The average homogenization temperature ( $T_h$ ) and salinity (in weight percent NaCl equivalent) are shown for each fluid inclusion assemblage.

From 461 m elevation in T-8.



Moore et al. (2008)

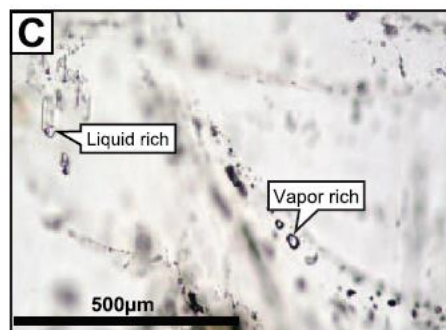
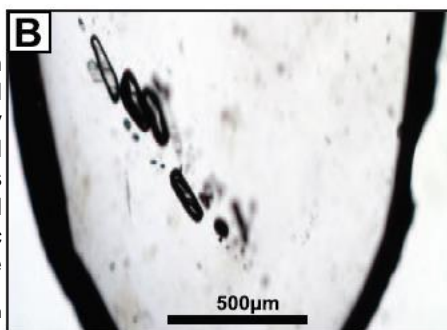


# Case study: The Karaha -Telaga Bodas geothermal field

## Examples of fluid inclusion types

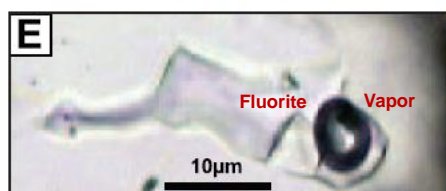
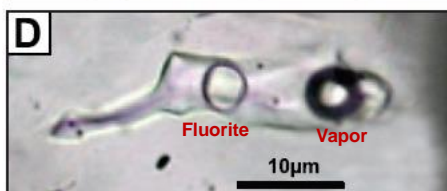
Growth zone in quartz defined by primary vapor-rich fluid inclusions trapped parallel to a rhombic face

From -222 m elevation in K-21



Pseudo-secondary inclusions trapped along healed fractures within a growth zone

From 878 m elevation in T-2



Liquid-rich fluid inclusions containing a fluorite daughter crystal

Moore et al. (2008)

From 528 m elevation in T-8

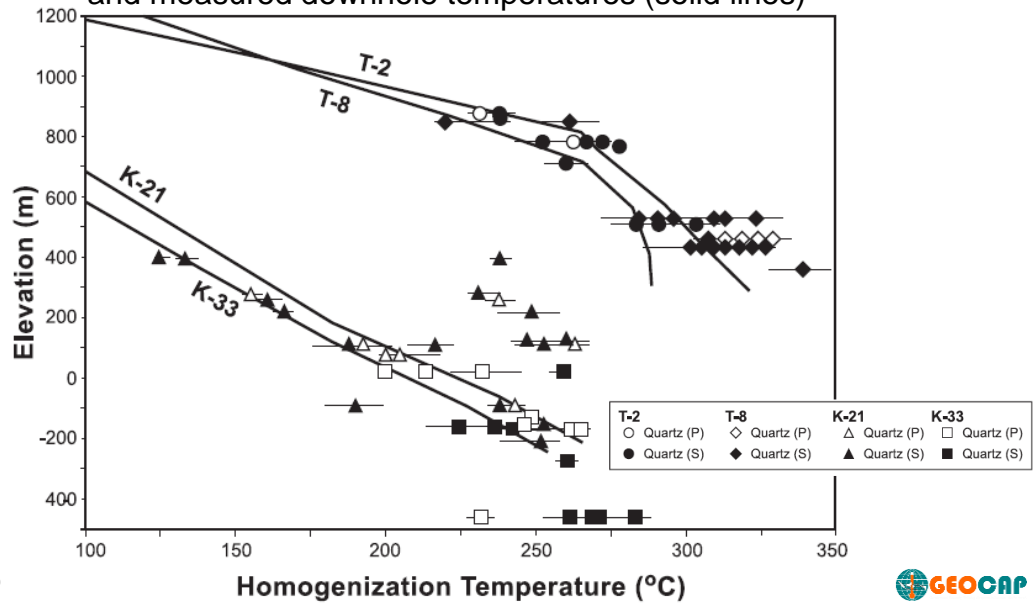






### Case study: The Karaha -Telaga Bodas geothermal field

Homogenization temperatures of fluid inclusions in quartz (assemblage 2) and measured downhole temperatures (solid lines)

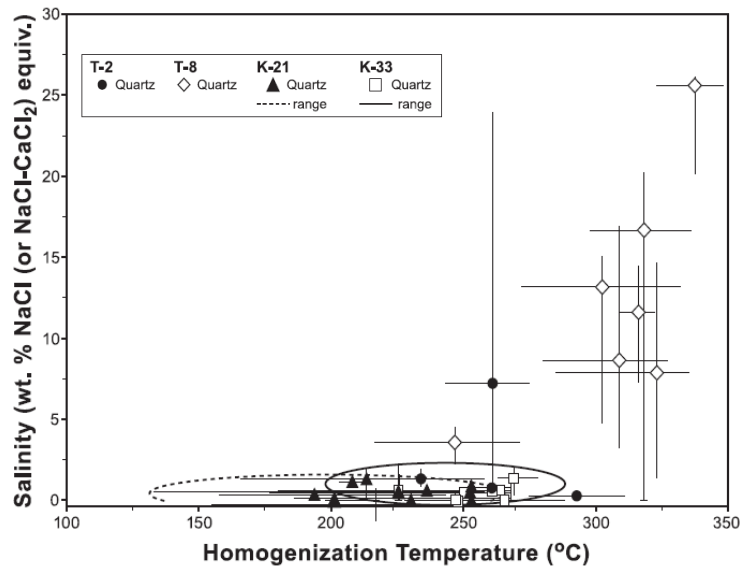


Moore et al. (2008)



### Case study: The Karaha -Telaga Bodas geothermal field

Homogenization temperatures and salinities of fluid inclusions trapped in quartz (assemblage 2)



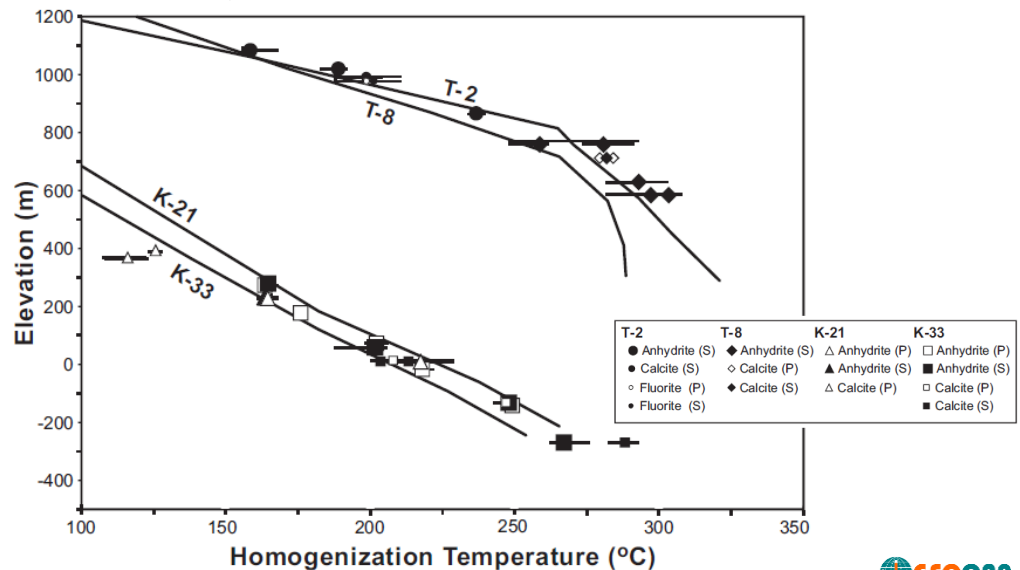
Moore et al. (2008)





### Case study: The Karaha -Telaga Bodas geothermal field

Homogenization temperatures of fluid inclusions trapped in anhydrite, calcite and fluorite (assemblage 3) and measured downhole temperatures (solid lines)



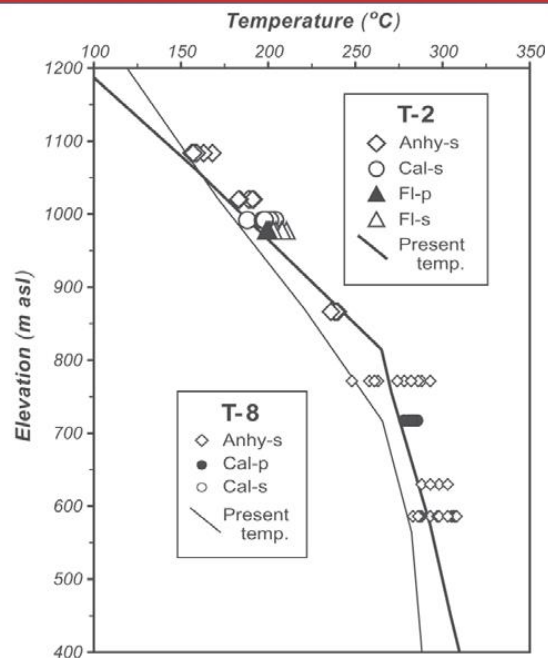
Moore et al. (2008)



### Case study: The Karaha -Telaga Bodas geothermal field

Homogenization temperatures of fluid inclusions in stage-3 minerals from core holes T-2 and T-8

Measured downhole temperatures shown for reference



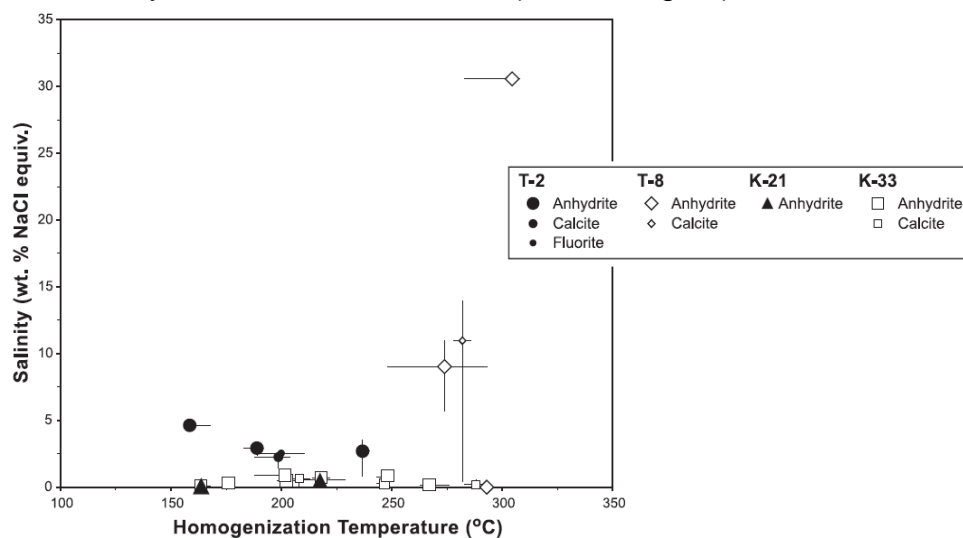
Moore et al. (2004)





### Case study: The Karaha -Telaga Bodas geothermal field

Homogenization temperatures and salinities of fluid inclusions trapped in anhydrite, calcite and fluorite (assemblage 3)

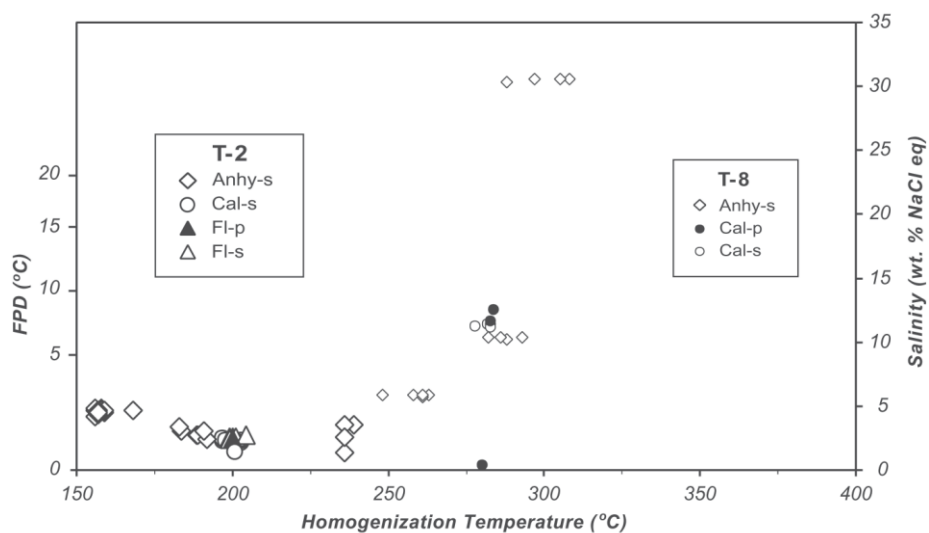


Moore et al. (2008)



### Case study: The Karaha -Telaga Bodas geothermal field

Homogenization temperatures and freezing-point depressions (FPD) of individual fluid inclusions from stage-3



Moore et al. (2004)

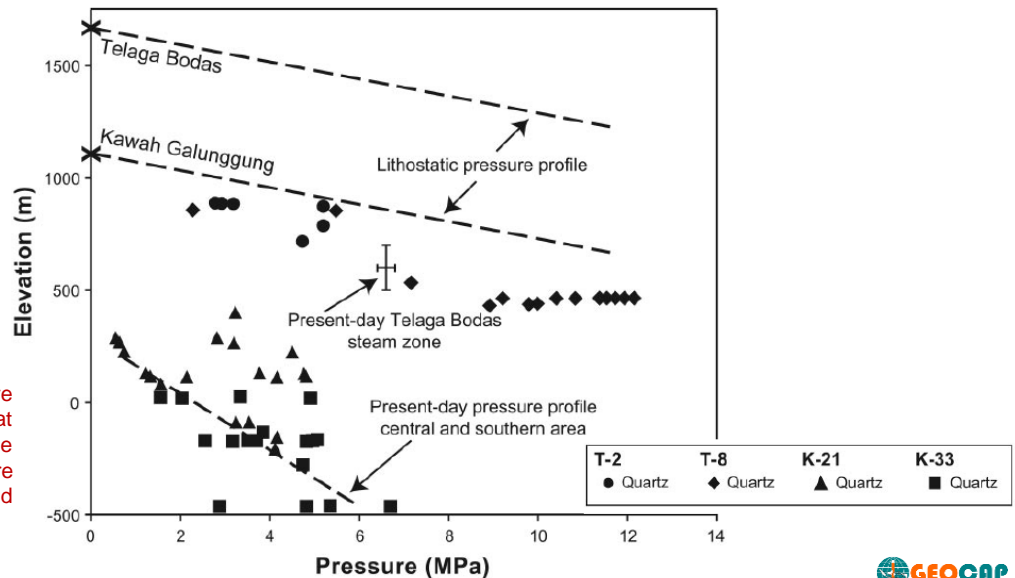






### Case study: The Karaha -Telaga Bodas geothermal field

Relationship between pressures calculated from the average homogenization temperature and salinity of each fluid inclusion assemblage and elevation



Moore et al. (2008)



### Case study: The Karaha -Telaga Bodas geothermal field

Schematic evolution of the geothermal system

Hydrothermal mineralogy as a function of depth and relative time

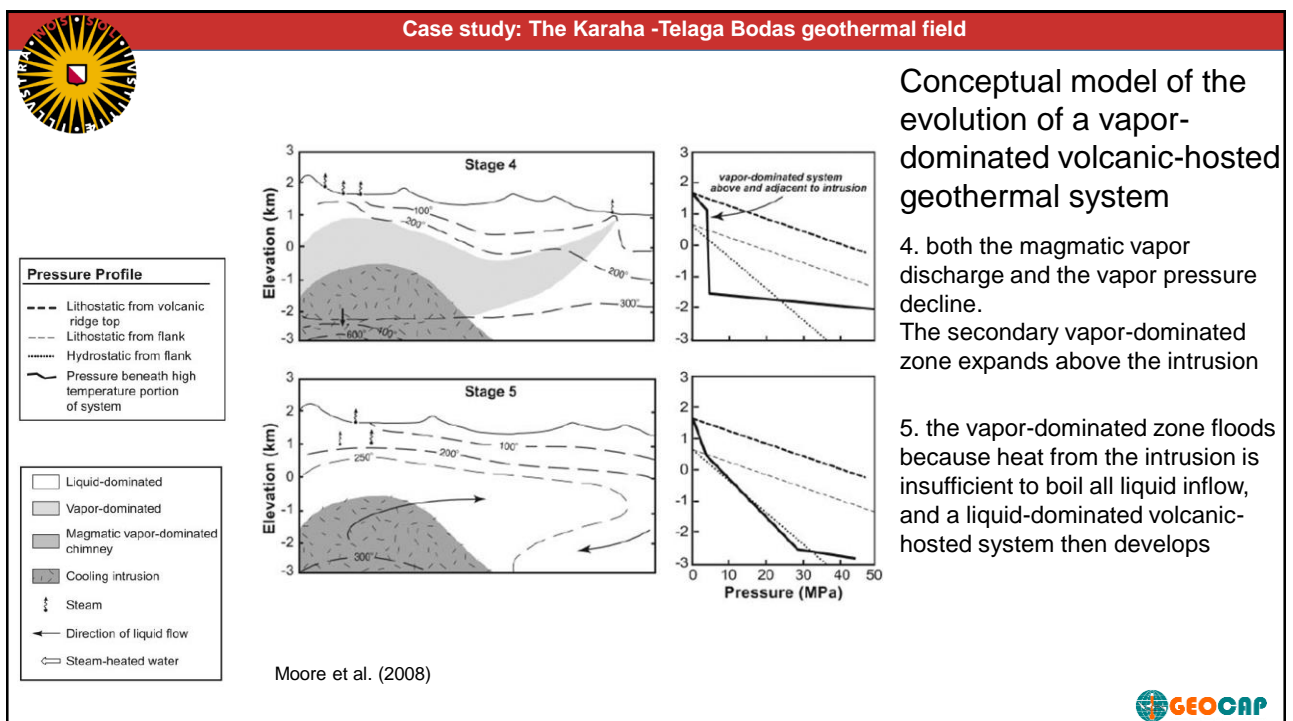
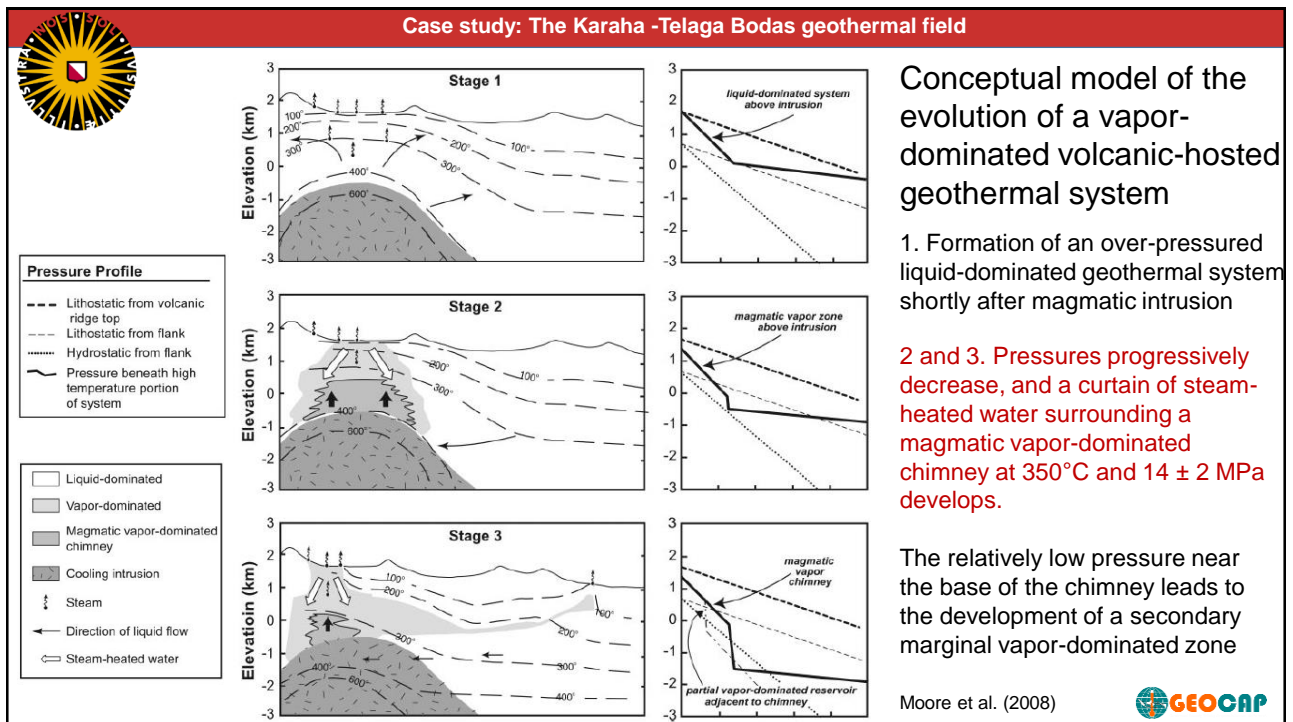
<sup>a</sup> Quartz and sulfides present in all assemblages

<sup>b</sup> Pyrite present in all assemblages

Depth	Time →		
	Liquid-dominated <sup>a</sup>	Transitional	Vapor-dominated <sup>b</sup>
Near surface			alunite, kaolinite, quartz
Shallow	smectite, carbonates zeolites	chalcedony, quartz	anhydrite, calcite
	illite-smectite, chlorite-smectite, calcite		
Deep	illite, chlorite	chalcedony, quartz	anhydrite, calcite, wairakite
	epidote, illite, chlorite actinolite, prehnite biotite, clinopyroxene actinolite, magnetite, epidote, chlorite, tourmaline.		

Nemčok et al. (2007)







### Case study: The Karaha -Telaga Bodas geothermal field

## SUMMARY 1

Karaha - Telaga Bodas is an active volcano-hosted geothermal system extending along a volcanic ridge northward from Galunggung Volcano

Information derived from deep drill holes includes temperature and pressure distributions, fluid compositions, and petrologic data on rock samples

Wells up to 3 km in depth have encountered

- temperatures as high as 353°C
- weakly altered granodiorite that intruded to within 2 to 3 km of the surface

The intrusion is shallowest beneath the southern end of the field where an acid lake overlies a nearly vertical low resistivity structure, interpreted to represent a vapor-dominated corridor to the surface for magmatic gases



### Case study: The Karaha -Telaga Bodas geothermal field

## SUMMARY 2

Four distinct hydrothermal mineral assemblages document the evolution of the geothermal system and the *transition from liquid- to vapor-dominated conditions*

### Assemblage 1 - Tourmaline, biotite, actinolite, epidote and clay minerals

- deposited at progressively greater distances from the intrusive contact
- represents the initial liquid-dominated system generated during emplacement of the granodiorite between  $5910 \pm 76$  and  $4200 \pm 150$  y BP

### Assemblage 2 - Chalcedony followed by quartz

- deposited upon early boiling of low salinity hydrothermal fluids
- boiling resulted from catastrophic decompression due to flank collapse and the formation of the Galunggung crater at  $4200 \pm 150$  y BP
- initial development of the modern vapor-dominated regime

### Assemblage 3 - Anhydrite and calcite

- formed from downward drained CO<sub>2</sub>- and SO<sub>4</sub>-rich steam-heated water in fractures as pressures declined, limiting further recharge

### Assemblage 4 - NaCl, KCl and FeCl<sub>x</sub>

- precipitated on rock surfaces in portions of the vapor-dominated zone that boiled dry







### Case study: The Karaha -Telaga Bodas geothermal field

## SUMMARY 3

Descending steam condensates produced advanced argillic alteration that is superseded at depth by veins with predominant anhydrite, pyrite, calcite and, locally, fluorite.

Fluid inclusions in anhydrite, calcite and fluorite record the chemical and thermal evolution of the fluids.

The freezing-point depressions and thus the apparent salinities of the fluids, first decrease as the homogenization temperatures increase from  $\sim 160^\circ$  to  $205^\circ\text{C}$ , then remain near constant to  $235^\circ\text{C}$ . At higher temperatures and greater depths, the fluids boil off, eventually becoming hypersaline as temperatures reach  $300^\circ\text{C}$ .

Vapor-dominated conditions extend over a distance of at least 10km and to depths below sea level. Deep wells drilled into the underlying liquid-dominated reservoir in the northern and central part of the volcanic ridge produce low salinity fluids representing recent recharge of meteoric and steam-heated water



### Case study: The Karaha -Telaga Bodas geothermal field

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