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Petrology and mineral alteration in hydrothermal systems: From diagenesis to volcanic catastrophes

by

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PETROLOGY AND MINERAL ALTERATION IN HYDROTHERMAL SYSTEMS: FROM DIAGENESIS TO VOLCANIC CATASTROPHES

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PREFACE

The 20th year of the UNU Geothermal Training Programme ended with an Anniversary Workshop and a lecture series given by Dr. Agnes G. Reyes, a former UNU Fellow, who was the UNU Visiting Lecturer of this anniversary year. She attended the first annual course of the Training Programme starting in May 1979. She had been working for one year with PNOC-EDC when she came to Iceland. Prior to that she had been working with the Commission on Volcanology for less than a year and in field mapping for a mining company. In a few years, she built up an excellent petrological laboratory in Manila from scratch and trained a very competent group of borehole geologists. She adopted the best techniques from Iceland and New Zealand to the conditions in the Philippines. She has made an outstanding contribution to geothermal science at the international level. She is presently conducting her research at the Institute of Geological and Nuclear Sciences in New Zealand.

In her lectures in Reykjavik presented here, the main theme was the application of petrological techniques to geothermal exploration and development. Few organizations in the geothermal community have relied as much on the results of petrological research in their geothermal development as PNOC/EDC in the Philippines, thanks to the excellent work of Agnes G. Reyes and her colleagues. We are very grateful to her for writing up her lecture notes and, thus, make the lectures available to a very much larger audience than those who were so fortunate to attend the lectures in Reykjavík. She has been and will be an inspiration for everybody who studies how a geothermal system functions.

Since the foundation of the UNU Geothermal Training Programme in 1979, it has been customary to invite annually one internationally renowned geothermal expert to come to Iceland as the UNU Visiting Lecturer. This has been in addition to various foreign lecturers who have given lectures at the Training Programme from year to year. It is the good fortune of the UNU Geothermal Training Programme that so many distinguished geothermal specialists have found time to visit us. Following is a list of the UNU Visiting Lecturers during 1979-1998:

1979 Donald E. White	United States	1989 Peter Ottlik	Hungary
1980 Christopher Armstead	United Kingdom	1990 Andre Menjoz	France
1981 Derek H. Freeston	New Zealand	1991 Wang Ji-yang	China
1982 Stanley H. Ward	United States	1992 Patrick Muffler	USA
1983 Patrick Browne	New Zealand	1993 Zosimo F. Sarmiento	Philippines
1984 Enrico Barbier	Italy	1994 Ladislaus Rybach	Switzerland
1985 Bernardo Tolentino	Philippines	1995 Gudmundur Bödvarsson	United States
1986 C. Russel James	New Zealand	1996 John Lund	United States
1987 Robert Harrison	UK	1997 Toshihiro Uchida	Japan
1988 Robert O. Fournier	United States	1998 Agnes G. Reyes	Philippines/ New Zealand

With warmest wishes from Iceland,

Ingvar B. Fridleifsson, director,
United Nations University
Geothermal Training Programme

TABLE OF CONTENTS

Page

PREFACE . . . 3

TABLE OF CONTENTS . . . 4

LIST OF FIGURES . . . 5

LIST OF TABLES . . . 6

LECTURE 1: THE APPLICATION OF PETROLOGICAL TECHNIQUES TO GEOTHERMAL EXPLORATION AND EXPLOITATION IN THE PHILIPPINES . . . 7
1. Geological setting of high-temperature geothermal systems in the Philippines . . . 7
2. Factors affecting hydrothermal alteration . . . 8
3. Data gleaned from petrographic techniques . . . 8
4. Temperature . . . 9
5. Fluid chemistry / source of fluids . . . 16
6. Permeability . . . 19
7. Processes . . . 20
8. Thermal history . . . 20
9. Pressure . . . 22
10. How are petrological data used in the study and operation of geothermal systems? . . . 22

LECTURE 2: NEUTRAL pH ALTERATION: FROM DIAGENESIS TO HYDROTHERMAL ALTERATION TO CONTACT METAMORPHISM . . . 26
1. Characteristics of neutral pH alteration in Philippine geothermal systems . . . 26
2. Alteration types . . . 28
3. Case study: Neutral pH alteration in Tongonan, the Philippines . . . 29
4. Diagenesis and hydrothermal alteration . . . 30

LECTURE 3: ACID ALTERATION IN PHILIPPINES: FROM THE VADOSE ZONE TO THE HYDROTHERMAL MAGMATIC INTERFACE . . . 33
1. Occurrences . . . 33
2. Mineralogy . . . 34
3. Types of alteration according to water composition . . . 35
4. Types of acid fluids according to the virulence and corrosivity of the associated fluids and the propensity of the assemblage to the rejuvenate fluid acidity . . . 36
5. Fluid inclusions . . . 36
6. Rock chemistry . . . 36
7. Fluid chemistry . . . 37
8. Origin and criteria for determining when acid alteration is active . . . 37
9. Notes on acidity of hydrothermal fluids according to Giggenbach (1977b) . . . 38
10. Magmatic-hydrothermal systems in the Philippines and their characteristics . . . 40

LECTURE 4: REDISTRIBUTION OF LIGHT ELEMENTS DURING HYDROTHERMAL ALTERATION: ELEMENTAL MOBILITY AND ION BEAM ANALYSIS . . . 41
1. Nomenclature . . . 41
2. Uses . . . 41

LECTURE 5: VOLCANIC ASH LEACHATE COMPOSITION AS A MEANS OF MONITORING VOLCANIC VAPOUR DISCHARGES DURING EXPLOSIVE ERUPTIONS . . . 43
1. Hydrothermal and magmatic components in the 1995-1996 Ruapheu ashes (abstract) . . . 43

Page

REFERENCES 44

APPENDIX I: Mineralogy, distribution and origin of acid alteration in Philippine geothermal systems (Reyes, 1991) 47

APPENDIX II: Petrological and geochemical characteristics of magmatic-hydrothermal systems in the Philippines (Reyes, 1994) 55

APPENDIX III: Petrology and fluid chemistry of magmatic-hydrothermal systems in the Philippines (Reyes and Giggenbach, 1992) 61

APPENDIX IV: Distribution of lithium, boron and chloride between fresh and altered rocks in the Kawerau geothermal system, New Zealand (Reyes and Vickeridge, 1996) 65

APPENDIX V: Litium and boron distribution in geological samples (Trompetter et al., 1999) 71

LIST OF FIGURES

1. Geochemical model of a typical Philippine geothermal system 7
2. $\delta^{18}O$ and δD of discharge fluids 8
3. Selected mineral geothermometers in Philippine geothermal systems 10
4. Range of stable temperatures for hydrothermal minerals in Wairakei 11
5. Mineral zones and sub-zones in various geothermal systems 12
6. Changes in epidote crystal occurrences and morphology 13
7. Organic and inorganic geothermometry in sedimentary basins and geothermal systems 14
8. Vitrinite reflectance data in geothermal systems plotted against temperature 14
9. Fluid inclusion temperatures in the Alto Peak wells 15
10. Stability of hydrothermal minerals as a function of f_{CO2} and temperature 15
11. R_H vs temperature and mineral sulphides 16
12. Using fluid inclusions to define fluid salinities, possible CO_2 contents and processes 17
13. Alteration types, assemblages and processes in Alto Peak 17
14. Types of hydrothermal alteration systems according to a qualitative "fluid/rock" ratio 18
15. Types of metasomatism according to "fluid/rock" ratio 18
16. Cross-section showing the various processes found in a hydrothermal system 19
17. Patterns formed by plotting homogenisation vs. freezing point temperatures 20
18. Stratigraphic column and thermal events in Palinpinon 21
19. Estimated thermal history of Palinpinon based on thermoluminescence 22
20. Mineral paragenesis in the Poihipi sector, Wairakei geothermal system, New Zealand 22
21. Example of a preliminary petrological output during drilling 23
22. Hydrological model of a geothermal system (plan view) 24
23. Hydrological model of a geothermal system (vertical view) 25
24. Variations in smectite:illite ratios with increase in temperature 26
25. Cross-section of mineral zones and sub-zones and stable temperature isotherms in Tongonan . . 27
26. Changes in Mg-rich clays with depth and temperature in Bac-Man wells 27
27. Juxtaposition of the two types of clay assemblages in Mahagnao 28
28. Variations in rock chemistry during neutral pH alteration 28
29. Temperature ranges of mineral zones and sub-zones in Tongonan 29

Page

30. Distribution of anhydrite and calcite in Tongonan 30
31. Permeable faults in Tongonan 30
32. Paragenesis in a New Zealand hydrocarbon system 32
33. Geologic model of Philippine geothermal systems 33
34. Distribution of acid alteration in Hatchobaru, Japan 34
35. Sharp boundaries between acid and neutral pH alteration in a core 34
36. Acid alteration zones in the Philippines 35
37. Variations in acidity due to HCl, with temperature 39
38. Stability of Al-silicates as a function of m_{HCl}/m_{KCl} and temperature 40
39. Example of a vapour-cored hydrothermal system in the Philippines 40
40. Variations in the relative elemental compositions of blue-luminescing feldspars 40
41. Variations in the concentrations of element in differently coloured quartz 41
42. Elemental maps of a sedimentary rock section 42

LIST OF TABLES

1. Examples of processes in Philippine geothermal wells/systems and their associated mineralogical, fluid inclusion and water compositions 21
2. Comparison between diagenesis and hydrothermal neutral pH alteration 31
3. Comparison between acid and neutral pH well discharges 37
4. Criteria for predicting the immediacy of acid fluid influx and effects in a geothermal well 38

LECTURE 1

THE APPLICATION OF PETROLOGICAL TECHNIQUES TO GEOTHERMAL EXPLORATION AND EXPLOITATION IN THE PHILIPPINES

1. GEOLOGICAL SETTING OF HIGH-TEMPERATURE GEOTHERMAL SYSTEMS IN THE PHILIPPINES

Tectonic setting. Most high-temperature geothermal systems in the Philippines are located within a region of active oblique plate convergence involving two sets of subduction zones to the east and west of the archipelago. Others are found in areas associated with post-collision volcanism, rifting in the Macolod Corridor and shearing along the Philippine Fault Zone.

Volcanic setting. Most geothermal areas are associated with Pleistocene to Recent calc-alkaline to alkaline volcanic complexes dominated by andesite, sometimes with domes of silicic andesite to dacite.

General well stratigraphy. From top to bottom the stratigraphy consists of Pliocene to Recent andesitic to dacitic extrusives, andesitic hyaloclastites and minor basalts; Miocene to Late Pliocene carbonaceous sedimentary rocks. These are intruded by dikes. Basement may be a massive diorite pluton or a heterolithologic sedimentary breccia with clasts of intrusive rocks, volcaniclastics and serpentinites.

Topography is very rugged and differences in elevation within a geothermal resource may vary from 750 to 2500 m. This affects the hydrology of the system such as the depth of the water table (200-800 m from surface), phase separation within the reservoir, the distribution and type of thermal manifestations (Figure 1). These in turn have a bearing on the hydrothermal alteration patterns and mineral assemblages.

Geochemical gradients. There are steep geochemical gradients. Reservoir Cl ranges from 3,000 to 10,000 mg/kg and is usually associated with high gas contents. Magmatic content based on $\delta^{18}O$ and δD of well discharges ranges from zero to 90% (Figure 2).

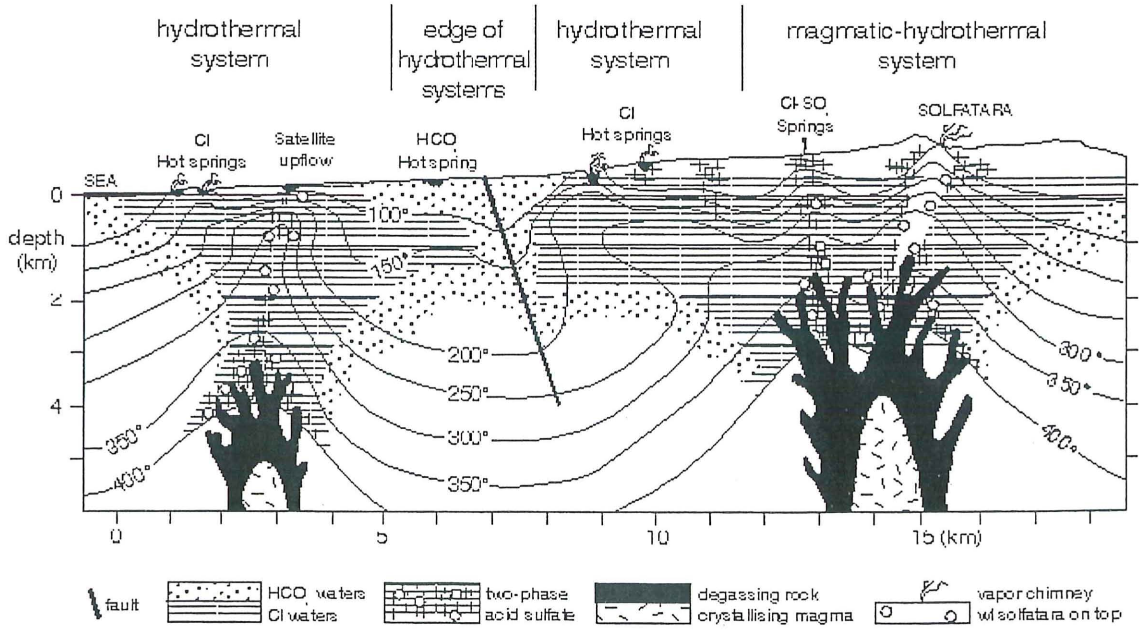


Figure 1: Geochemical model of a typical Philippine geothermal system (Reyes, 1995)

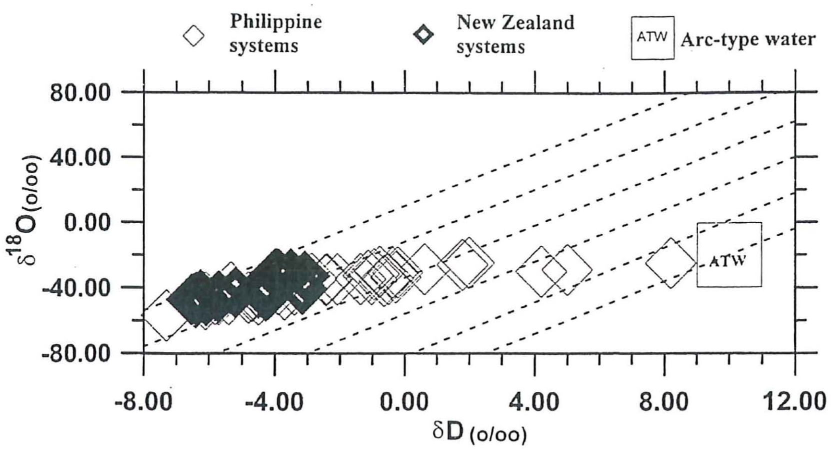


Figure 2: $\delta^{18}O$ and δD of discharge fluids in Philippine and New Zealand geothermal systems (Reyes, 1995)

2. FACTORS AFFECTING HYDROTHERMAL ALTERATION

- Temperature;
- Permeability (related to gas contents and hydrology of a system);
- Fluid composition (acid, neutral pH; high or low gas; vapour- or water-dominated; magmatic, meteoric);
- Initial composition of rocks;
- Duration of activity (immature, mature);
- Number of superimposed hydrothermal regimes (overprinting of alteration);
- Hydrology (affected by topography).

3. DATA THAT CAN BE GLEANED FROM VARIOUS PETROGRAPHIC TECHNIQUES (Reyes, 1992)

- Temperature from:
  - Hydrothermal mineralogy;
  - Fluid inclusions;
  - Vitrinite reflectance.

- Fluid chemistry/Source of fluids from:
  - Hydrothermal mineralogy;
    - *Neutral pH alteration assemblage,
    - *Acid alteration assemblage.
  - Stability diagrams;
  - Fluid inclusion data;
    - *Salinity,
    - *CO_2 contents,
    - *Presence of other gases and fluids.

- Permeability from:
  - Structures;
  - Mineralogy;
  - Rock types;

- Processes from:
  - Mineralogy;
  - Fluid inclusions;
  - Rock structures.

  These processes include:
  - Steam-heating;
  - Condensation;
  - Boiling of hot aquifer fluids;
  - Incursion of cool groundwaters;
  - Neutralisation of acid waters;
  - Formation of vapour-dominated zones;
  - Influx of magmatic fluids;
  - Formation of sealed zones.

  Geological processes that produce secondary minerals in Philippine geothermal systems:
  - Weathering;
  - Serpentinisation;
  - Devitrification of glass;
  - Diagenesis;
  - Hydrothermal;
  - Magmatic-hydrothermal;
  - Contact metamorphism.

- The thermal history of a system can be unravelled using:
  - Mineral paragenesis
  - Cross-cutting relationships among veins, intrusives;
  - Palaeontology;
  - Thermoluminescence;
  - K/Ar dating of alteration minerals.

- Rough estimate of the thickness of eroded overburden.

4. TEMPERATURE

Temperature not only controls, to a degree, the composition of secondary mineral assemblages but also the rate of alteration processes. Figure 3 lists common minerals used as geothermometers in Philippine geothermal systems. Temperatures are often ± 20°C.

Setting up mineral geothermometers in individual Philippine geothermal systems

Assumptions:

A. There has been a single field-wide hydrothermal pulse that is presently active and thus secondary minerals reflect present conditions;
B. No large fault displacements have occurred since the onset of the hydrothermal activity;
C. There is minimal internal flow in the wells that may mask stable well temperatures;
D. There is little variation in rock compositions in the stratigraphic column.

However, most Philippine systems are characterised by:

A. The occurrence of at least two pulses of hydrothermal activity as indicated by multi-modal fluid inclusion homogenisation temperatures, retrogradation of alteration minerals, crosscutting veins and the presence of multiple intrusive events;
B. The occurrence of large normal fault displacements (350 m) after rock alteration;
C. Wells with multi-feed zones that cause internal flows are common.

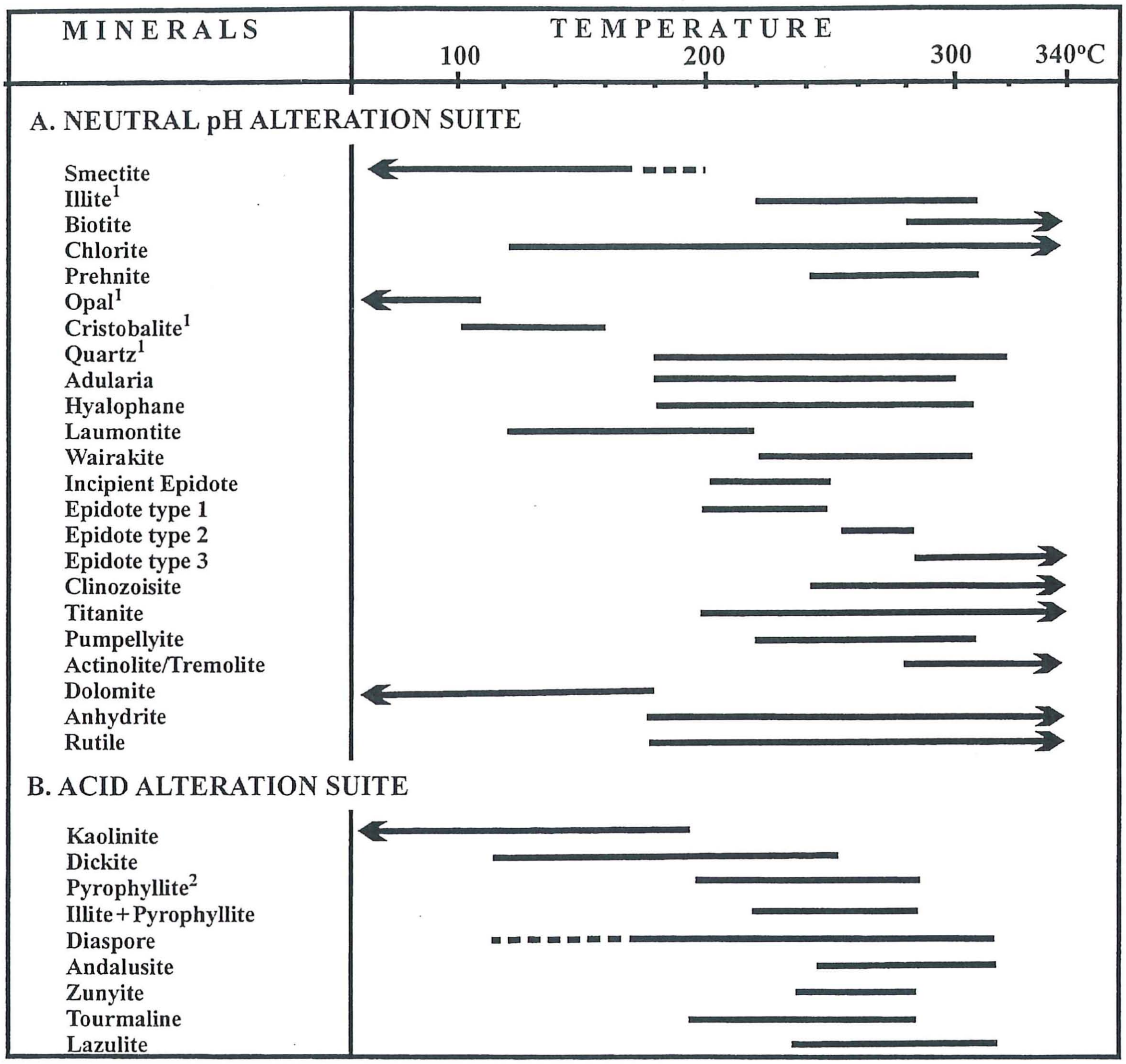


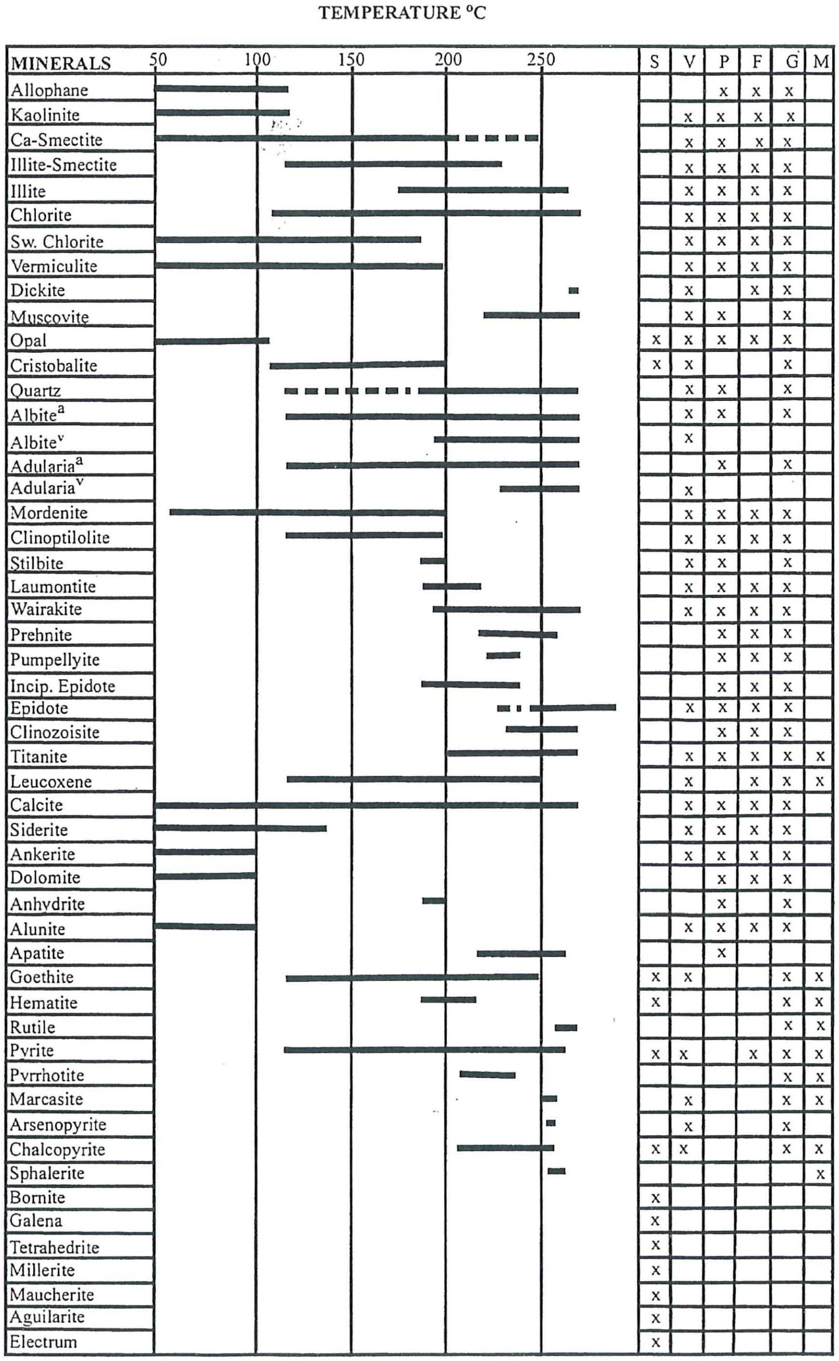
Figure 3: Selected minerals in Philippine geothermal systems commonly used as geothermometers (Reyes, 1990)

Despite these encumbrances, fluid inclusions and measured stable temperatures were gathered from more than 100 deep geothermal wells, sampled every 3-5 m, and compared to secondary mineral occurrences. When determining possible mineral geothermometers, a list of hydrothermal minerals and their stable temperature ranges in a geothermal system, such as in Wairakei (Figure 4), are first drawn up. From this list, common minerals with specific temperature ranges are selected and used as geothermeters as shown in Figure 3 for the Philippines.

As a shortcut, the various minerals can be grouped into zones and subzones associated with characteristic mineral assemblages. Such zones are used to give gross approximations of well temperatures.

Often minerals are divided into clay zones and calc-silicate sub-zones because of

- their common occurrence and abundance;
- their sensitivity to thermal and fluid composition changes;
- the easy megascopic identification of epidote, wairakite, garnet, smectite and actinolite-tremolite in the field using a light microscope (Figure 5).



MINERALS	S	V	P	F	G	M
Allophane			x	x	x	
Kaolinite		x	x	x	x	
Ca-Smectite		x	x	x	x	
Illite-Smectite		x	x	x	x	
Illite		x	x	x	x	
Chlorite		x	x	x	x	
Sw. Chlorite		x	x	x	x	
Vermiculite		x	x	x	x	
Dickite		x		x	x	
Muscovite		x	x		x	
Opal	x	x	x	x	x	
Cristobalite	x	x			x	
Quartz		x	x		x	
Albite^a		x	x		x	
Albite^v		x				
Adularia^a			x		x	
Adularia^v		x				
Mordenite		x	x	x	x	
Clinoptilolite		x	x	x	x	
Stilbite		x	x		x	
Laumontite		x	x	x	x	
Wairakite		x	x	x	x	
Prehnite			x	x	x	
Pumpellyite			x	x	x	
Incip. Epidote			x	x	x	
Epidote		x	x	x	x	
Clinozoisite			x	x	x	
Titanite		x	x	x	x	x
Leucoxene		x		x	x	x
Calcite		x	x	x	x	
Siderite		x	x	x	x	
Ankerite		x	x	x	x	
Dolomite			x	x	x	
Anhydrite			x		x	
Alunite		x	x	x	x	
Apatite			x			
Goethite	x	x			x	x
Hematite	x				x	x
Rutile					x	x
Pyrite	x	x		x	x	x
Pyrrhotite					x	x
Marcasite		x			x	x
Arsenopyrite		x			x	
Chalcopyrite	x	x			x	x
Sphalerite						x
Bornite	x					
Galena	x					
Tetrahedrite	x					
Millerite	x					
Maucherite	x					
Aguilarite	x					
Electrum	x					

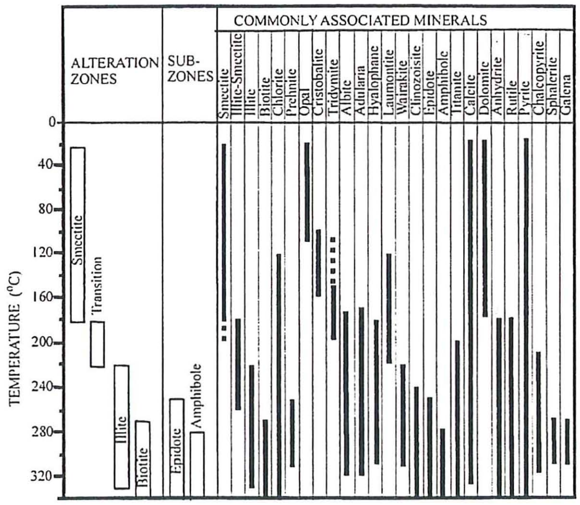
Figure 4: Range of stable temperatures for hydrothermal minerals in Wairakei; mineral occurrences: S = scale material, V = vein or vug mineral, P = secondary mineral replacing feldspars, F = minerals replacing ferromagnesians, G = minerals replacing the groundmass, M = minerals replacing titanomagnetite, a = alteration, v = vein (compiled by Reyes et al., 1994)

Further temperature predictions within the calc-silicate sub-zone of Philippine geothermal systems can be made by

- the appearance of hydrogrossular/grossular garnet (>260°C), wairakite(>230°C) and actinolite-tremolite (>280°C);
- the occurrences and crystal morphology of epidote (Figure 6).

ZONE	SUB-ZONE	MINERAL ASSOCIATION	TEMPERATURE RANGE (°C)
Montmorillonite	Mordenite	Smectite, mordenite, siderite goethite, chlorite, pyrite, pyrrhotite. Primary andesine usually unaltered	Ambient to 230°C
	Laumontite	Laumontite, carbonates, goethite, chlorite, iron sulfides	(180-230°C)
Intermediate	Upper	Plagioclase is replaced by wairakite, albite, calcite, illite-smectite, quartz, chlorite	230-240°C
	Lower	Mineralogy as above but with the appearance of epidote and illite	>240°C
K-Feldspar		Characterised by presence of adularia and intense silicification. Plagioclase is replaced by adularia, albite, wairakite and illite in various associations	>240°C

A



B

Figure 5. Mineral zones and sub-zones in various geothermal systems; A. Wairakei (Steiner, 1977); B. Neutral pH alteration in the Philippines (Reyes, 1990); C. Iceland (Kristmannsdóttir, 1982).

Rock Temperature oC	Alteration zones	Index Minerals	Mineralogical Characteristics	Regional Metamorphic Facies
50	I a	Chabazite Smectite Scolecite Stilbite Laumontite	Low temperature zeolites and smectite forms	Zeolite
100			Low temperature zeolites → laumontite	Facies
150	b		Smectite interlayered	
200		Wairakite	Laumontite → wairakite Smectite → mixed-layer clay minerals	
	II	Mixed-layer clay minerals	Mixed-layer clay minerals → chlorite	
250	III	Chlorite Epidote	Epidote - continuous occurrence	
			Actinolite forms	Greenschist
300	IV	Chlorite Actinolite	Plagioclase commonly albitized	Facies

C

Temperature also affects the metamorphism of organic material in geothermal areas where carbonaceous sedimentary rocks can be intersected in deep wells such as in the Philippines, New Zealand, Mexico and the USA. The reflectance in oil (R_{oil}%) of organic fragments or macerals, especially vitrinite, increases proportionally with temperature. Figure 7 shows a comparison among organic and inorganic geothermometers in sedimentary basins and geothermal systems with increasing reflectance (R_{oil}%) and temperature. The metamorphic zones in Figure 7 refer to organic material alteration.

PROCESSES	<180°C	180-220°C	240-260°C	>280°C	Cooling and/or change in chemical environment
Primary	Ti-magnetite ↓ Leucoxene	TiO_2 polymorphs ↓ Fine-grained titanite	TiO_2 polymorphs ↓ → Epidote	TiO_2 polymorphs ↓ Epidote	
Mineral		Glass ↓ Fine-grained highly birefringent "incipient" epidote	→ Epidote	→ increase in Epidote abundance and crystal size	Crystal "clouding" due to formation of brown amorphous material
					Crystals become etched
			Plagioclase + Ferromagnesians ↓ partial alteration to Epidote	→ Epidote replacement becomes pervasive	Epidote becomes stained with goethite
Transformations		Titanite appears	→ Epidote	→ increase in Epidote abundance and crystal size	
Vein epidote				Vein Epidote becomes common	
Other associated minerals	Deposition of calcite and/or anhydrite	Calcite and anhydrite persist			

PROGRADATION, increasing alteration rank and generally, alteration intensity → RETROGRADATION

Increase in Epidote abundance, crystal size, →

Figure 6: Changes in epidote crystal occurrences and morphology with increase in temperature (Reyes, unpublished results)

Vitrinite reflectance in geothermal systems, such as in various geothermal areas in New Zealand, Cerro Prieto, Salton Sea and the Philippines have been measured. These points are plotted in Figure 8. Initially these were compared to the regression line for Cerro Prieto drawn up by Barker (1979). Analyses from the Philippines (p) fall along the Cerro Prieto line. The Salton Sea samples (s) lie along its own, steeper, correlation line. Above 200°C vitrinite reflectance data from New Zealand geothermal systems (Struckmayer, 1983; Gonzales, 1985) cluster within a narrow range for a given temperature. However, below 150°C, vitrinite reflectance values are scattered due probably to the role of kinetics in altering maceral compositions (Figure 8).

Fluid inclusion homogenisation temperatures are commonly measured in anhydrite, quartz, calcite, wairakite, K-feldspar and sphalerite occurring in veins or as replacement material. Both primary and secondary fluid inclusions are studied, although results from the latter often match measured well temperatures. In the Philippines, material from both cuttings and cores are collected and analysed. To circumvent any contamination from shallower levels in cuttings, homogenisation temperatures are always measured in at least six different crystals from each sampled depth, since fluid inclusion results are basically statistical. Temperature histograms in most Philippine studies tend to show more scatter at temperatures higher than measured in the well. Thus contamination from shallower depths, may often not be as serious as anticipated. An example of fluid inclusion results in Alto Peak, the Philippines, is shown in Figure 9.

Fluid inclusion homogenisation temperatures

- provide a more precise picture of thermal pulses;
- often reflect stabilised well temperatures.

The stability of hydrothermal minerals as a function of f_{CO_2} and temperature (Figure 10) can be determined using thermodynamic data, as used by Giggenbach (1997a).

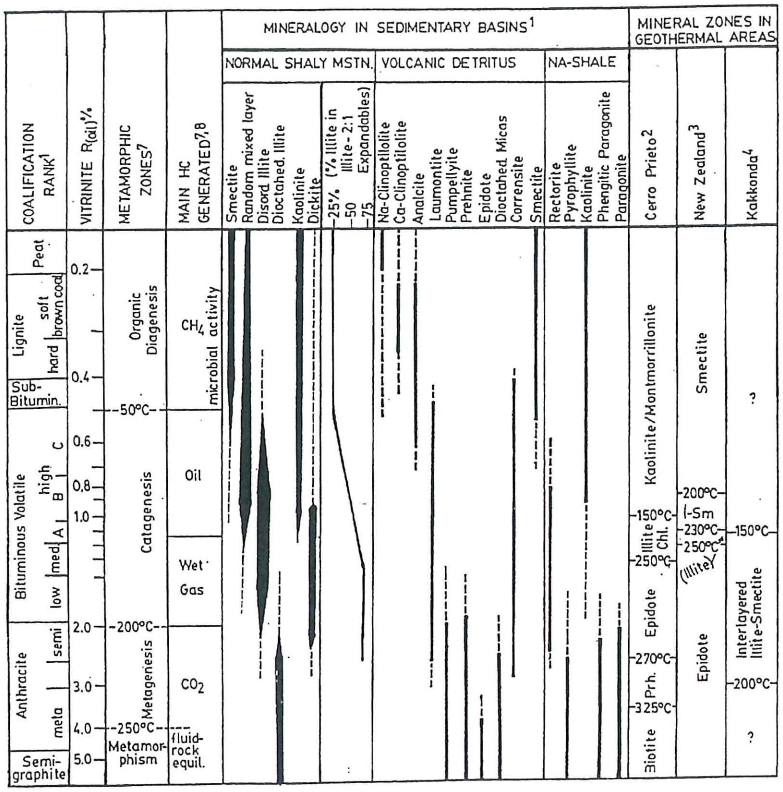


Figure 7: A diagram comparing organic and inorganic geothermometry in sedimentary basins and geothermal systems; organic geothermometry is based on the reflectance in oil (R_o%) of vitrinite macerals and inorganic geothermometry on secondary minerals ([1]Heroux et al. (1979); [2]Barker (1979); [3]Struckmayer (1983); [4]Taguchi et al. (1983); [5]Diessel and Offer (1975); [6]Stach et al. (1982); [7]Giggenbach (1997a); [8]Tissot and Welte (1984))

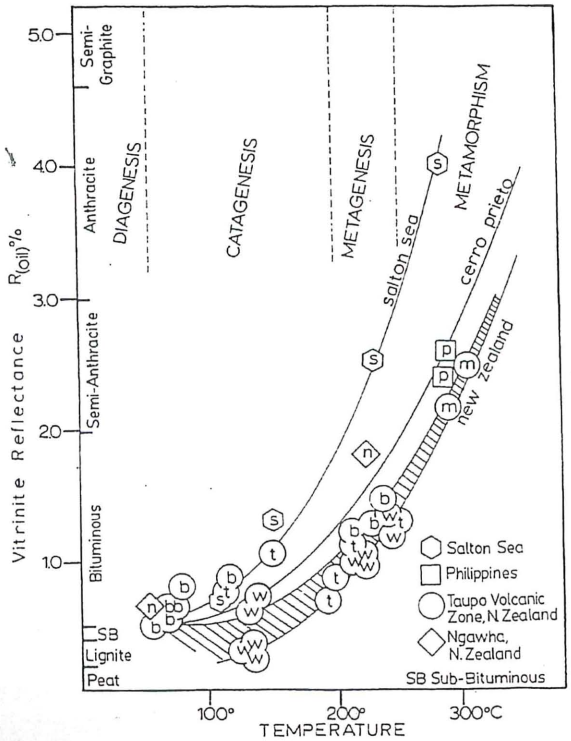


Figure 8: Vitrinite reflectance data in Philippine, New Zealand, Salton Sea and Cerro Prieto geothermal systems plotted against measured well or fluid inclusion temperatures (data from Bostick, 1971; Barker, 1979; Struckmayer, 1983; Reyes, 1984; Gonzales, 1985); explanations: s = Salton Sea; n = Ngawha; b = Broadlands; w = Wairakei; t = Tauhara; m = Ngatamariki; p = the Philippines

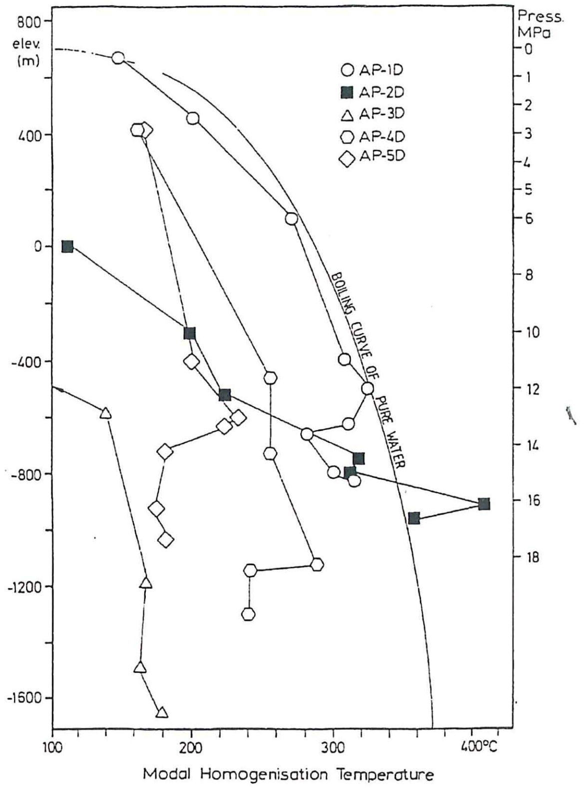


Figure 9: Fluid inclusion temperatures in the Alto Peak wells, the Philippines, plotted against elevation and compared to the boiling point curve for pure water (Reyes et al., 1993)

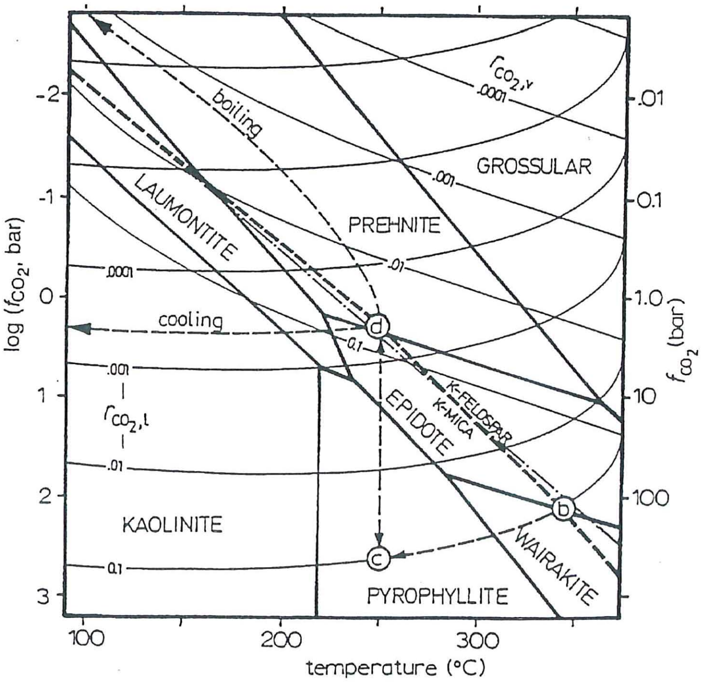


Figure 10: Stability of hydrothermal minerals as a function of f_{CO_2} and temperature (Giggenbach, 1997b)

5. FLUID CHEMISTRY/SOURCE OF FLUIDS

The hydrothermal mineral assemblages, both non-opaque (Figure 3) and opaque minerals in combination with mineral thermodynamic data and activity diagrams (Figs 10 and 11) can be used to predict the probable water and gas compositions of aquifers in a well during drilling. Fluid inclusion petrographic characteristics and freezing point measurements can be used to determine past and present water salinities and relative gas contents (Figure 12). The source of fluids can be determined from stable isotope compositions, such as $\delta^{18}O$, δD (Figure 2) and $\delta^{32}S$, of mineral components or well discharges.

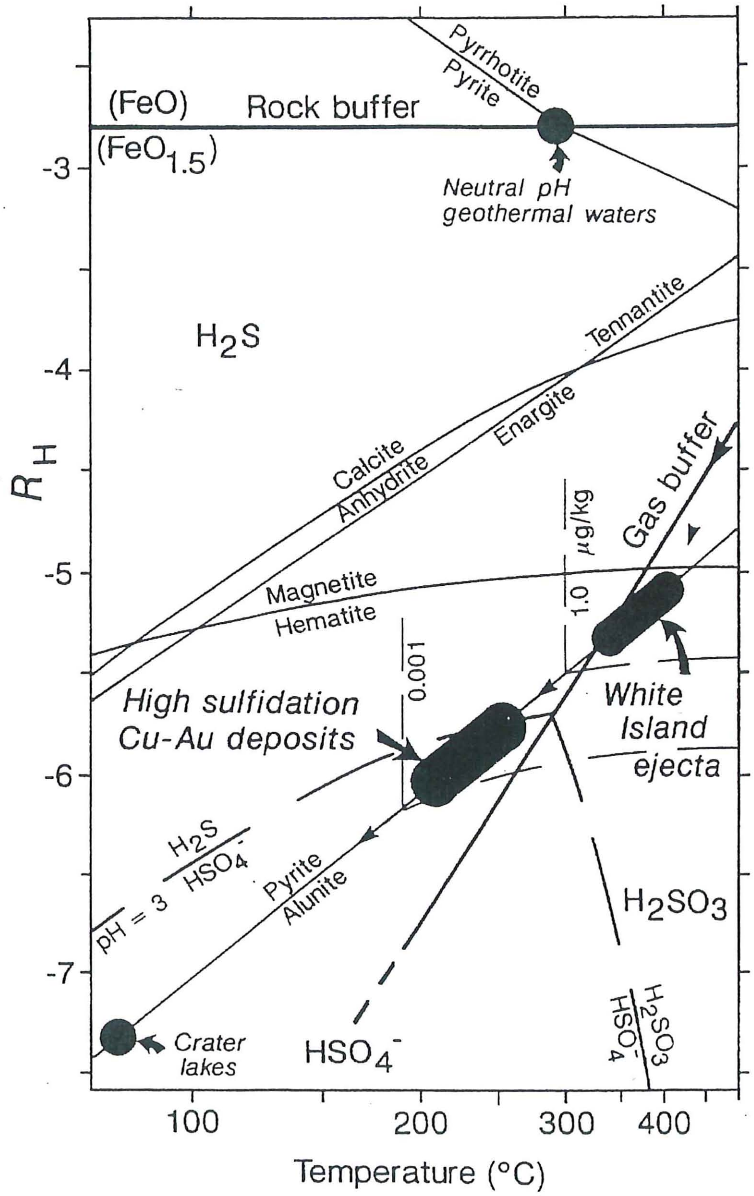


Figure 11: R_H vs temperature and mineral sulfides (Hedenquist et al, 1993)

Types of hydrothermal alteration. Alteration mineral assemblages may indicate the acidity and corrosivity of hydrothermal fluids and are divided into two major types:

Neutral pH alteration associated with *mature* geothermal systems;
Acid alteration associated with *immature* geothermal systems or upflows. Acid alteration can be divided into three major types, each with their characteristic mineral assemblages, temperature ranges and associated water compositions.

Examples of minerals in each alteration suite are shown in Figure 4 and alteration types, alteration assemblages and alteration processes in Alto Peak are shown in Figure 13.

Fluid/Rock ratio. Hydrothermal alteration systems may be subdivided into two main types depending on the relative proportions of fluid and rock involved in the hydrothermal process (Figure 14):
- Rock-dominated and
- Fluid-dominated

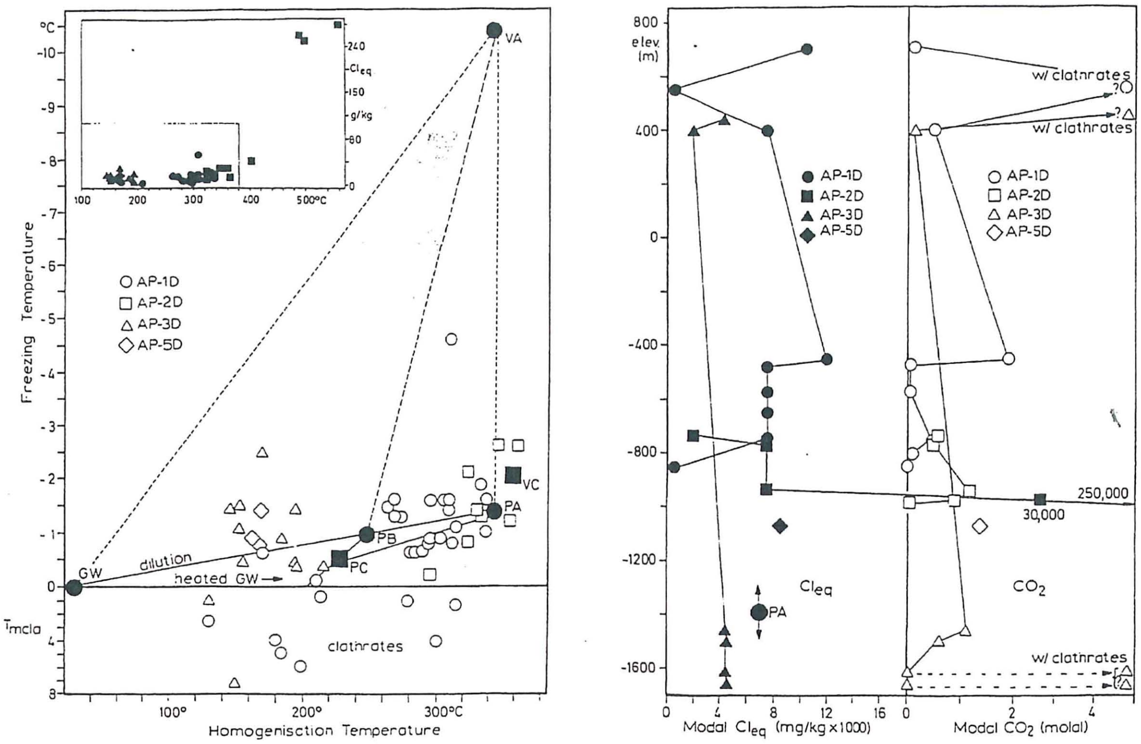


Figure 12: Using fluid inclusions to define fluid salinities, possible CO_2 contents and processes in the Alto Peak wells, the Philippines (Reyes et al., 1993)

Fluid/rock ratios are defined rigorously only in closed or stagnant systems. In natural generally open and dynamic systems, the fluid/rock ratio cannot be quantified but can still be used qualitatively to refer to relative effects, rather than quantities of fluid and rock involved in the hydrothermal process. With increasing effective fluid/rock ratios, the following four major situations can be delineated:

- In the absence of a fluid, such as in highly impermeable formations, the primary rock remains;
- The presence of a minor, essentially stagnant fluid phase facilitates isochemical recrystallization, accompanied by hydration;
- At high fluid/rock ratios, the alteration process is increasingly dominated by the introduction and removal of fluid phase components leading to the replacement or metasomatism of primary minerals;
- At very high fluid/rock ratios, in sufficiently aggressive environments, the rock may dissolve altogether as in acid environments.

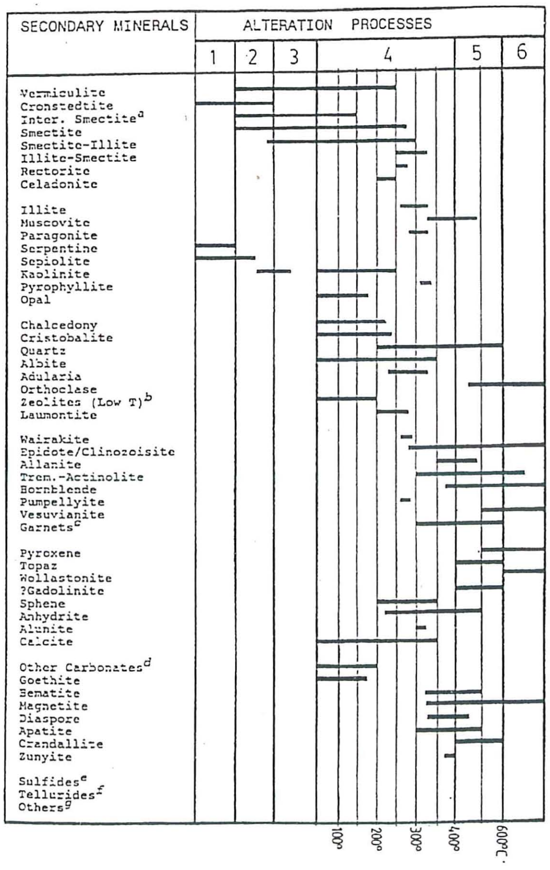


Figure 13: Alteration types, assemblages and processes in Alto Peak, the Philippines (Reyes et al., 1993)

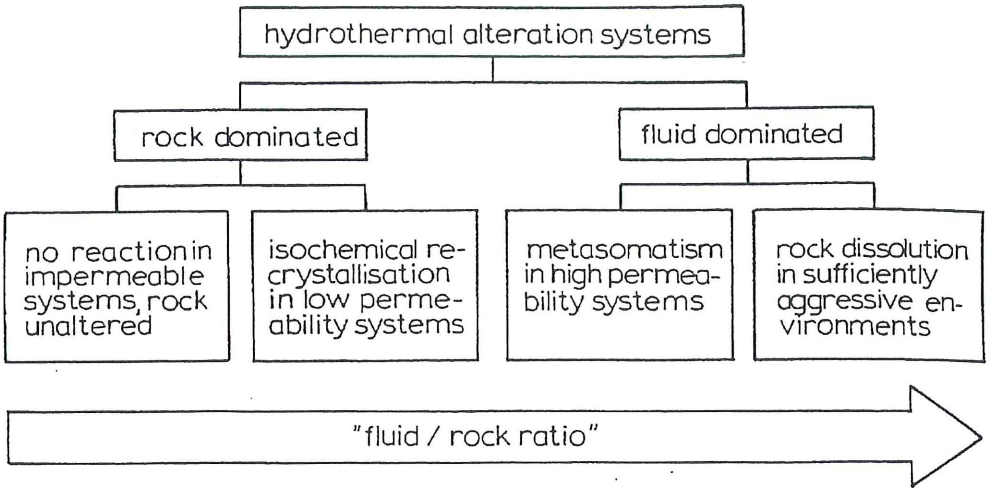


Figure 14: A Giggagram showing types of hydrothermal alteration systems according to a qualitative fluid/rock ratio (Giggenbach, 1997b)

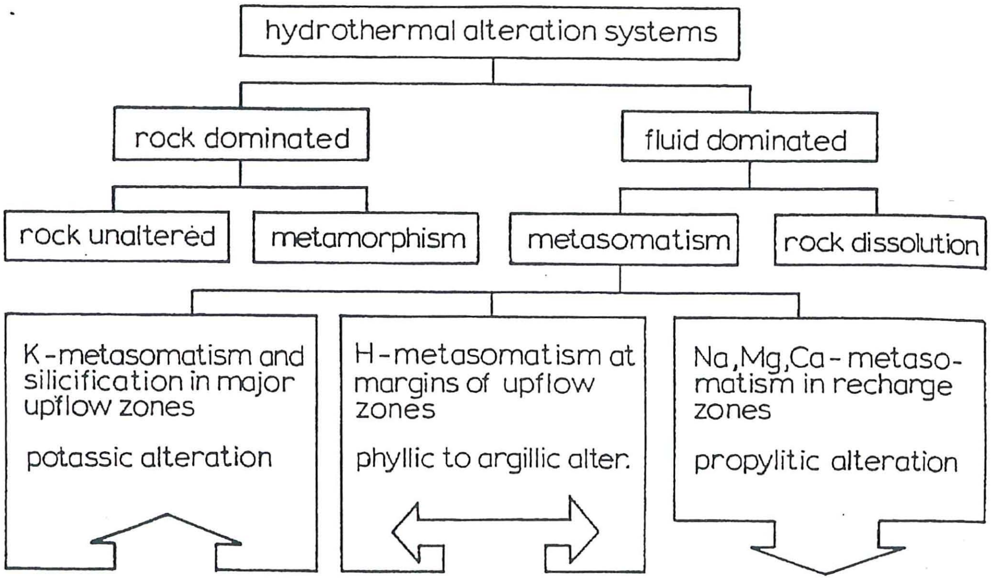


Figure 15: A Giggagram showing various types of metasomatism according to "fluid/rock" ratio (Giggenbach, 1997b)

Metasomatism during fluid-dominated alteration processes may be subdivided into three sub-processes (Figures 15 and 16):

- K-metasomatism accompanied by silicification in major upflow zones, giving rise to potassic alteration;
- H-metasomatism due to rapid cooling along the margins of upflow zones leading to argillic and phyllic alteration;
- Na, Mg, Ca metasomatism in response to increasing temperatures in recharge zones leading to propylitic alteration (Giggenbach, 1997b).

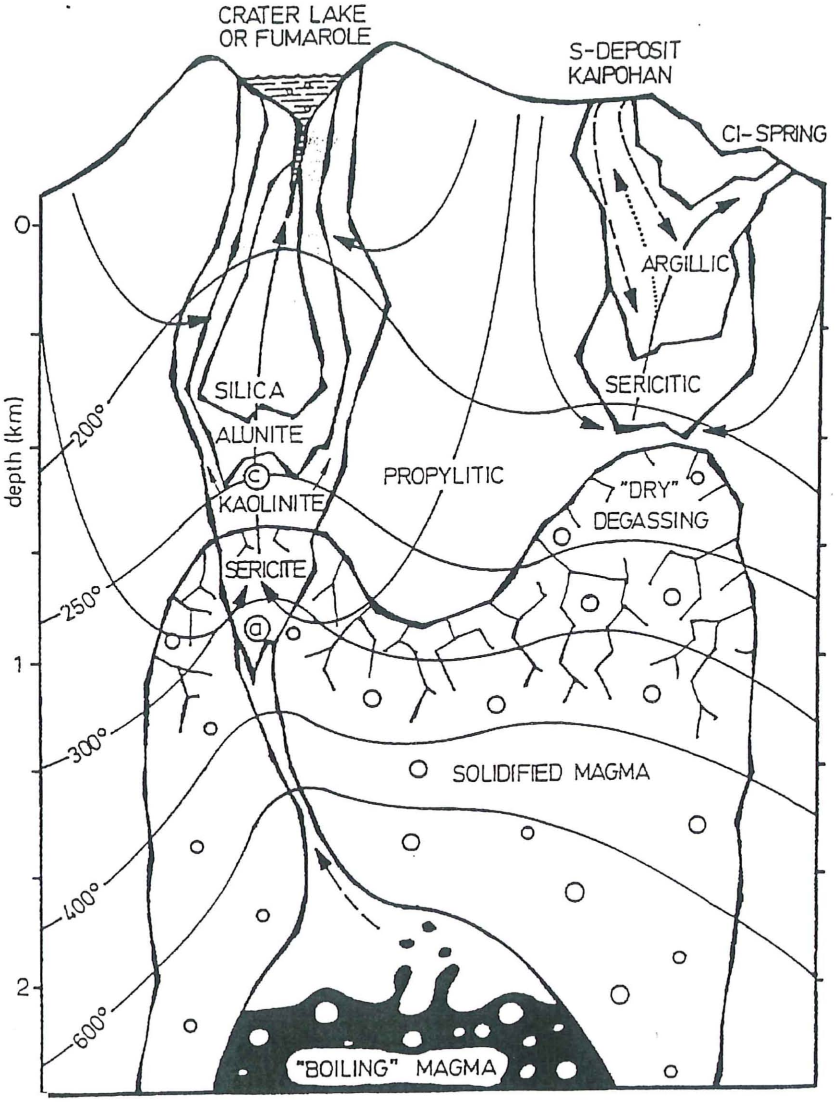


Figure 16: Cross-section showing the varióus processes found in a hydrothermal system (Giggenbach 1997b)

6. PERMEABILITY

Sources of permeability in Philippine geothermal systems are the following:

- Faults with dips of 60° - 90° (mostly normal, rarely reverse faults);
- Fractures or joints due to intrusions and along edges of plugs and domes;
- Lithological contacts;
- Clast:matrix or fragment:fragment contacts in breccia, especially hyaloclastites;
- Paleosols.

Fault intersections are the major sources of permeability in Philippine systems. Most wells in the Philippines are drilled directionally because of rugged topography in most geothermal sites. These wells have an advantage, too, in intersecting more faults that may provide permeable zones. Evidences used to infer faults during or after drilling, as shown below, should be used together:

- Permeable zones detected during well completion tests;
- Bit walks during drilling;
- Drilling losses with or without subsequent blind drilling;
- Intense to complete alteration of rock samples;
- Abundant veins;
- Presence of mylonites and fault-comminuted rock samples;
- Presence of acid alteration below 200 m.

Types of faults according to their role in the geothermal reservoir and the type of fluids they channel:

- Conduits for hot aquifer fluids;
- Channels for cooler, often dilute groundwaters;
- Pathways for acid solutions;
- Conduits for magmatic fluids.

Rock characteristics indicative of possible aquifers:

- Presence of sheared rock and its association with abundant veins, drusy minerals and high alteration intensity.

Minerals indicative of good permeability in Philippine geothermal wells:

- Quartz, adularia, anhydrite, Wairakite, illite, hyalophane, abundant pyrite, abundant calcite (often drusy minerals).

Poor permeability indicators:

- Low alteration intensity, absence of the aforementioned minerals; presence of prehnite, pumpellyite, pyrrhotite and abundant laumontite and titanite; persistence of smectite and illite-smectite at >230°C; persistence of matrix dolomite or siderite at >180°C

7. PROCESSES

Characteristic mineralogical and fluid inclusion signatures can define certain hydrological processes, as listed in Table 1. Figure 17 shows patterns formed by plotting homogenisation vs. freezing point fluid inclusion temperatures. These are characteristic of certain well conditions or processes.

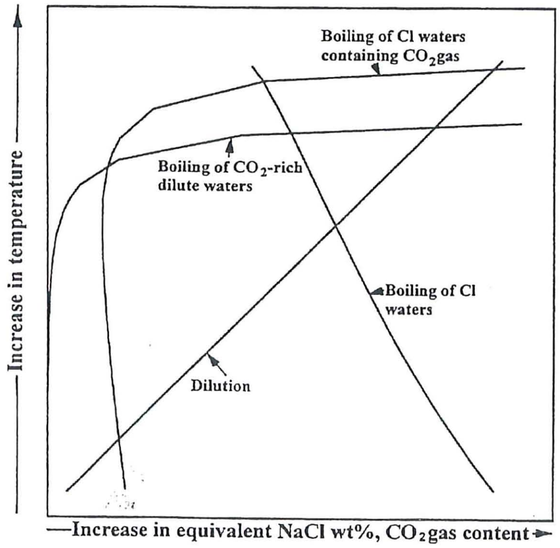


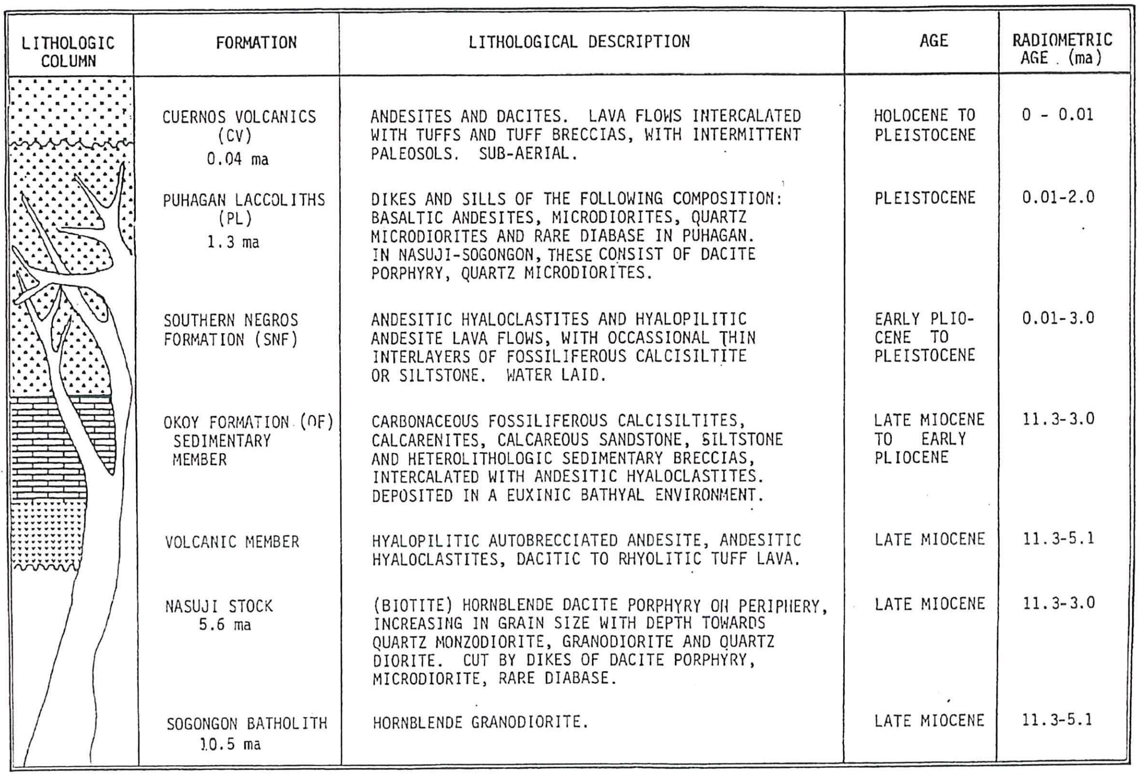
Figure 17: Patterns formed by plotting homogenisation vs freezing point fluid inclusion temperatures, characteristic of certain well conditions or processes

8. THERMAL HISTORY

By dating fossils in the sedimentary formations found in most geothermal systems and by dating intrusives using K-Ar dating methods, it was found that in most Philippine geothermal areas, the Upper Miocene to Early Pliocene sedimentary formations are affected by hydrothermal alteration, indicating that hydrothermal systems were initiated after the Pliocene (Figure 18). Another method used in dating thermal events is thermoluminescence, as in the Palinpinon geothermal region in the Philippines, illustrated in Figure 19.

Table 1: Examples of processes or conditions in geothermal wells/systems in the Philippines and their associated mineralogical, fluid inclusion and discharge or downhole water compositions (Reyes, unpublished results)

Process	Mineralogical indications	Fluid inclusion indications	Others
1. Condensation			
CO_2 to HCO_3 waters	Kaolinite + Marcasite + Chalcedony + Smectite + Calcite/Dolomite/Ankerite	Very dilute waters + CO_2	
H_2S to SO_4 waters	Kaolinite + Opal + Pyrite + Marcasite + Alunite + Chalcocite + native Sulfur		
2. Boiling of hot aquifer fluids	Drusy quartz, wairakite, anhydrite, adularia and/or hyalophane with or without associated illite ± epidote	Vapour-filled FI associated with liquid-filled ones have similar homogenisation temperatures (T_h). Pattern formed when plotting T_h vs T_m (ice melting temperatures) as shown in Figure 17.	
3. Cold water incursion	Abundant goethite in veins, as clots on matrix, as replacement of ferromagnesians and magnetite; Abundant Mg-rich minerals such as vermiculite, vermiculite-talc, dolomite, ankerite, Mg-rich chlorite, kerolite; Abundant montmorillonite; abundant calcite; Siderite and/or huntite may be present; Overlap of low- and high-temperature minerals	Bimodal T_h; near-zero T_m associated with low Th; pattern exhibited by plotting Th vs Tm	Downhole fluid chemistry shows a decrease in Cl and SiO_2 associated with an increase in Mg; measured well tempera-tures (T_{msd}) <175°C; depth <2700 m



LITHOLOGIC COLUMN	FORMATION	LITHOLOGICAL DESCRIPTION	AGE	RADIOMETRIC AGE (ma)
	CUERNOS VOLCANICS (CV) 0.04 ma	ANDESITES AND DACITES. LAVA FLOWS INTERCALATED WITH TUFFS AND TUFF BRECCIAS, WITH INTERMITTENT PALEOSOLS. SUB-AERIAL.	HOLOCENE TO PLEISTOCENE	0 - 0.01
	PUHAGAN LACCOLITHS (PL) 1.3 ma	DIKES AND SILLS OF THE FOLLOWING COMPOSITION: BASALTIC ANDESITES, MICRODIORITES, QUARTZ MICRODIORITES AND RARE DIABASE IN PUHAGAN. IN NASUJI-SOGONGON, THESE CONSIST OF DACITE PORPHYRY, QUARTZ MICRODIORITES.	PLEISTOCENE	0.01-2.0
	SOUTHERN NEGROS FORMATION (SNF)	ANDESITIC HYALOCLASTITES AND HYALOPILITIC ANDESITE LAVA FLOWS, WITH OCCASSIONAL THIN INTERLAYERS OF FOSSILIFEROUS CALCISILTITE OR SILTSTONE. WATER LAID.	EARLY PLIOCENE TO PLEISTOCENE	0.01-3.0
	OKOY FORMATION (OF) SEDIMENTARY MEMBER	CARBONACEOUS FOSSILIFEROUS CALCISILTITES, CALCARENITES, CALCAREOUS SANDSTONE, SILTSTONE AND HETEROLITHOLOGIC SEDIMENTARY BRECCIAS, INTERCALATED WITH ANDESITIC HYALOCLASTITES. DEPOSITED IN A EUXINIC BATHYAL ENVIRONMENT.	LATE MIOCENE TO EARLY PLIOCENE	11.3-3.0
	VOLCANIC MEMBER	HYALOPILITIC AUTOBRECCIATED ANDESITE, ANDESITIC HYALOCLASTITES, DACITIC TO RHYOLITIC TUFF LAVA.	LATE MIOCENE	11.3-5.1
	NASUJI STOCK 5.6 ma	(BIOTITE) HORNBLENDE DACITE PORPHYRY ON PERIPHERY, INCREASING IN GRAIN SIZE WITH DEPTH TOWARDS QUARTZ MONZODIORITE, GRANODIORITE AND QUARTZ DIORITE. CUT BY DIKES OF DACITE PORPHYRY, MICRODIORITE, RARE DIABASE.	LATE MIOCENE	11.3-3.0
	SOGONGON BATHOLITH 10.5 ma	HORNBLENDE GRANODIORITE.	LATE MIOCENE	11.3-5.1

Figure 18: Stratigraphic column and thermal events in Palinpinon, the Philippines, showing ages based on paleontology and K-Ar dates (PNOC-EDC unpublished data, 1990)

The relative history of a hydrothermal system can be unravelled using crosscutting relationships among veins and mineral paragenesis, together with fluid inclusion and measured downhole temperatures. In Poihipi, New Zealand, for example, this method has been used to determine changes in temperature and fluid type (Figure 20).

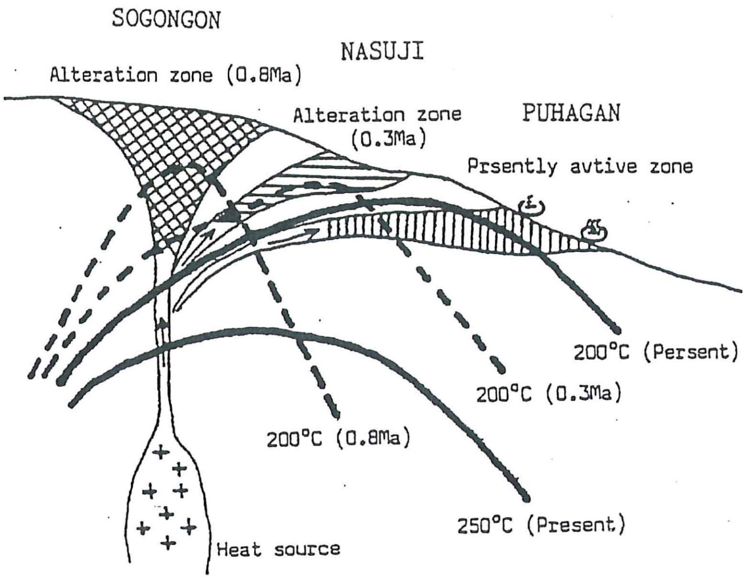


Figure 19: Esitmated thermal history of Palinpinon, the Philippines, based on thermoluminescence (Takashima and Reyes, 1990)

9. PRESSURE

The effects of pressure on hydrothermal alteration reactions involving only minerals and aqueous solutions can generally be neglected.

10. HOW ARE PETROLOGICAL DATA USED IN THE STUDY AND OPERATION OF GEOTHERMAL SYSTEMS?

Petrological findings and interpretations are widely used during operations work in geothermal systems in various stages of exploration and exploitation. Enumerated below are several immediate uses of petrology in Philippine geothermal systems, often used together with findings from other geoscientific and engineering disciplines (Reyes, 1991).

During surface geoscientific studies, petrological techniques are employed to:

- Analyse rock samples to determine lithologies and stratigraphy;
- Analyse thermal manifestation deposits and alteration assemblages to describe the general type of fluids harboured by a system of thermal manifestations and also to define the thermal history of an area.

During drilling, petrological findings are employed:

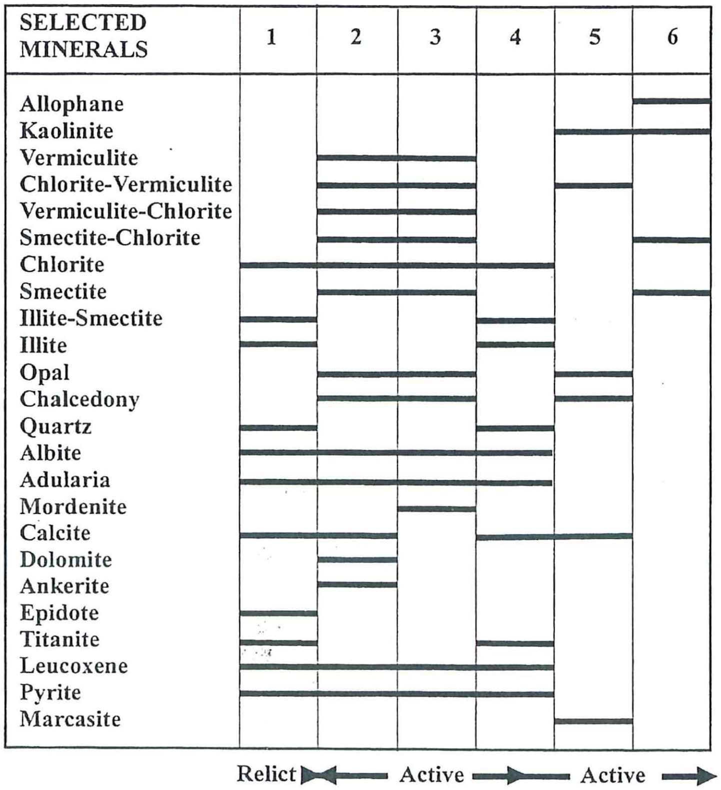


Figure 20: Mineral paragenesis in the Poihipi sector of the Wairakei geothermal system, New Zealand (Reyes and Giggenbach, 1999)

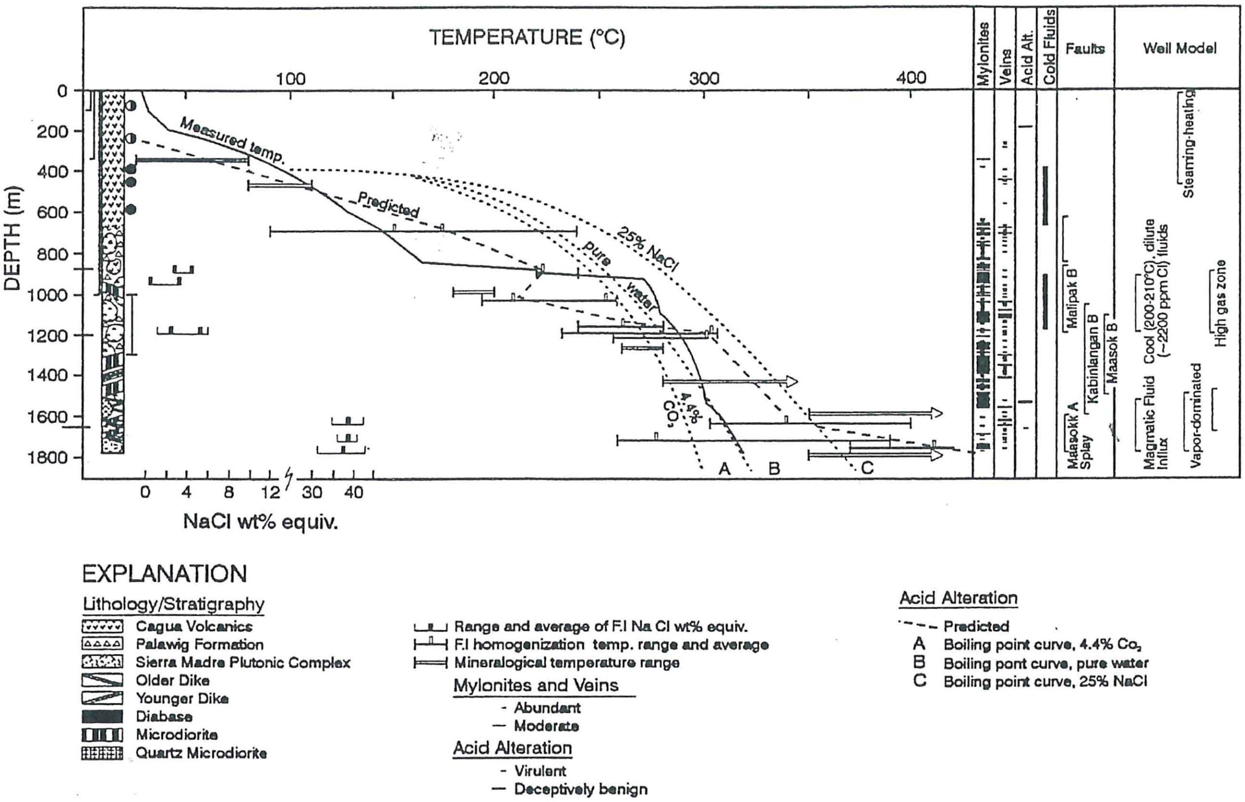


Figure 21: Example of a preliminary petrological output submitted to PNOC-EDC management right after a well is drilled. The main data shown are probable temperatures, permeable zones, acid fluid incursion, cold water input, vapour zone locations and possible magmatic influx (Reyes, unpublished results)

- To assist rig personnel and management in deciding the depths at which to set the production casing shoe, when to change the well track or the well drift angle, and when to stop drilling;
- To assist in anticipating or defining drilling problems such as stuck pipes caused by swelling clays or sloughing of rock formations, short bit lives due to the rock type or extremely high temperatures, degeneration of drilling mud due to very high temperatures;
- As an "early warning device" in cases where a magmatic-hydrothermal zone is intersected, which harbour highly acid waters, high gas contents, noxious gases and extremely high temperatures.

The outcome of a well can be predicted (Figure 21), during drilling and/or before well measurements and discharge analyses are available, in terms of:

- Temperatures with depth;
- Permeable depths and type of permeability;
- Zones of cold water influx or temperature reversals;
- Depths where there may be hot fluid influx;
- Steam-dominated horizons;
- Possible existence of high gas zones;
- Approximate reservoir salinity;
- Variations in fluid acidity with depth, depths of acid fluid influx ;
- Possible direct magmatic input;
- Possible corrosion and scaling tendencies of well fluids.

The hydrology of a geothermal system (Figures 22 and 23) can be defined by:

- Locating the upflow and outflow regions using secondary mineral assemblages and fluid inclusion studies;

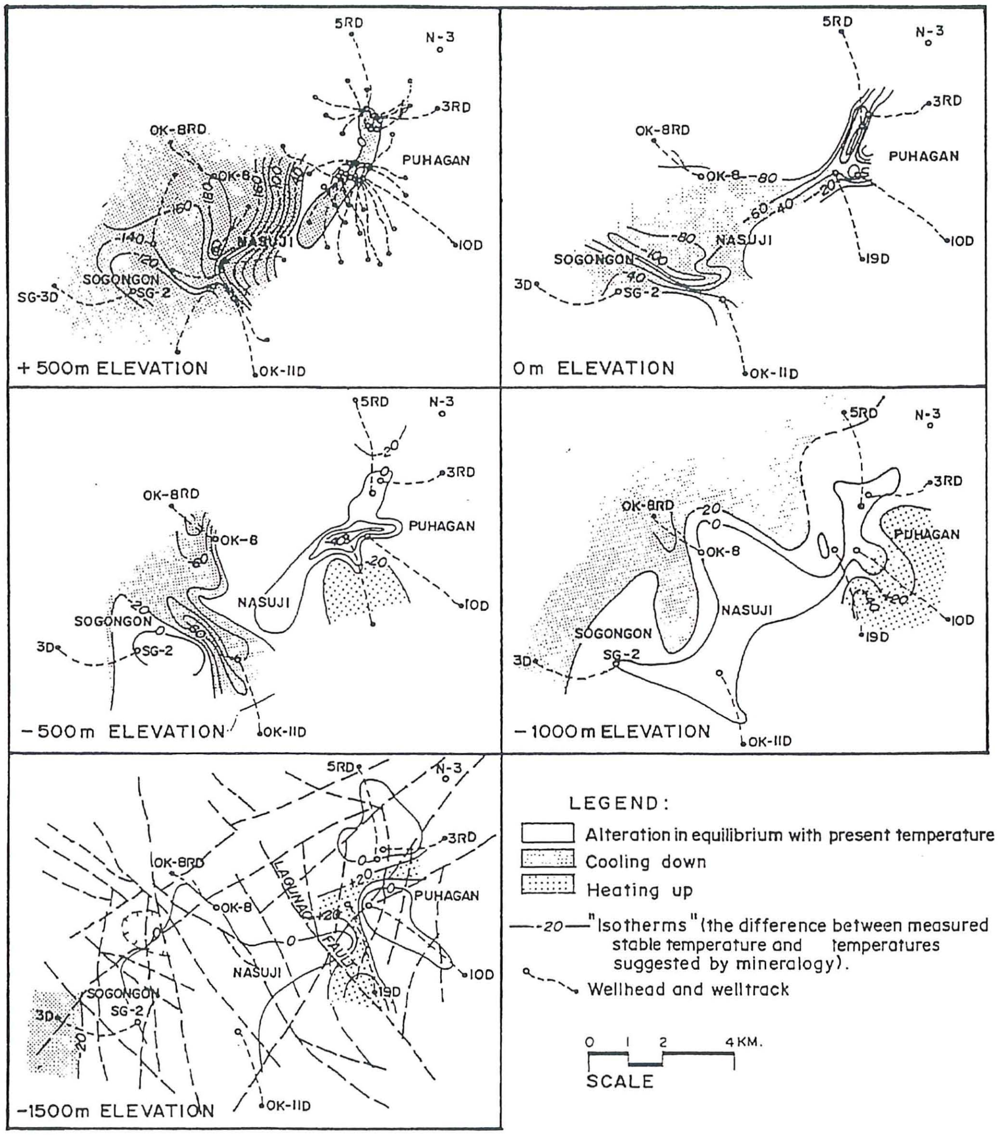


Figure 22: Defining the hydrology of a geothermal system using fluid inclusion and mineralogical data (plan view) in Palinpinon, the Philippines (Reyes, 1990)

- Characterising faults cutting across the resource in terms of the fluids they channel and their permeability;
- Identifying sectors of the resource where thermal fluctuations have occurred.

By defining the hydrology of the system, new areas for production and reinjection drilling can be pinpointed.

After drilling, other materials from wells are studied to provide more information. These include:
- Well scales to determine the chemical composition and temperature of fluids entering the well at a given depth and in so doing, define the well hydrology e.g., presence of internal flows;
- Well ejecta to provide information on the depths and types of aquifers that may possibly occur in the well especially within depths drilled blindly.

The identification and study of scales extends to those deposited in the fluid collection and disposal system and the information gleaned from these can be used to:

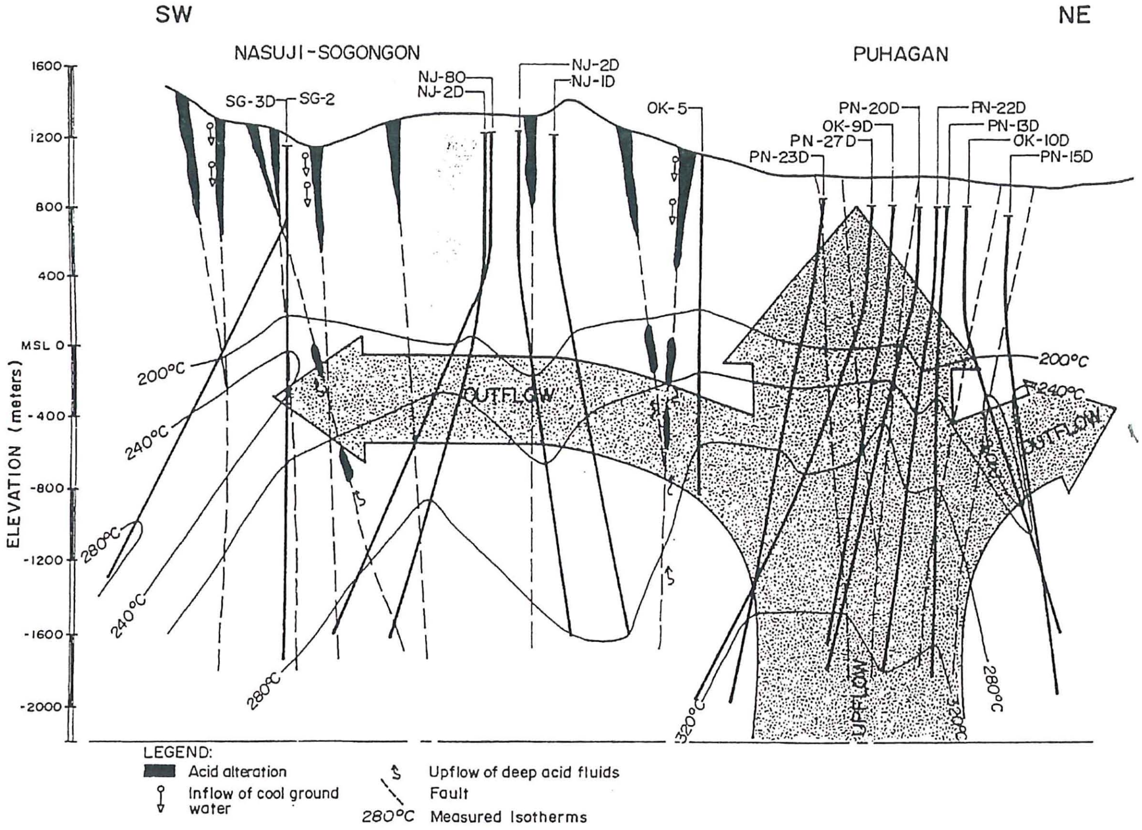


Figure 23: Defining the hydrology of a geothermal system using fluid inclusion and mineralogical data (vertical view) in Palinpinon, the Philippines (Reyes, 1990)

- Determine flow regimes along the length of the pipelines;
- Determine any corrosion along the pipelines;
- Delineate changes in water composition and temperature along the pipelines by measuring homogenisation and freezing temperatures in the silica scales.

The identification of scales in turbines have been used to:

- Determine degree and type of corrosion in the blades;
- Determine if the steam is clean and if water was introduced into the system and in so doing settle disputes between the steam provider and buyer.

Petrological techniques have also been used to study other materials such as:

- Drilling clays to determine if the mud used during drilling may later contribute to the formation of clays scales in the wells or if the mud can be prevented from deteriorating when drilling very high temperature wells;
- Cement to determine changes in the material with time, upon exposure to geothermal fluids and high temperatures;
- Dust from the environment to determine the relative amounts and type of pollutants for a given time and place.

The lessons learned from studying the petrology of active hydrothermal systems have been successfully used in the investigation of fossil hydrothermal systems such as epithermal mineral deposits and diagenetic processes in sedimentary basins

LECTURE 2

NEUTRAL pH ALTERATION: FROM DIAGENESIS TO HYDROTHERMAL ALTERATION TO CONTACT METAMORPHISM

1. CHARACTERISTICS OF NEUTRAL pH ALTERATION IN PHILIPPINE GEOTHERMAL SYSTEMS

- Pervasive, dominant alteration type;
- Temperature range - ambient to >400°C;
- Depths of occurrence - surface to >3000 m;
- Occurs throughout the stratigraphic sequence in the wells, affecting volcanics, calc-alkaline intrusives and sedimentary rocks;
- More than 55 secondary minerals have been identified, 28 of which are relatively common, cation aluminosilicates are dominant;
- Two general types divided according to main clay zones, but affected by rock type:
  - More common are mineral zones defined by the successive appearances of smectite, interlayered illite-smectite and illite clays, wherein montmorillonite and illite ratios vary with increasing temperature and depth (Figure 24). A cross-section in Tongonan, the Philippines, shows the distribution of mineral zones with temperature (Figure 25);
  - Less common, found sporadically and often lithologically controlled (occur where basalt, diabase and andesite hyaloclastites are present) are clay zones consisting mainly of the Mg-clays vermiculite and chlorite, and interlayering between the two minerals (Figures 26 and 27).

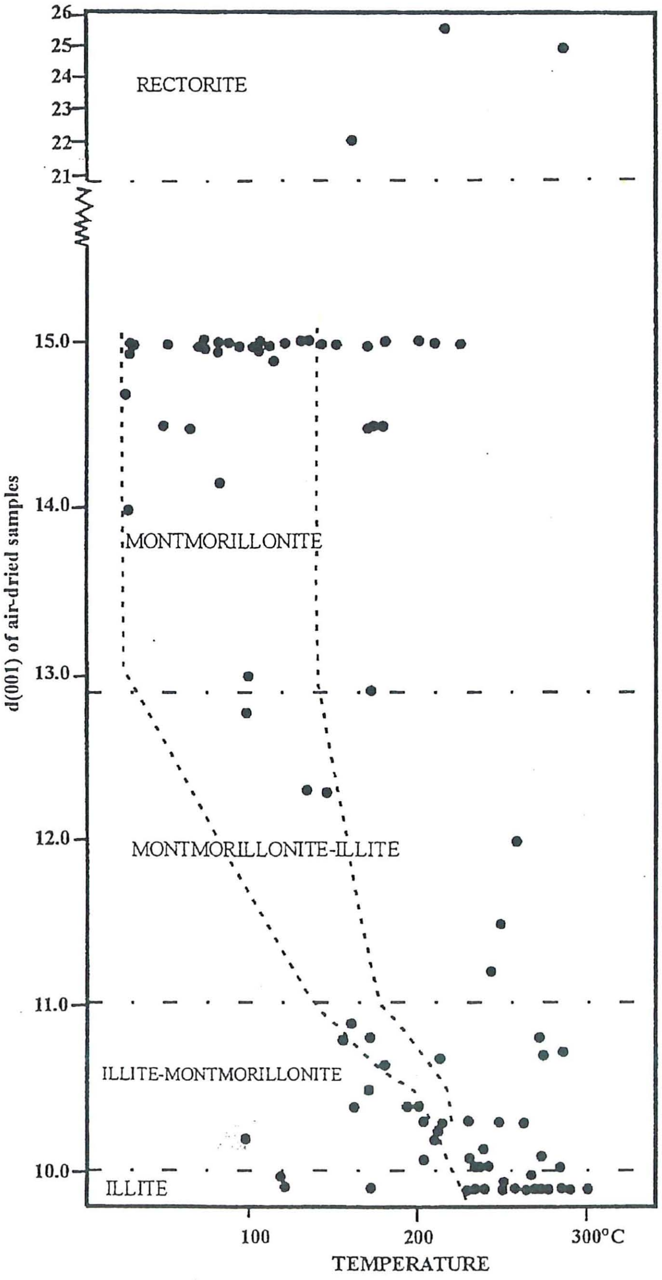


Figure 24: Variations in smectite:illite ratios with increase in temperature as indicated by changes in d(001) spacing with temperature (Reyes, 1984)

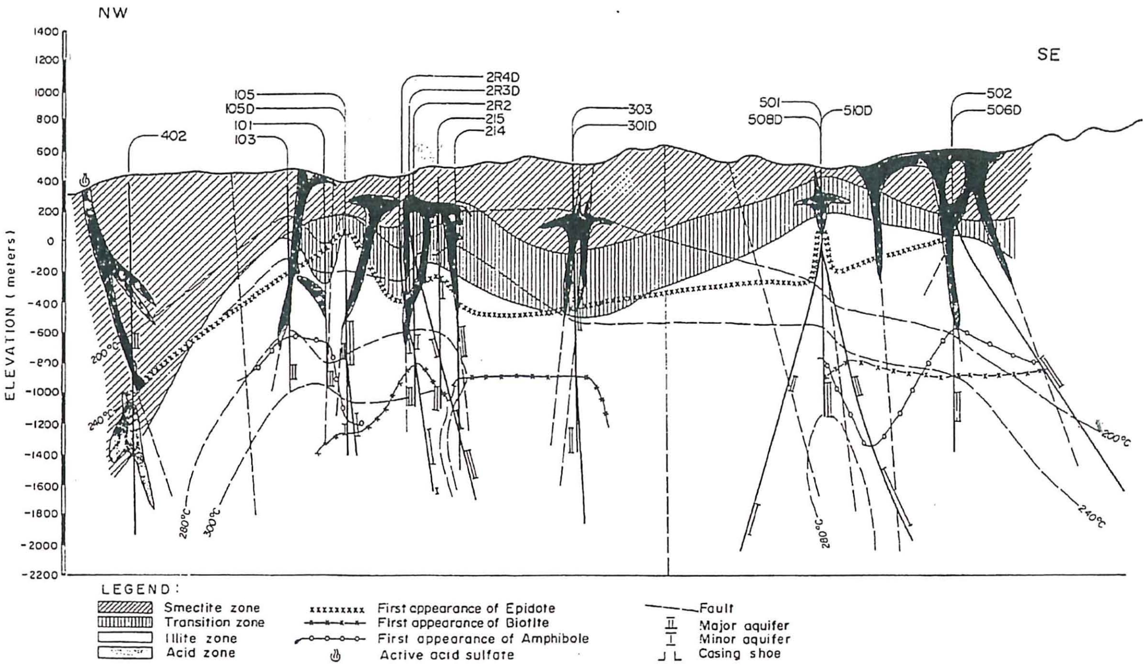


Figure 25: Cross section of mineral zones and sub-zones and stable measured temperature isotherms in Tongonan, the Philippines (Reyes, 1990)

- Origin of altering fluids is meteoric, although some components may be magmatic. Magmatic components in terms of δD and $\delta^{18}O$ range from zero to 40% (Figure 2);
- Mineralogy and mineral associations are the basis for most of the uses of petrology in the exploration and development of geothermal systems (refer to Lecture 1);
- Thermal fluctuations can be adduced from mineralogy and fluid inclusion data. Cooling may be indicated by the retrogradation of epidote, amphibole, biotite (to chlorite) and illite to lower temperature minerals, intense pitting in epidote, cold water incursion (see Lecture 1), reappearance of opal at depth, etc. Heating may be observed in the conversion of smectite to illite, vermiculite to chlorite, opal to quartz, tourmaline to andalusite;
- Ore textures and common ore elements: brecciation, open-space filling; Cu, Pb, Zn, Sb, As, Ag, Hg, Tl, Au.

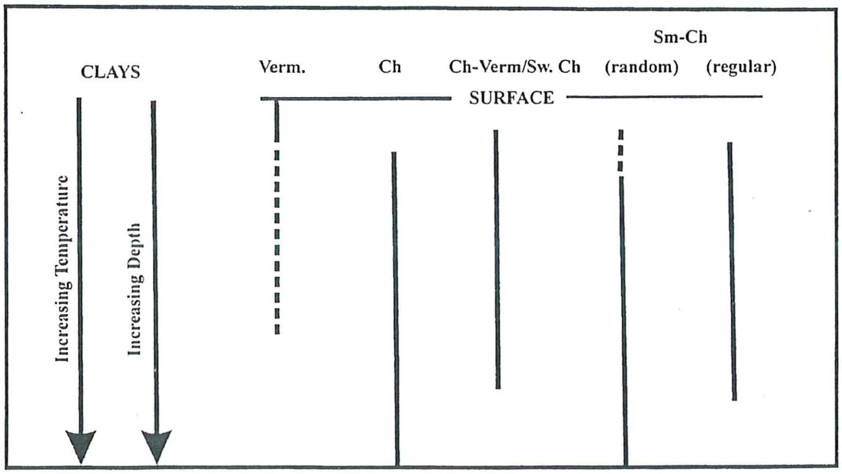


Figure 26: Changes in Mg-rich clays with depth and temperature in Bac-Man wells, the Philippines. Verm= Vermiculite, Ch= Chlorite, Sw= Swelling, Sm= Smectite (Reyes, 1984)

2. ALTERATION TYPES

- Neutral pH alteration ranges from low-temperature hydrothermal to magmatic-hydrothermal to contact metamorphism; the latter often occurs adjacent to intrusives;
- Alteration by neutral pH waters consists mainly of "reshuffling" of elements into new minerals (Figure 28);
- Types of rock-dominated alteration:
  - Zeolitization at <220°C;
  - Propylitic alteration characterised by presence of chlorite and epidote at 220-340°C; by the appearance of actinolite-tremolite at 280-350°C; and by secondary pyroxene or hornblende at >350°C (at slightly higher "fluid/water" ratios, hornblende forms).
- Types of alteration affected by neutral pH chloride waters and associated with higher fluid/rock ratios:
  - Argillic alteration at <200°C;
  - Phyllic alteration at 200-320°C;
  - Biotitic alteration at >320°C
- Types of metasomatism found in Philippine geothermal systems:
  - *K-metasomatism* associated with the upflow of >180°C waters within permeable zones, often accompanied by hydrolytic attack followed by deposition of adularia in veins or vugs. Illitic clay deposition is always preceded by the dissolution of primary andesitic components such as plagioclase;
  - *Na-metasomatism* involves widespread albitisation of plagioclase. Albite is only precipitated in vugs and fractures at >280°C;
  - *Mg-metasomatism* is widespread and Mg-bearing minerals are highly varied. Their prevalence in the Philippines may be due to the abundance of ferromagnesians in the andesitic host rocks; their greater variety to the steep geochemical gradients associated with the rapid neutralisation of initially highly acid fluids. At <180°C kerolite and vermiculite occur, while actinolite-tremolite appears at >320°C. Where acid waters are rapidly neutralised by rock or mixing with neutral pH waters, sepiolite is deposited at <180°C and at >270°C, Mg partitions into a phosphate mineral, lazulite.

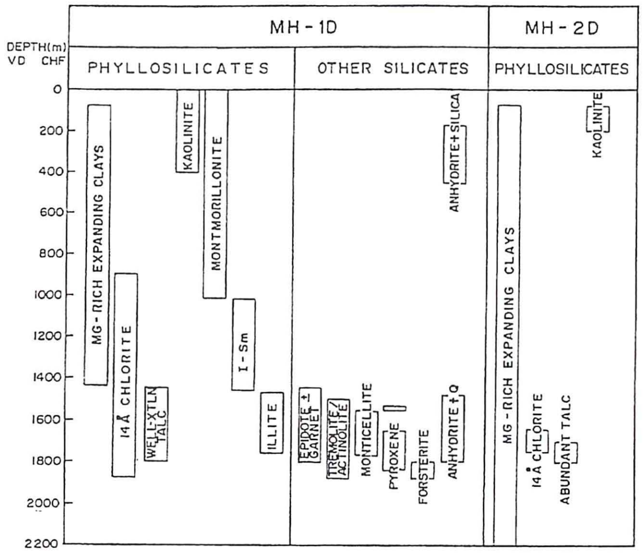


Figure 27: Juxtaposition of two types of clay assemblages in Mahagnao, the Philippines (Reyes, unpublished results)

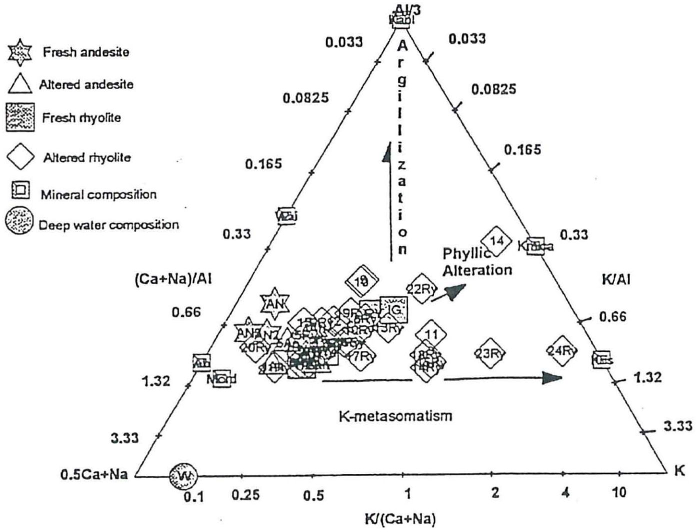


Figure 28: Neutral pH alteration often involves reshuffling of elements in the original rock to form new minerals in Wairakei, New Zealand (Reyes et al, 1994)

3. CASE STUDY: NEUTRAL pH ALTERATION IN TONGONAN, THE PHILIPPINES

The Tongonan geothermal system consists of four sectors: Mahiao-Sambaloran, Malitbog, Mamban and Mahanagdong. Prograde alteration zones are associated with the active hydrothermal system in Mahiao-Sambaloran and Mahanagdong (Figures 25 and 29).

Cooling and several alteration events had occurred in Malitbog and Mamban, as indicated by the superposition of the smectite over the illite zone and the occurrence of the top of the illite zone at lower than "equilibrium" temperatures. As much as 250 m uplift probably occurred in Malitbog and Mamban. Within Mahiao-Sambaloran and Mahanagdong, anhydrite is abundant in hotter portions of the system, near the main upflow zone while calcite occupies the cooler peripheral and shallower regions. Where cold waters intrude, calcite becomes dominant over anhydrite, such as in Malitbog and Mamban (Figure 30).

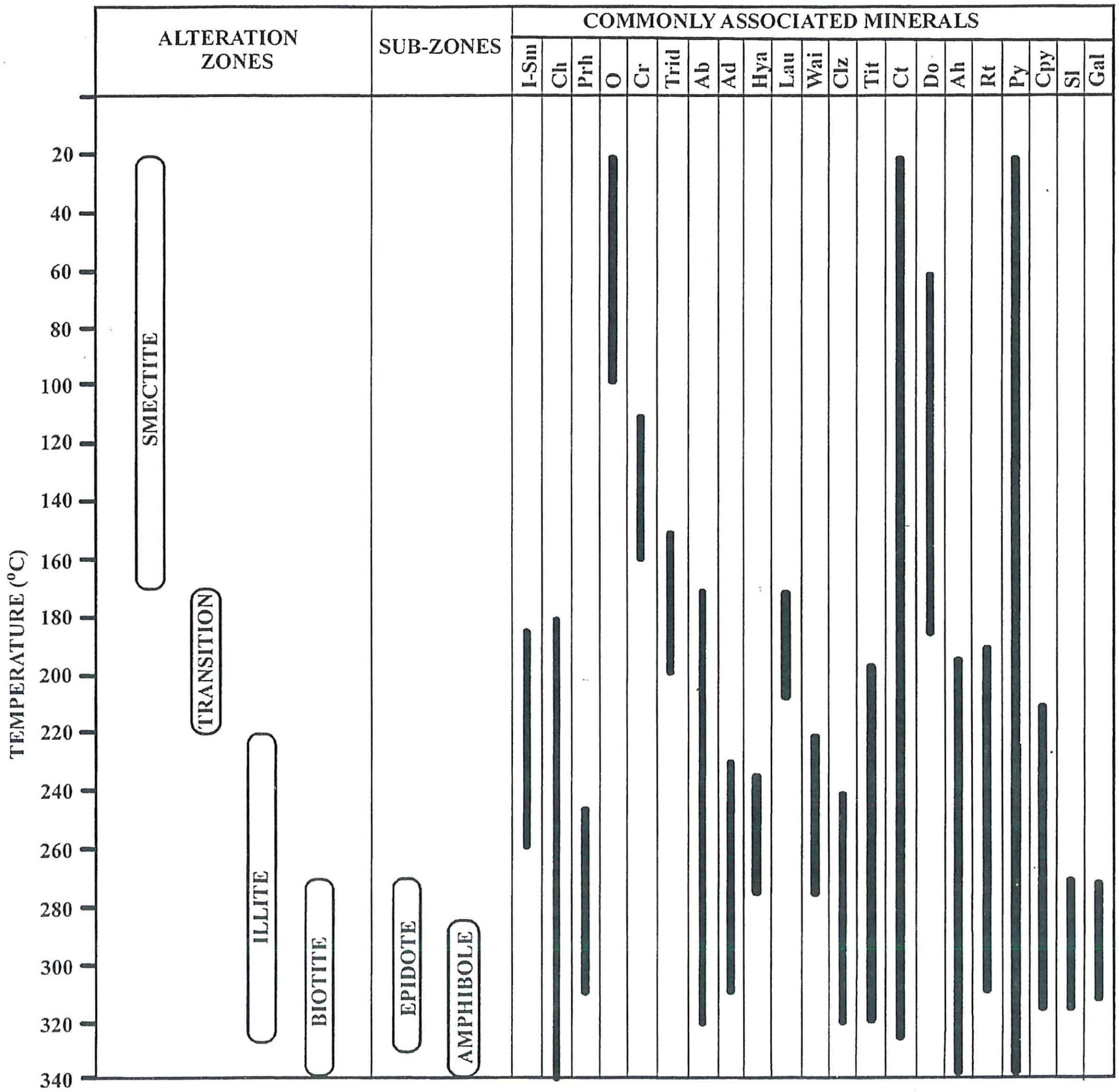


Figure 29: Temperature ranges of mineral zones and sub-zones in Tongonan. I-Sm= Illite-smectite, Ch= Chlorite, Prh= Prehnite, O= Opal, Cr= Cristobalite, Trid= Tridymite, Ab= Albite, Ad=Adularia, Hya= Hyalophane, Lau= Laumontite, Wai= Wairakite, Clz= Clinozoisite, Tit= Titanite, Ct= Calcite, Do-= Dolomite, Ah= Anhydrite, Rt= Rutile, Py= Pyrite, Cpy= Chalcopyrite, Sl= Sphalerite, Gal= Galena. Quartz is often present from 180°C (Reyes et al, 1988 and 1990)

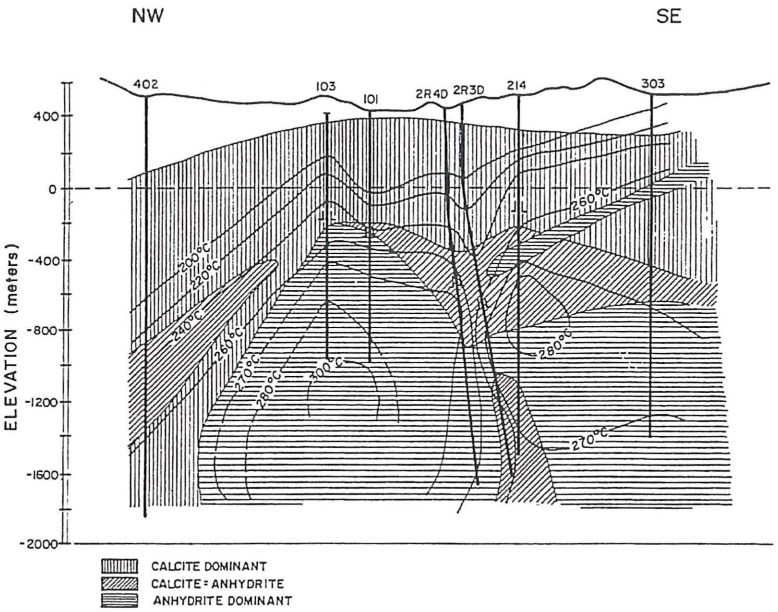
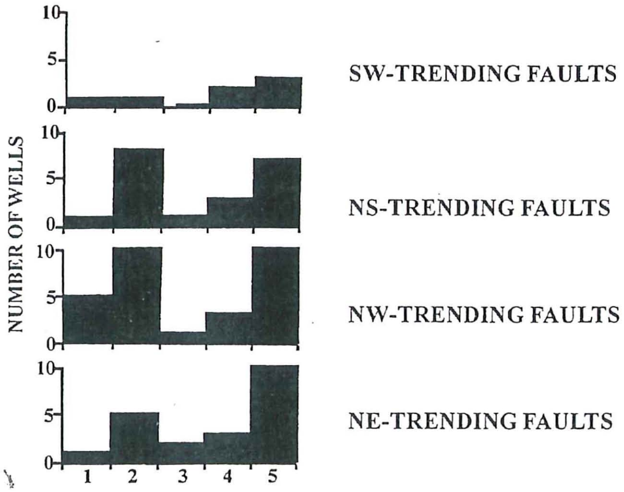


Figure 30: Distribution of anhydrite and calcite in Tongonan, the Philippines (Reyes, 1990)

Cooling in a geothermal system may be caused by (1) structurally-controlled incursion of cold groundwater into the system, (2) thermal decline of the heat source with time and (3) shifting of the focus of fluid flow in response to renewed intrusion. Cooling and heating trends can be used to define the hydrology of a system. These are based on a comparison between hydrothermal mineral occurrences, fluid inclusion homogenisation results and measured well temperatures.

Relict alteration at the surface of Malitbog and Mamban indicate cooling by as much as 250°C while no cooling is observed in Mahiao-Sambaloran. Apparent heating trends observed in some wells are caused by poor permeability, enabling smectite and low-temperature zeolites to persist at >200°C. True heating trends are observed in wells located within the main upflow.

Faults are the major sources of permeability in Philippine systems. The presence of faults along a well are based on combined evidences from petrographic observations, drilling parameters such as drilling losses, blind drilling and bit walks and well measurements indicative of permeability. From detailed petrological studies and comparison with well measurements, it was found that in Tongonan, the northeast trending faults are the most permeable whilst the least permeable are the E-W striking ones (Figure 31).



1 No associated aquifer/ non-commercial well
2 Associated with minor aquifer
3 Injectivity <20 l/s MPa
4 Injectivity: 20-30 l/s MPa
5 Injectivity >30 l/s MPa

Figure 31: Permeable faults in Tongonan, the Philippines (Reyes at al, 1990)

4. DIAGENESIS AND HYDROTHERMAL ALTERATION

Studies on alteration in a hydrocarbon-bearing sedimentary basin are based on the premise that diagenesis is a low-temperature type of hydrothermal alteration, wherein fluids and temperature play major roles in mineral precipitation, dissolution and transformation. Thus, petrological principles gained from hydrothermal studies can be extended to understanding hydrocarbon reservoirs.

Like hydrothermal alteration, authigenic mineral formation in sedimentary basins are induced by fluid flow and influenced by heat and mass transfer. Comparison between diagenesis and low-temperature hydrothermal alteration is shown in Table 2.

In the study of diagenesis more analytical techniques are employed to unravel the changes in types and modes of mineralisation, fluid compositions, hydrocarbon generation and formation porosity with time and temperature in hydrocarbon systems. These include petrographic techniques such as transmitted and reflected light microscopy, X-ray diffractometry (XRD), cathodoluminescence (CL), fluorescence, fluid inclusion determinations, scanning electron microscopy (SEM) and particle-induced X-ray emission (PIXE) analysis.

Figure 32 shows an example from New Zealand, alteration in an 800 m thick rock formation progressed from initial argillisation or smectitic cementation of clasts upon burial where temperatures were ambient, to transformation of smectite to illite-smectite and illite at temperatures of 150° ±20°C by the circulation of silica-saturated waters in equilibrium with opal. Silica-saturated solutions seem to have circulated in the formation throughout most of its diagenetic history, causing quartz overgrowths, healing quartz fractures and precipitating chalcedonic quartz mosaics on the matrix.

Table 2: Comparison between diagenesis and hydrothermal neutral pH alteration (Reyes, unpublished results)

Factors	**Diagenesis**	**Low-temperature hydrothermal**
Temperature	<180°C, affects the types of minerals deposited; but often changes in temperature with depth are very gradual and variations in temperature narrow	>180°C, affects the type of minerals deposited and their compositions
Geothermal gradients	<50°C/km	>100°C/km
Geochemical gradient	Very gradual; affected more by the basin history than the present topography	May be very steep especially in rugged country; affected to large degree by topography
Time span for alteration to occur	May take tens of millions of years	May take days to as long as its lifetime (0.1 to 1.0ma)
Main factors affecting mineral formation	Kinetic factors (hydrostatic gradient affects mineral associations/assemblages)	Near-equilibrium conditions
Alteration type	Rock-dominated	Ranges from rock- to fluid-dominated
Pressure conditions	Pressure in the sedimentary basic affects absolute gas pressures and this in turn affects the type of mineral assemblages formed	Mostly unimportant
Alteration of carbonaceous material	Important under redox conditions and during decarboxylation processes. Alteration affects CO_2 generation in the system	Merely gets cooked and does not participate in inorganic mineral deposition above about 120°C
Elemental mobility during alteration	Subtle	Drastic changes observable
Factors affecting variations in mineralogy with depth	Redox conditions, fluid acidity, gas contents, porosity	See Lecture 1 and 2 notes

Apart from chalcedonic quartz and illitic clays other authigenic minerals, occurring as replacement phases or as cementing material, include siderite, ankerite, dolomite, kaolinite, pyrite, goethite and minor calcite. Siderite and Fe- bearing dolomite and ankerite are prevalent, reflecting the overall redox condition of the system, wherein the oxidation of hydrocarbon gases and decarboxylation generated CO_2 that in turn promoted siderite deposition. As temperature decreased and as CO_2 was used up, solutions became slightly acid, resulting in the kaolinisation of illitic clays and muscovite fragments and the precipitation of kaolinite aggregates. As the acid solutions were neutralised by interaction with rock and more CO_2 is produced by the system, calcite was deposited. Porosity and permeability had been diminished by diagenetic reactions (Figure 32).

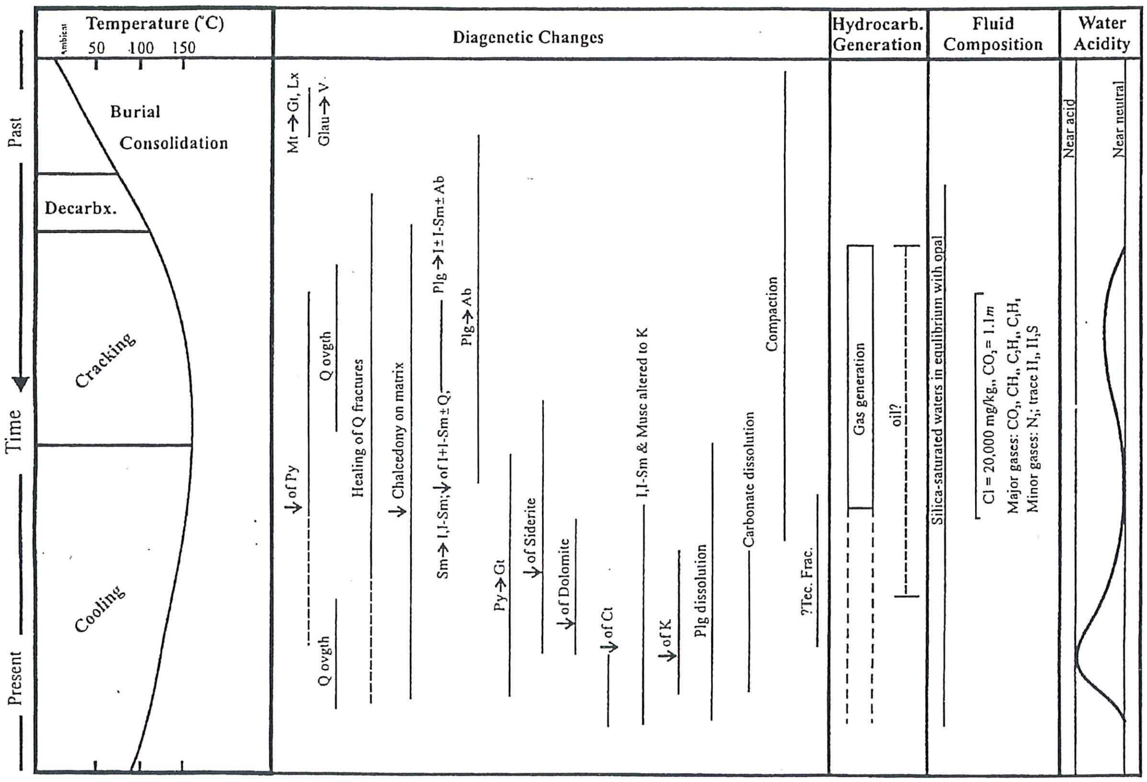


Figure 32: Paragenesis in a New Zealand hydrocarbon system that attained maximum temperatures of about 150°C; estimated fluid compositions are based on fluid inclusion studies whilst temperatures are based on fluid inclusion data, well measurements and authigenic mineral associations (Reyes, 1998)

LECTURE 3

ACID ALTERATION IN THE PHILIPPINES: FROM THE VADOSE ZONE TO THE HYDROTHERMAL MAGMATIC INTERFACE

1. OCCURRENCES

Acid alteration occurs under various circumstances as given by the following list:

- Structurally-controlled (Figures 33 and 34);
- Often narrow (a few cm to as much as 750 m) (Figure 33);
- Forms contemporaneously with neutral pH alteration (Figures 33 and 34);
- Sharp boundaries with neutral pH alteration (Figure 35);
- Some shallow occurrences may be buried solfataras (Figure 33);
- Occurs as deep as 2500 m in the Philippines, mostly at 1600-1800 m (Figure 33);
- Temperature range: ambient to >400°C (Figure 36);
- Often found where there was or still is high gas content;
- Often associated with abundant veins and intense to complete alteration (Figure 34);
- Fluid dominated alteration - immature hydrothermal systems.

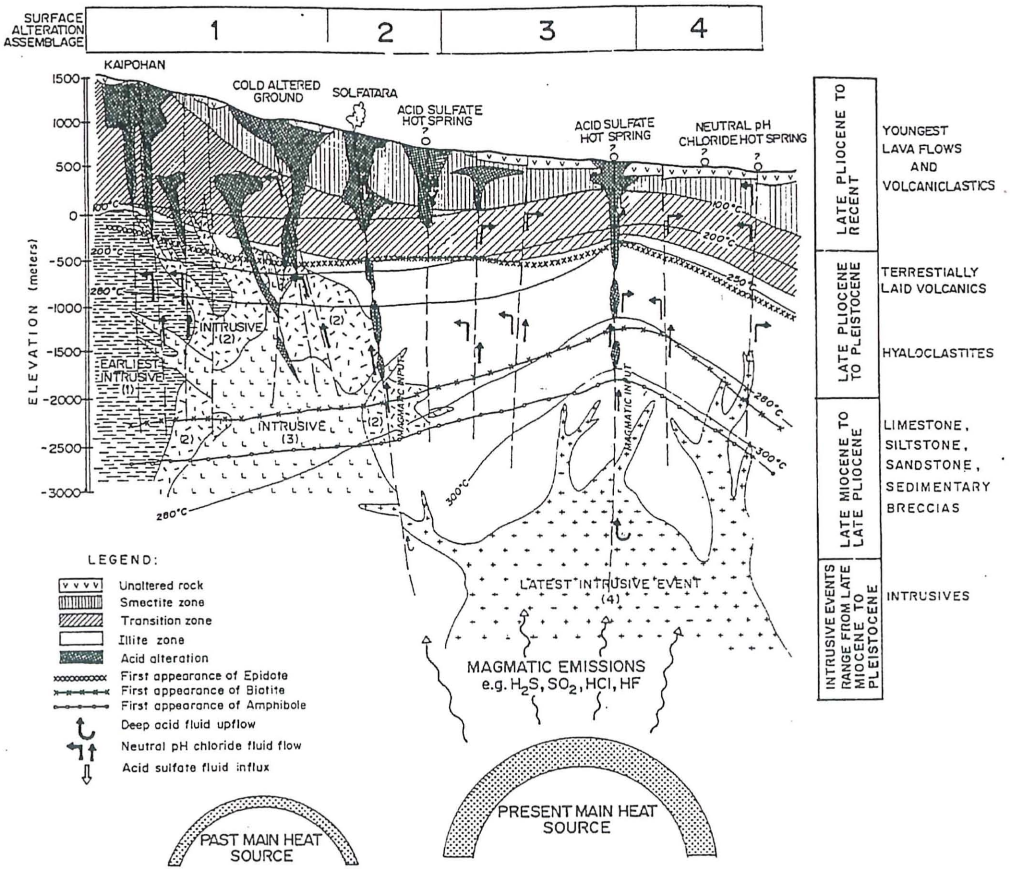


Figure 33: Geologic model, alteration patterns, including acid alteration, distribution, and stratigraphy typical of Philippine geothermal systems; note that acid alteration is structurally controlled (Reyes, 1990)

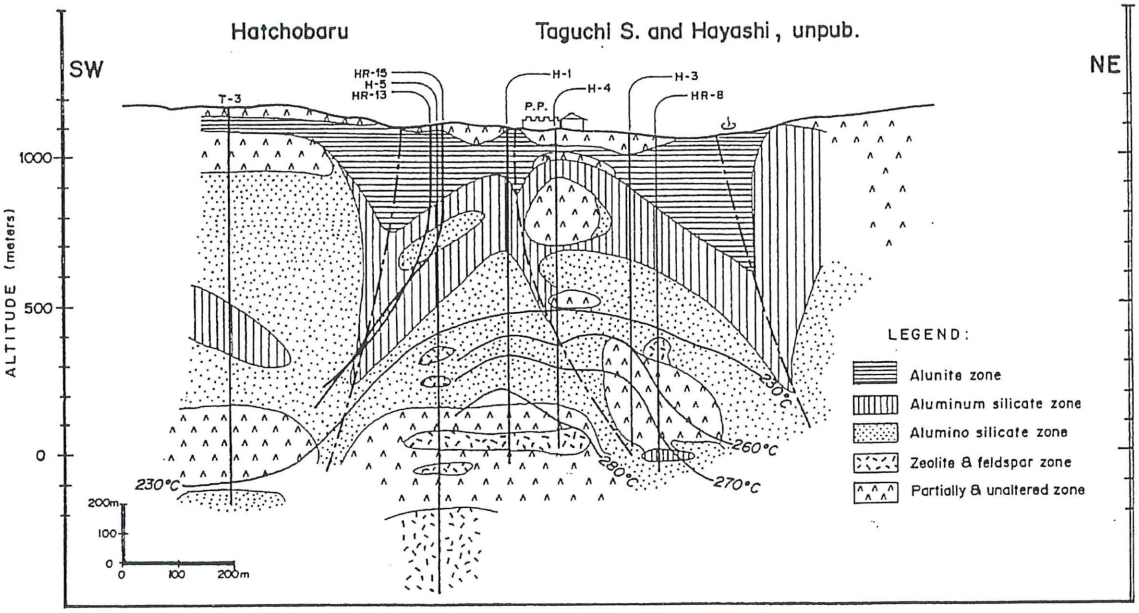
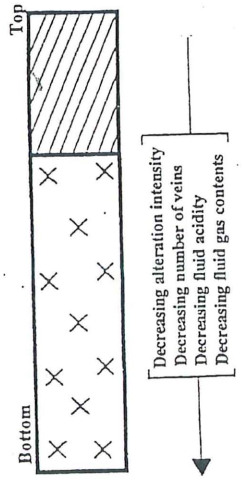


Figure 34: Distribution of acid alteration in Hatchobaru, Japan; note the tapering of the acid alteration zones with depth

2. MINERALOGY

More than 35 minerals have been identified, including opaques, 18 of which are common. Zones consist of Kaolinite, Dickite ± Kaolinite, Dickite ± Pyrophyllite, Pyrophyllite + Illite and Muscovite as temperatures, fluid pH, silica activity and alkali cations increase. From the Kaolinite to Muscovite zones, clays increasingly become dehydrated and become more crystalline and anhydrite increases relative to alunite (Figure 36). Retrogradation or fluctuations in fluid chemistry are best observed in opaque minerals.



ALTERATION SUITE	ASSEMBLAGE	VEINS
Acid Alteration	Illite, Pyrophyllite, Anhydrite, Quartz, Diaspore	Anhydrite ± Diaspore, Anhydrite ± Illite ± Pyrophyllite + Pyrite + Quartz
Neutral	Illite, Chlorite, Quartz, Anhydrite, Pyrite, Titanite	Anhydrite + Illite + Pyrite ± Quartz
pH Alteration	Chlorite, Quartz, Illite, Anhydrite, Albite, Pyrite, Leucoxene, Titanite, Epidote, Calcite	Anhydrite + Epidote + Pyrite + Illite, Illite + Anhydrite + Calcite Open fractures partially filled with Calcite

Figure 35: Sharp boundaries between contiguous acid and neutral pH alteration in a core (Reyes, unpublished results)

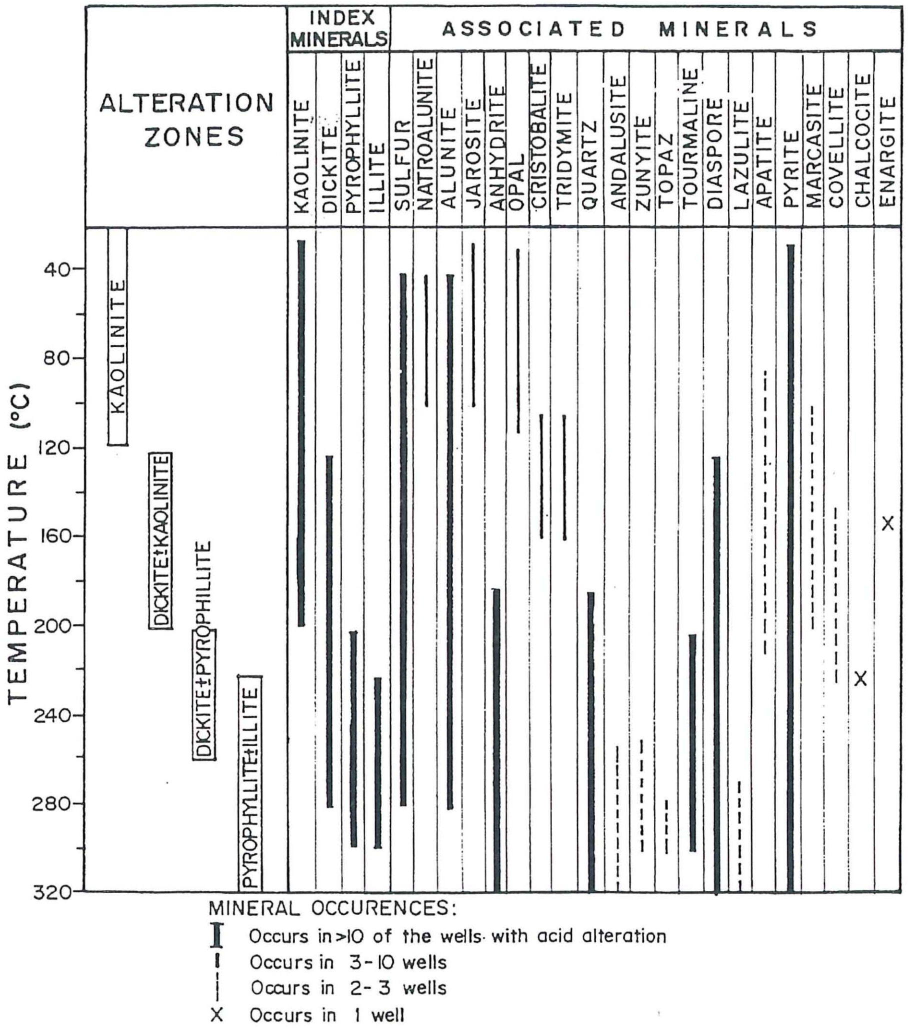


Figure 36: Acid alteration zones in the Philippines (Reyes, 1990)

3. TYPES OF ACID ALTERATION ACCORDING TO WATER COMPOSITION

Acid alteration is associated with low temperature (<160°C) bicarbonate waters producing an assemblage containing smectite and kaolinite with or without associated pyrite, goethite and/or calcite.

Acid alteration associated with acid-sulphate waters produces an assemblage commonly containing alunite, kandites, silica polymorphs and sulphides such as pyrite, bornite, enargite, covellite and chalcocite. As the acid waters become slightly neutralised by reaction with rock, pyrophyllite, illite, diaspore and anhydrite appear. In areas where topography is steep and rugged and normal faults are present, as in Philippine hydrothermal systems, such shallow acid waters may percolate to a few hundreds of metres. Temperatures vary from near-ambient to about 300-330°C.

Acid alteration associated with deep magmatic-hydrothermal fluids may overlap with the above type. Alteration mineralogy is similar to above except that at temperatures >330°C, muscovite instead of illite forms and minerals such as andalusite and cordierite appear. Temperatures >330°C based on measured downhole data, mineral assemblages and fluid inclusion homogenisation temperatures.

4. TYPES OF ACID FLUIDS ACCORDING TO THE VIRULENCE AND CORROSIVITY OF THE ASSOCIATED FLUIDS AND THE PROPENSITY OF THE ASSEMBLAGE TO REJUVENATE FLUID ACIDITY

The types are:

- *Virulent acid* alteration, consists of sulfur + alunite + abundant pyrite/marcasite;
- *Deceptively benign* acid alteration characterised by the absence of sulphur and alunite and the presence of kandites, pyrophyllite, diaspore, anhydrite and pyrite;

Acid alteration often changes from a virulent to a deceptively benign type and then onto neutral pH alteration with depth, along a fault. It also changes laterally away from the main acid fluid channel and across narrow <1 m zones as found in several cores.

When encountered within permeable zones in wells the presence of virulent acid alteration portends immediate acid fluid discharges and intense corrosion of pipes. Acid fluids also corrode casing. Even when relict, virulent acid assemblages may rejuvenate fluid acidity particularly at high temperatures

Deep acid alteration and wells that discharge acid fluids are common in andesitic- to dacitic-hosted geothermal systems. Examples of such are found in Matsukawa, Hatchobaru and Komatsu in Japan; Tatun in Taiwan; Indonesia; Mexico; Costa Rica; and the Philippines

Other characteristics are:

- Acid alteration is found in 90% of the wells studied (about 200-300) in the Philippines, with 45% having the potential to discharge acid fluids upon field exploitation. However, at present, only about 25 wells have confirmed acidic discharges;
- Often acid wells have low mass flows and relatively low permeabilities;
- Acid sulphate surface thermal manifestations, whether relict or not, are often harbingers of subsurface acid alteration although their absence does not preclude the latter.

5. FLUID INCLUSIONS

Homogenisation (T_h) and freezing temperatures (or temperatures of ice melting, T_m) are measured in anhydrite, quartz, diaspore, alunite. The range of T_h is 90° to >400°C, similar to those in adjacent neutral pH altered rocks

High gas fluid inclusions are more common in acid alteration zones than in adjacent neutral pH alteration minerals; clathrates commonly disappearing at +1 to +10°C signify the presence of dissolved CO_2. When CO_2 is low and salinities may be derived from fluid inclusions' freezing temperatures, fluid salinities of adjacent acid and neutral pH minerals are similar.

6. ROCK CHEMISTRY

Acid fluid influx results in complete recrystallization of rock and mobilisation of cations, sometimes leaving only pockmarked quartz. Acid-altered rocks are composed largely of residual oxides:

- Ca is fixed in anhydrite at >180°C;
- K forms alunite at low pH, at high sulphate activity and at temperatures of <50 - 330°C; and illite and muscovite at higher pH, silica activity and temperatures of 220 - >400°C;
- Na is rarely partitioned into natroalunite at <150°C;
- Mg does not form any stable minerals within the acid zone but commonly precipitates out as sepiolite, lazulite, Mg-rich chlorite at the interface between acid and neutral pH alteration;
- High total sulfur is found as native sulfur, sulfides, and sulphates;
- Arsenic increases in acid zones but Cu and Zn decrease dramatically.

7. FLUID CHEMISTRY

A summary comparing neutral pH acid water discharge compositions is listed in Table 3.

Table 3: Comparison between acid and neutral pH well discharges (Reyes, 1991)

Fluid component	Characteristics	Comments
pH (ambient)	<5.5 for acid fluids being discharged by wells	Acid and neutral pH waters often enter a well through different openings and intermix during well discharge
Cl	Generally lower for acid water well discharges at about 3700-13600 mg/kg as opposed to 8100-25700 mg/kg for most neutral pH water discharges. Where magmatic acid fluids enter the well, there is excess Cl in the water and vapour phases	Excess Cl may be due to HCl
Ca	Generally lower in acid discharges at 40-200 mg/kg compared to 160-500 mg/kg for neutral pH well discharges	
Mg	May be as much as 50x greater in acid fluids, at 0.5 to 170 mg/kg compared to neutral pH waters at 0.01-1.3 mg/kg	
Fe	May be as much as 400x greater in acid fluids, at 4.0-445 mg/kg than in neutral pH waters at <9.0 mg/kg	Most of the Fe may originate from the casing
SO_4	May be as much as 35x in acid fluids at 50-3200 mg/kg compared to 15-50 in neutral pH well discharges	
F	High in magmatic-hydrothermal well discharges	May be from HF
H_2 (gas)	Discharge values may be as much as 35x in acid compared to neutral pH gases	Some H_2 may originate from the casing

8. ORIGIN AND CRITERIA FOR DETERMINING WHEN ACID ALTERATION IS ACTIVE

Acid alteration originates from various sources, such as:

- In surface manifestations, condensation and subsequent oxidation of H_2S-laden steam;
- Reaction of groundwater with sulfur that has sublimated from H_2S;
- Fossil solfataras;
- Regeneration of acid sulphate fluids from reaction of groundwaters or upflowing fluids with relict acid sulphate minerals;
- H_2S rising from the reservoir is oxidised in the vadose zone and the resulting acid fluids channelled to deeper levels by faults. Due to the strong neutralising effect of rocks such fluids and alteration are confined to shallow levels at, perhaps, <200 m;
- A variation of the above sources may occur when extreme drawdown during the exploitation of a system creates a steam cap. Acid fluids are then generated when cooler groundwaters enter the system, react with "acid" gases and percolate to deeper levels. Fluid acidity is augmented when virulent acid alteration is intersected by these fluids along its way to deeper depths;
- Reaction of deep aquifer fluids with magmatic volatiles such as HCl, H_2S, SO_2, HF;
- Direct magmatic input as in Pinatubo, Cagua, Mahagnao, Biliran, Alto Peak, portions of Tongonan, Palinpinon and Bac-Man.

The following criteria can be used to determine when acid alteration is active in a geothermal well:

- Acid influx was identified from the chemical composition of well waters;
- Anhydrite- and/or barite-scales and As-bearing sulphides deposit at the point of inflow of acid fluids in the well;
- Measured well temperatures are similar to fluid inclusion data, acid mineral geothermometry and temperatures indicated by contiguous neutral pH alteration assemblages;
- More than 5% alunite/natroalunite and/or sulfur are present in a sample;

- Acid minerals, other than above, are abundant (>20% of sample if not magmatic in origin; 5% if magmatic), with thickness of the acid horizon >20m if not magmatic, >3m if magmatic;
- Associated solfatara, kaipohan or acid-sulphate-(chloride) thermal manifestations occur along the strike of a fault, projected to be intersected by the well at depth;
- Corrosion pits are absent in diaspore, topaz, andalusite, tourmaline, fluorite, etc;
- Fluid inclusions exhibiting unusual characteristics and behaviour are abundant. Examples include abundant and varied daughter minerals, formation of yellow fluid upon heating, presence of at least two types of fluids in an inclusion, etc;
- The geothermal system is closely associated, in space and time, with young silicic and andesitic domes and volcanoes.

Table 4 shows criteria for predicting the immediacy of acid fluid influx and effects in a geothermal well., in relation to various types of active acid faults. The numbers on top indicate the immediacy of acid fluid effect after a well is drilled.

Table 4: Criteria for predicting the immediacy of acid fluid influx and effects in a geothermal well

Criteria	**1**	2	3
1. Intersection of acid-water feed zones in wells	*		
2. Formation of anhydrite- barite- and/or As-bearing sulfide-scales at the point of acid fluid inflow into the well	*		
3. Intersection of alunite/natroalunite- and/or sulfur-bearing rocks	*		
4. Thickness of the formation containing acid alteration is >20m	*	*	
5. The geothermal system is associated with active solfatara, kaipohan or acid-SO_4^--Cl thermal manifestations and very recent volcanism	*	*	*
6. Relict virulent acid alteration assemblages were intersected on the surface by faults that may be intersected by wells at depth	*	*	*

(1) Virulent acid sulphate waters will be discharged by wells even during the first days of well testing and discharge ;
(2) Indications for acid fluid influx in the well discharge may be detected only months after the well had been first discharged; and
(3) Acid fluid influx into the geothermal system is induced by exploitation effects such as drawdown, and detection of acid input may take months or years after drilling (Reyes, unpublished results).

9. NOTES ON ACIDITY OF HYDROTHERMAL FLUIDS ACCORDING TO GIGGENBACH (1997b)

The acidity of a solution is generally measured in terms of the concentration of hydrogen ions H^+, protons, or "hydronium ions", H_3O^+. Since the concentration of hydrogen ions is usually small, the acidity is expressed as the pH of the solution, the p standing for –log 10. Therefore $pH= -\log 10 a_H+$ where a_H+ is the activity of H^+, or in dilute solutions, its molality, the number of moles of H^+ per kg of water. pH provides a convenient way to express acidity in lower-temperature solutions where it can often be measured directly. In close to neutral solutions it is only a very minor acidity-generating species. This role can be played by a number of other species such as CO_2, HSO_4^-, HCO_3^-, HCI, Al^{3+}, or even mineral species, such as clays.

In intermediate-temperature hydrothermal systems, at <350°C, the major acid-generating species is CO_2; in higher-temperature, up to magmatic systems, a suitable variable to describe acidity-dependent reactions is the ratio HCl/KCl. In a high-temperature (600°C), close to magmatic, system, the HCl/KCl ratio of fluids in equilibrium with an average crustal rock is close to 0.1 (Figure 37). With decreasing temperature, the equilibrium HCl/KCl ratio decreases to 0.01 at about 500°C, to 0.001 at about 400°C

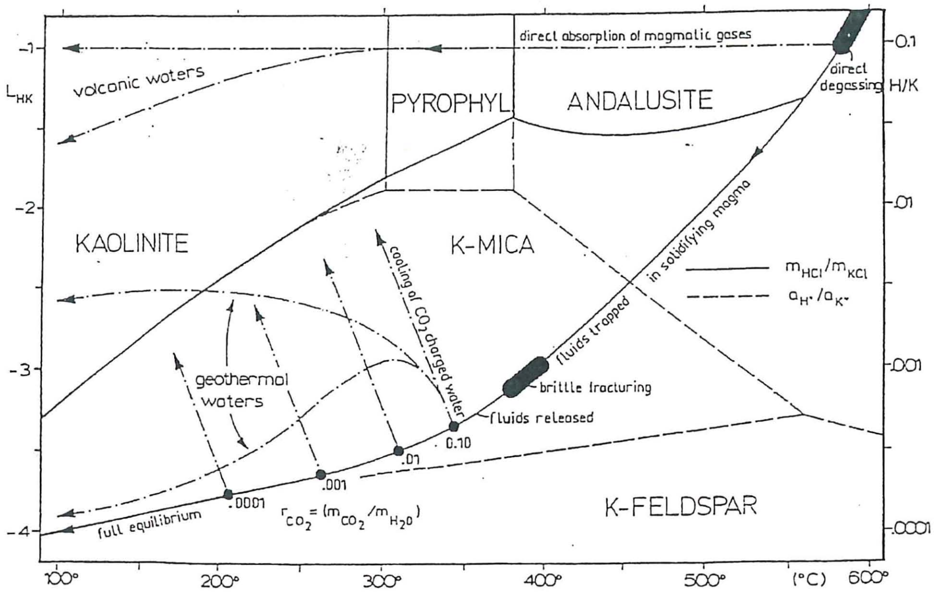


Figure 37: Variations in acidity due to HC1, with temperature (Giggenbach, in prep.)

and 0.0001 at about 100°C. The major process facilitating this decrease in HCl/KCl, or "acidity" is conversion of framework silicates, such as feldspars, to layer silicates, such as micas, according to:

$$3\ KAlSi_3O_8 + 2\ HCl \rightarrow KAl_3Si_3O_{10}(OH)_2 + 2\ KCl + 6\ SiO_2$$

"Full equilibrium" cooling of a solution, interacting with an average crustal rock, leads to a drastic reduction in the HCl/KCl ration and, therefore, in the acidity-generating potential of HCl.

Removal of an equilibrium fluid at high temperatures, e.g. in a volcanic system, preserves high-temperature HCl/KCl rations. Interaction of these highly acid fluids can be expected to lead to intense rock alteration, as observed in crater lakes and at volcanogenic, so-called high-sulphidation ore deposits. Acidity-dependent water-rock interaction in magmatic-hydrothermal systems can, therefore, be described in terms of two end-member processes:

- Full-equilibrium cooling along the feldspar-mica coexistence boundary; and
- Non-equilibrium cooling preserving high-temperature acidities.

The ever-increasing gap between these two cooling paths is a major driving force behind hydrothermal alteration in magmatic-hydrothermal systems.

In the case of most geothermal systems, interaction of circulating groundwater with magmatic material is likely to take place at temperatures (~400°C), allowing fluid pathways generated through brittle fracturing to remain open. Under such sub-solidus conditions, release of originally magmatic volatiles corresponds essentially to a leaching process. Because of the long residence of the fluids trapped in the vesicles and along grain boundaries, acid components, such as HCl, can be expected to become largely neutralised allowing CO_2 to take over as the major acid-generating species. Under hydrothermal conditions, CO_2 becomes reactive with respect to the conversion of feldspars to mica, according to the reaction:

$$CaAl_2Si_2O_8 + KalSi_3O_8 + CO_2 + H_2O \leftrightarrow CaCO_3 + Kal_3Si_3O_{10}(OH)_2 + SiO_2$$

but only at temperatures below 350°C. With decreasing temperature, its reactivity increases rapidly and CO_2-charged waters move quickly into the stability field of layer silicates, with framework silicates, feldspars, becoming unstable (Figure 38).

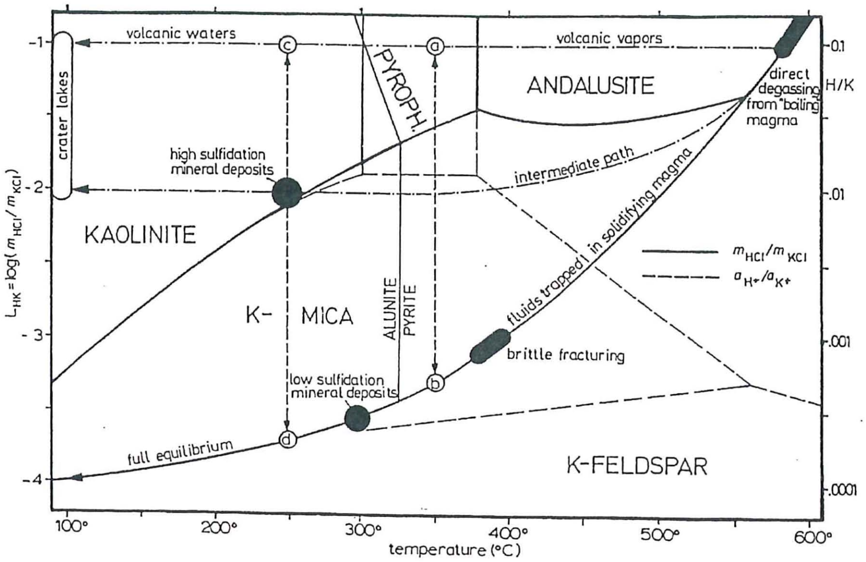


Figure 38: Stability of Al-silicates as a function of m_{HCl}/m_{KCl} and temperature (Giggenbach, 1997b)

A good review on the mineralogy and distribution and origin of acid alteration in Philippine geothermal systems is given in the reprinted paper by Reyes (1991) in Appendix I.

10. MAGMATIC-HYDROTHERMAL SYSTEMS IN THE PHILIPPINES AND THEIR CHARACTERISTICS

A typical magmatic-hydrothermal system in the Philippines is shown below in Figure 39. Two papers (Reyes, 1994; Reyes and Giggenbach, 1992) cover the characteristics of these systems and are presented here in Appendix II and Appendix III.

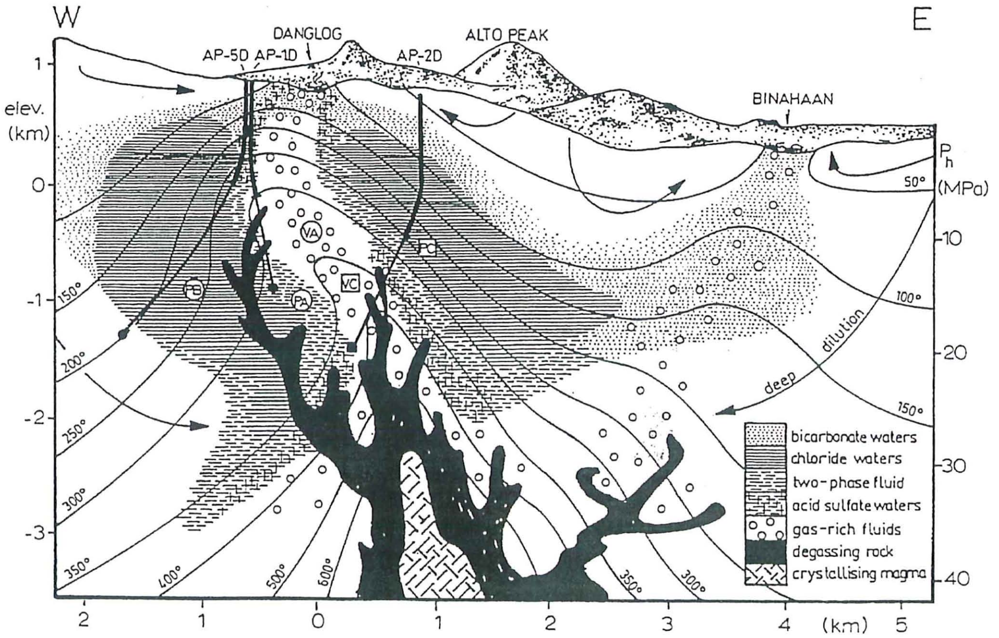


Figure 39: Example of a vapour-cored hydrothermal system in the Philippines with magmatic acid fluids closely associated with recent volcanism (Reyes et al., 1993)

LECTURE 4

REDISTRIBUTION OF LIGHT ELEMENTS DURING HYDROTHERMAL ALTERATION: ELEMENTAL MOBILITY AND ION BEAM ANALYSIS

1. NOMENCLATURE

PIXE:	Particle induced X-ray emission using proton rather than electron beams
IBA:	Ion beam analysis
NRA:	Nuclear reaction analysis
Light elements:	Elements with relative atomic masse of <19, e.g. Li, B, F, N_2, Be, O_2.

2. USES

The macro- and microbeam IBA system at the Institute of Geological and Nuclear Sciences in Lower Hutt, New Zealand was developed in-house, employing a 3 MeV Van der Graaf accelerator, to study the occurrences, distribution and redistribution of a wide range of elements in biological and geological environments. Earlier studies using this system have, for example, mapped the distribution of fluoride in teeth and bones of man and animals. The system is also used to study the composition of air pollutants and changes in their spatial and temporal distribution. Both coal and rocks have been analysed using this system for the last five years.

In the study of rocks, both electron and proton (IBA) beam methods were used to determine rock powder or mineral compositions in conjunction with various petrographic techniques. Electron beam techniques include EMP (electron microscope) and XRF (X-ray fluorescence) whilst petrographic procedures consist of transmitted and reflected light microscopy, cathodoluminescence, fluorescence, XRD (X-ray diffractometry) and SEM (scanning electron microscopy).

One of the main reasons for employing IBA methods in geological studies is their ability to measure light elements that may be used to unravel various diagenetic, volcanic and alteration processes. These various studies are discussed below.

Use in diagenetic studies:

- Under cathodoluminescence, minerals such as quartz and feldspars show textures, structures and colours not seen under normal polarised and plain light microscopy. To determine the reason for the range of cathodoluminescent colours found in these minerals, areas in a number of minerals were point-analysed and plotted in a log (X/Si) vs. X graph (Figures 40 and 41) where X means the element. Blue colours in plagioclase are induced by the presence of trace amounts of Ti,

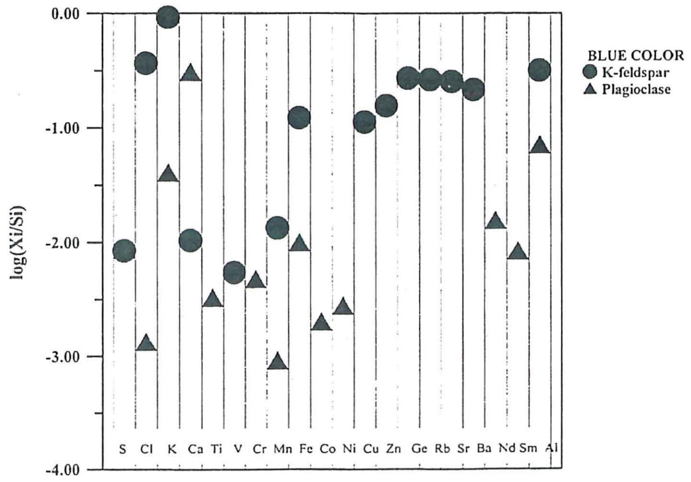


Figure 40: Variations in the relative elemental compositions of blue-luminescing plagioclase and K-feldspar in terms of log (X_i/Si) (Reyes, 1998)

Mn, Co and Ni (Figure 40), while blue cathodoluminescence in K-feldspars are activated by trace contents of V, Zn, Cu, Ge and perhaps Rb, Sr and Ba. Blue cathodoluminescence in quartz can be associated with the trace occurrences of S and relatively high amounts of Ti, V and Mn. Non- luminescent quartz has very low amounts of V, Cu, Mn, Co and Zn (Figure 41).

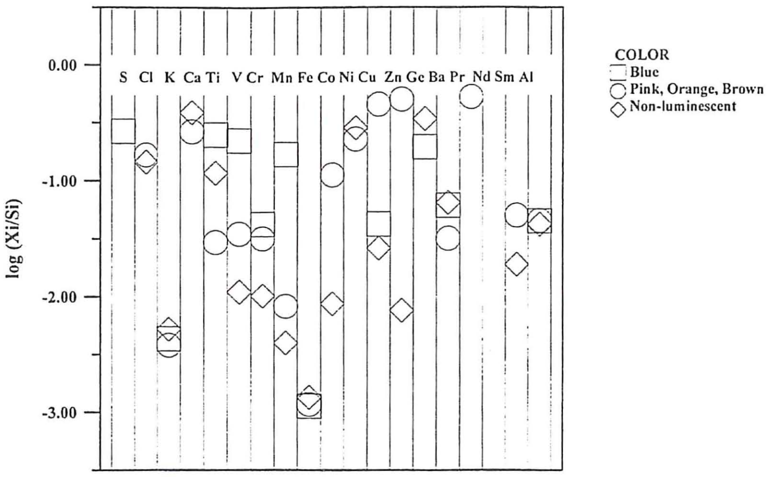


Figure 41: Variations in the concentrations of elements (X_i) with respect to Si concentrations expressed as log (X_i/Si) in blue-, pink- and non-luminescent quartz (Reyes, 1998)

- Mineral deposition is a slow process during diagenesis in hydrocarbon systems (Table 2), and elemental mobility is not easy to discern. Figure 42 illustrates how various elements in permeable sandstone are more mobile than apparent, using IBA mapping techniques.

Further discussion on the distribution of light elements is referred to two papers in appendices. Appendix IV includes a paper on the distribution of Li, B and Cl in the Kawerau geothermal field , New Zealand (Reyes and Vickridge, 1996) and Appendix V a paper on the distribution of Li and B in geological samples (Trompetter et al., 1999).

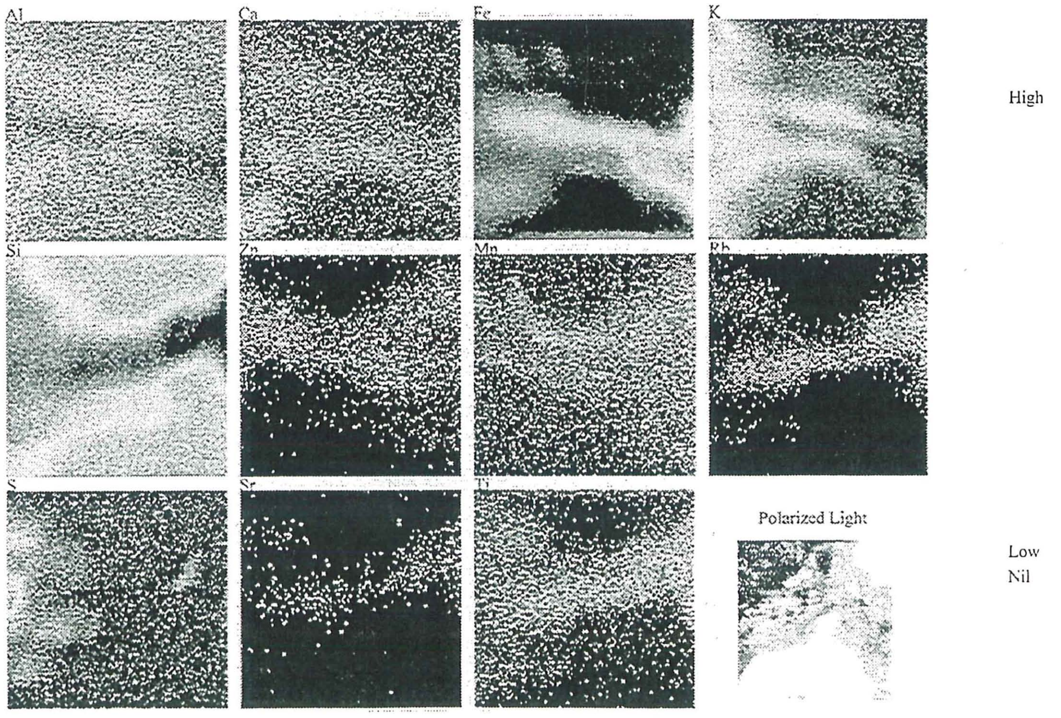


Figure 42: Elemental maps, using IBA, showing the distribution of Al, Ca, Fe, K, Si, Zn, Mn, Rb, S, Sr and Ti in a 1.2 × 1.0 mm^2 section of a sandstone composed mainly of various authigenic carbonates and detrital quartz grains (Reyes, 1998)

LECTURE 5

VOLCANIC ASH LEACHATE COMPOSITIONS AS A MEANS OF MONITORING VOLCANIC VAPOUR DISCHARGES DURING EXPLOSIVE ERUPTIONS

1. HYDROTHERMAL AND MAGMATIC COMPONENTS IN THE 1995-1996 RUAPHEU ASHES (Reyes, 1997)

Petrographic and SEM analyses of bombs and ashes from the 1995 and 1996 eeruptions of Mt. Ruapehu showed that they contained 8-20% hydrothermally altered fragments. Major and trace element contents of ash leachates and leached ashes were compared with each other and with those of Ruapehy Crater Lake. The June 1996 ashes contained up to 1100 mg/kg of F. Ingestion of ash-contaminated vegtation caused fatalities among farm animals. In comparison to the leached ashes, the crater lake waters and leachates are enriched in Cl, C, B. Pb, As and Li, and depleted in Cr and V. Most of the adsorbed material appears to represent evaporated lake water.

The composition of the hydrothermal products from the 1996 eruption, consisting of kaolinite, pyrite marcasite, gypsum, smectite, vermiculite and opal points to predominantly shallow formation, probably within the lake and at the contact of lake water with bedrock. Minor alteration products include cristobalite, alunite, quartz, anhydrite, illite, chlorite, biotite and magnetite. Alteration products indicative of >250°C hydrothermal conditions in Ruapehu are scarce. Less than 0.1% of the ashes is made up of illite, chlorite, biotite, quartz, anhydrite, bornite and magnetite suggesting that only a small high-temperature hydrothermal system existed within the Ruapehu volcanic structure, unlike at Mt. Pinatubo where as much as 12% of the volcanic ejecta consisted of fragments hydrothermally alterred at high temperatures. Assuming boiling-point-vs. depth conditions, the magmatic-hydrothermal interface Ruapehu would lie at a minimum depth of 1600 m.

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APPENDIX I

Geological Survey of Japan Report, No. 277, 1991, p. 59-65

Mineralogy, Distribution and Origin of Acid Alteration in Philippine Geothermal Systems

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Introduction

Overview of Philippine Geothermal Systems

Seventeen of the thirty geothermal systems in the Philippines have deep wells (depth$>$1500 m), four of which provide 894 MWe or 15.4% of the country's electrical power needs.

Philippine geothermal areas are closely linked with Pleistocene to Recent calc-alkaline volcanic complexes, dominated by andesite; or with smaller silicic andesite to dacitic domes. A cross-section of a typical Philippine geothermal system is shown in Fig. 1.

It is common for Philippine geothermal systems to have had several hydrothermal regimes, one of which is presently active, and the rest extinct or waning. In geothermal systems like Palinpinon, portions of the extinct hydrothermal system/s are exposed on the surface and are sometimes explored for epithermal deposits.

The major sources of permeability in the wells are gravity or normal faults with dips of 70-90°C. However, lithological contacts, breccias, fractures, and joints may also provide permeability (Reyes, 1990).

Objectives of Study

The presence of acid sulfate fluids has a debilitating effect in the development of a geothermal system, and may drastically limit the resource. Thus, detailing the occurrences of acid alteration, and understanding its origins and hydrology, may assist in planning the exploration and development strategy of a geothermal resource. The study of acid alteration in active hydrothermal systems may also contribute to an understanding of certain ore deposits such as the high sulfidation type associated with the enargite group of minerals. This study reviews the occurrences, geochemistry, temperature ranges, and mineral assemblages of acid alteration in Philippine geothermal systems, except for Tiwi and Makban, which are privately developed.

Occurrences

Patches of acid alteration common on the surface of most geothermal areas in the world usually form as products of steam-heated acid sulfate fluids when H_2S-laden steam condenses into surficial water (White, 1957). Reaction of groundwaters with sulfur sublimating from H_2S, or relict acid sulfate minerals may also produce a new generation of acid sulfate fluids and alteration as in Rotokawa, New Zealand (Browne, pers. comm., 1985).

However, the propensity for the formation of deep acid alteration, i.e., $\geq$500 m

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Keywords: Philippine geothermal systems, acid alterations, fluid inclusions, fluid chemistry

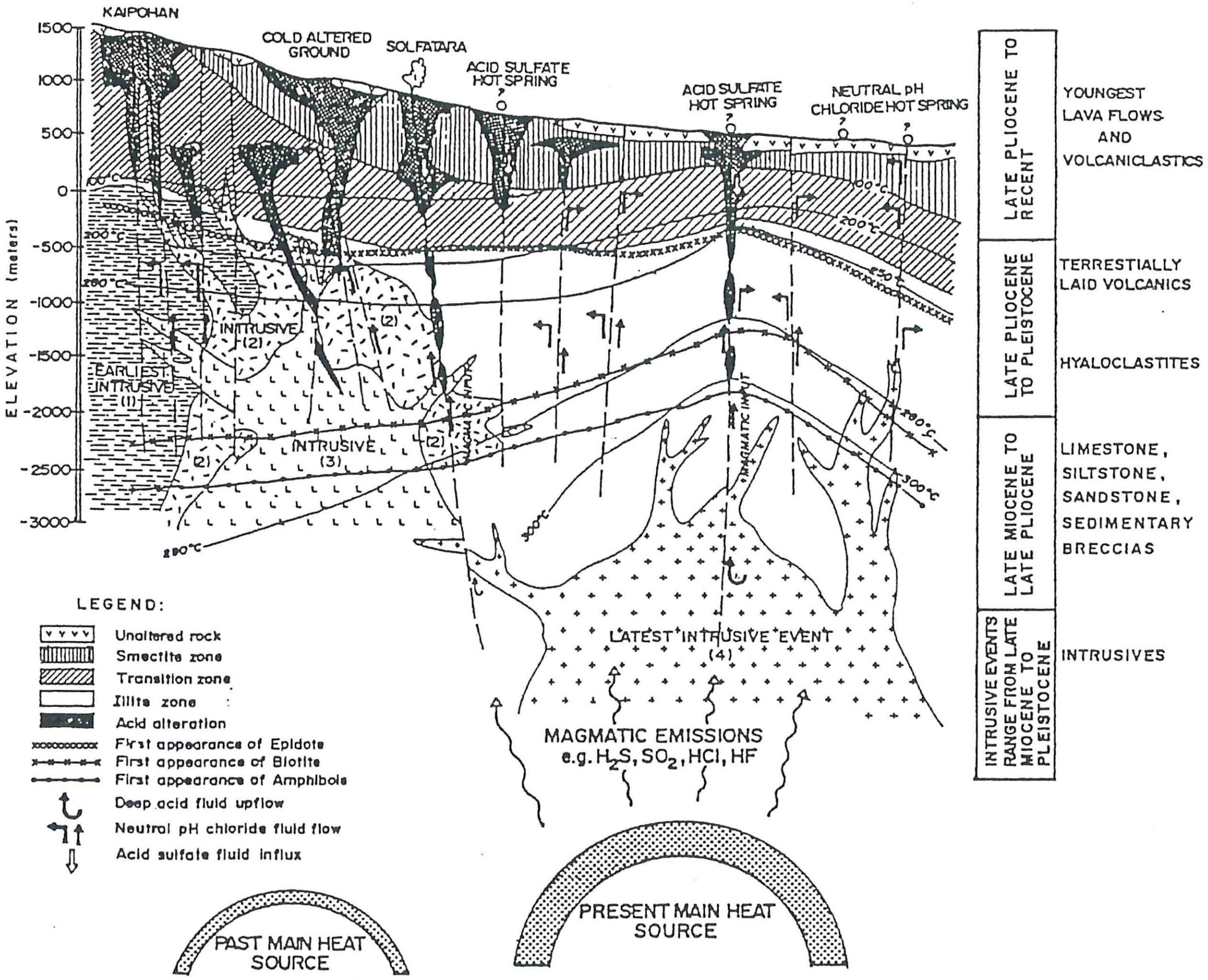

Fig. 1. Geologic model, alteration patterns, and stratigraphy typical of a Philippine geothermal system. The lateral extent of this model is 2-15 km. Note that downflowing acid sulfate fluids may occur throughout the system; but deep acid fluid upflow is associated with young intrusives and deeply-penetrating structures.

depth, and the presence of acid fluid discharging from wells, are common in andesitic to dacitic-hosted geothermal systems (Henley, 1985) e.g., Matsukawa, Otake, Hatchobaru, and Komatsu, in Japan (Sumi, 1969; Sumi and Maeda, 1970; Hayashi, 1973; Browne, 1978; Manabe and Ejima, 1984), Tatun in Taiwan (Chen, 1970), Indonesia (Browne, 1978), Mexico (Cathelineau *et al.*, 1985), Costa Rica (Corrales, pers. comm., 1986), and the Philippines.

Acid alteration in the Philippines occurs in about 90% of the wells reviewed, with about 45% having the potential to discharge acid fluids upon field exploitation. However, to date, only 17 wells are confirmed acid, with some having acid influx occurring only at certain borehole conditions. In general, acid wells have low mass flows and relatively low permeabilities.

Acid alteration in wells may be related to a buried hot spring system or solfatara; or localized along structural zones. These usually form sharp boundaries with the rest of the rock, which is pervaded by neutral pH alteration. Acid altered rocks are usually only a few tens of centimeters thick. However, thicknesses may be greater in volcaniclastics, as in well OK-11D in Palinpinon, where as much as 750 m is observed. On the average, acid alteration occurs sporadically down to 1600-1800 m, rarely extending down to 2500 m, with thickness and frequency diminishing with depth.

Acid sulfate surface thermal manifestations, whether relict or not, are usually harbingers of subsurface acid alteration, although their absence does not preclude the latter. For example, in the western sector of Palinpinon, ~85% of the surface faults are associated with acid altered ground. Subsequent examination of cuttings confirmed the presence of acid minerals along their subsurface intersections. Since structures are the main avenues for acid fluids deep in the system, study is focussed on structures to determine if the faults channel deep acid fluids (with magmatic input) or merely act as conduits of acidified fluids from the surface.

Mineralogy

About 35 minerals were identified in acid alteration assemblages. Due to extreme depletion in alkali cations, there are little, if any, interlayered clays in this assemblage.

Acid alteration minerals are divided into 5 zones based on the sequential appearance of index clays and associated minerals, with increasing depth, temperature, and distance from the main source of acid fluids (Fig. 2). From the kaolinite to the muscovite zone, there is an increase in the dehydration of the clays, crystallinity, silica content of the clays and aluminosilicates, and the ratio of anhydrite to alunite. Thus, as the acid fluids react with the rock, pH increases, the silica activity of the environment increases and the sulfate activity decreases. Minerals characteristic of acid fluids, e.g., quartz, diaspore, sulfates, sulfides, and iron oxides, are not inert, as suggested by dissolution and reprecipitation textures observed under the SEM.

Types of Acid Alteration

Aside from temperature-based zonations, acid minerals can be divided into two types, based on the virulence and corrosivity of the associated fluids and the propensity of the assemblage to rejuvenate fluid acidity. These are:

1) *Virulent* acid alteration characterized mainly by the presence of sulfur ± alunite ± abundant pyrite/marcasite, and

2) *Deceptively benign* acid alteration characterized by the absence of sulfur and alunite; and the presence of kaolinite, dickite, pyrophyllite, diaspore, anhydrite, and pyrite.

Virulent acid alteration occurs at shallower levels than the other type. In the Bacon-Manito geothermal system, the former persists down to a maximum of 1250 m while the latter can persist to 2500 m. Acid alteration often changes from a virulent to a relatively benign type to neutral pH alteration with depth, along a structure; or laterally, away from the main acid sulfate fluid channel.

When encountered within well aquifers, virulent acid minerals portend immediate acid fluid discharges from a well and intense corrosion of well pipes. Even when relict, the reaction of neutral pH fluids with virulent mineral assemblages rejuvenates fluid acidity- a mechanism that may be aggravated by high temperatures. The second type is deceptively benign as acid fluids may not be apparent during initial well discharges, as in some wells in Tongonan, Palinpinon, and

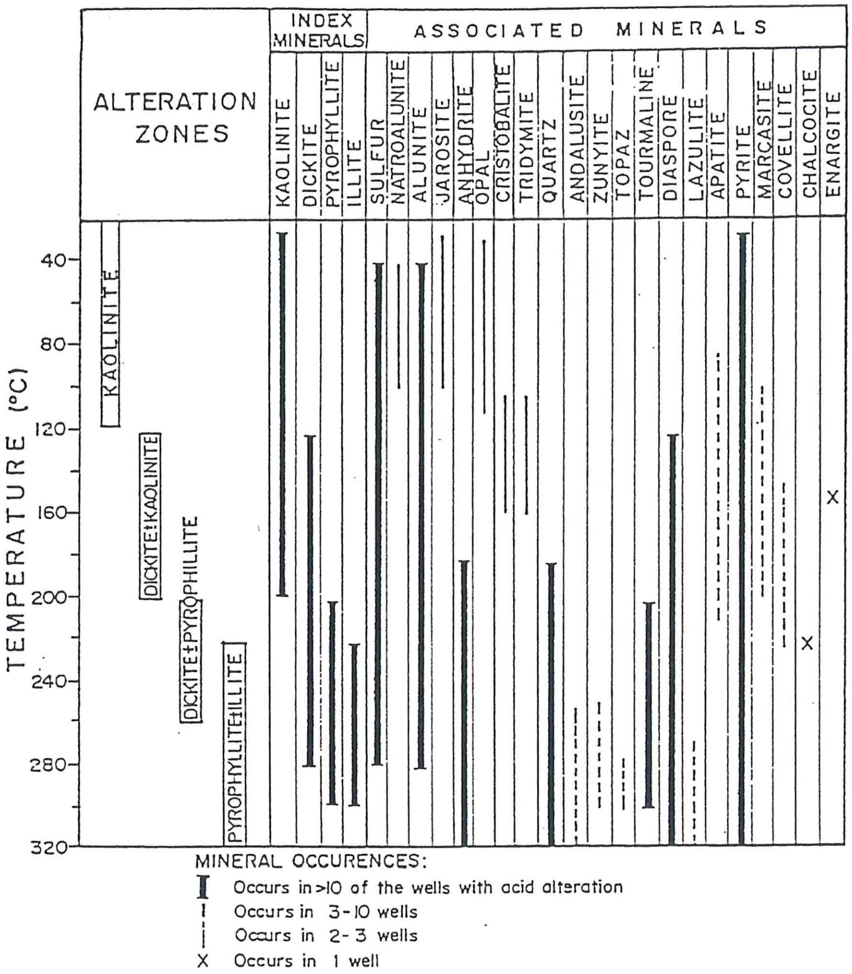

Fig. 2. Acid alteration zones and temperature ranges. Temperatures are based on direct measurement and fluid inclusion homogenization data, as well as temperatures of contiguous neutral pH alteration assemblages.

Bacon-Manito. Exceptions are a well in Mt. Pinatubo, and OK-11D in Palinpinon. The former intersected pyrophyllite + diaspore + anhydrite + abundant pyrite ± lazulite. OK-11D encountered minor acid alteration, but not in the aquifer zones. The Mt. Pinatubo well produced acid fluids upon discharge (Villarosa, pers. comm., 1989), while OK-11D produced molten sulfur nearly two years after drilling (Sarmiento, pers. comm., 1985). Both wells show active magmatic input based on fluid chemistry (Ruaya, pers. comm., 1990) and are adjacent to one of the latest volcanic edifices in each area. In fact, Mt.Pinatubo volcano started to erupt in June 1991.

Rock Chemistry and Mineralogy

Acid sulfate fluid incursion usually results in the complete recrystallization of the rock and mobilization of base cations, leaving hardly any primary minerals. Deep acid assemblages are often closely associated with fractures/faults.

Acid altered rocks are composed largely of residual oxides. Calcium is usually fixed in anhydrite. Potassium forms alunite at low pH, high sulfate activity, and low to moderate temperatures; and illite and muscovite at higher temperatures, pH, and silica activity. Sodium is rarely partitioned into natroalunite, usually at temperatures below 150°, while magnesium forms hardly any stable mineral in acid zones except for rare lazulite or ralstonite. Mg-rich clays, such as sepiolite, form abundantly at the contact of acid and neutral pH alteration. Total sulfur increases in acid assemblages and occurs in the form of sulfur, sulfides, and sulfates. In Bacon-Manito, there is an increase in arsenic and a depletion in copper and zinc in acid zones. In Palinpinon, arsenopyrite forms as well scales where there is acid sulfate fluid influx.

Fluid Inclusion Studies

Fluid inclusion homogenization and freezing temperatures were measured in anhydrite, quartz, diaspore, and rarely, alunite. Homogenization temperatures usually range from 90° to $\geq$ 420°, similar to those of fluid inclusions in adjacent neutral pH altered rocks. In general, fluid inclusions high in gas are more common in acid assemblages, often forming clathrates that disappear at about 1 to 11°C. Inclusions in diaspore and alunite are often vapor-rich, and in the case of diaspore from Bacon-Manito, homogenize to the vapor-phase. Where clathrates are absent, fluid inclusion equivalent salinities in acid assemblages are similar to those associated with contiguous neutral pH minerals; and when applicable, to well aquifer fluids.

In cases where magmatic input is suspected, based on mineralogy and well fluid chemistry, fluid inclusions show the following characteristics:

1) abundance and variety of isotropic to anisotropic daughter minerals, with

Table 1 A comparison of acid and neutral pH fluids in Tongonan and Palinpinon. These are discharge data from selected wells, analysed at 25°.

FLUID COMPONENT	CHARACTERISTICS
pH	<5.5 for acid fluids
Cl	Generally lower for acid fluid discharges at~3700-13600 ppm
	~8100-25700 ppm for neutral fluids
Ca	Generally lower in acid discharges at~40-200 ppm
	~160-500 ppm for neutral fluids
Mg	May be as much as 50 X greater in acid fluids at~0.5-170 ppm
	~0.01-1.3 ppm in neutral fluids
Fe	May be as much as 400 X greater in acid fluids, at~4.0-445 ppm
	~0.0-9.0 ppm in neutral fluids
SO_4	May be as much as 35 X in acid fluids at~50-3200 ppm
	~15-50 ppm in neutral fluids
H_2 (gas)	Discharge values may be as much as 35 X in acid fluids

some deemed to be copper sulfates,

2) very high salinities (≥ 17 wt% Cl eq., based on melting point of salt crystals),

3) very high temperatures, exceeding 400°, with some inclusions homogenizing at the critical point, and

4) presence of fluid inclusions that form a yellow liquid (sulfur ?) usually starting at~80°, and darkening to deeper yellow with increase in temperature, as in samples from wells in Biliran and Cagua.

Fluid inclusions in acid altered dacitic rocks are richer in daughter minerals than those in andesites.

Fluid Chemistry

Acid fluids from downhole samples and well discharges are often high in sulfate and chloride, and are believed to be a mixture of acid sulfate and neutral pH fluids coming from multi-feed zones in a well. However, the possibility of high chloride coming from HCl associated with magmatic contributions may be present in some wells where Cl is in excess and SO_2 is also detected (Ruaya, pers. comm., 1989). Table 1 shows selected fluid components whose ranges are characteristic of well discharges in Tongonan and Palinpinon. Acid discharges in both systems have higher Ca, Mg, Fe, SO_4 and H_2 gas than neutral fluids. In general, Cl is lower in acid fluids in Tongonan and Palinpinon, probably because acid wells in these areas usually occur at the outflow and/or the acid fluids tapped by the wells originate from the surface. High Mg may suggest the association of some acid fluids with dilute groundwaters.

Origins of Acid Alteration in Philippine Geothermal Systems

There are three major, possibly four, models for the formation of acid alteration and fluids in Philippine geothermal systems:

1) H_2S rising from a boiling aquifer to be oxidized in the vadose zone, and percolation of the resulting acid sulfate fluids along faults. Due to the strong neutralizing effect of the rock, such fluids are limited to shallow levels, perhaps down to 500 m from the surface, at the maximum. A variation of this may occur when extreme drawdown in a system creates a steam cap. Acid fluids are then generated when cooler groundwaters enter the system, react with the gases, and percolate to deeper levels along structures. Fluid acidity may be further aggravated when a virulent acid assemblage is intersected, along its way to deeper levels.

2) Reaction of deep aquifer fluids with magmatic volatiles such as SO_2, H_2S, HF, and HCl. This is supported by the presence of SO_2 and excess Cl in the fluid discharges; minerals like lazulite, topaz, ralstonite, danburite, gadolinite, and zunyite; and fluid inclusion characteristics.

3) Rejuvenation of acidity when neutral pH fluids react with formations enriched in alunite ± sulfur ± pyrite. This is corroborated by isotope studies in Palinpinon (Villasenor, pers. comm., 1988).

4) The possibility of deep aquifer acid fluids (not simply acid volatiles), related to Model 2 and exemplified by wells in Mts. Pinatubo and Cagua.

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APPENDIX II

Petrological and geochemical characteristics of magmatic-hydrothermal systems in the Philippines

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The chemical and isotopic compositions of water and gas discharges from geothermal wells, alteration mineralogy and fluid inclusion characteristics strongly indicate that ten of the more than 400 geothermal wells drilled in the Philippines contain active magmatic components. They are found at Biliran, Mt Pinatubo, Mt Cagua, Alto Peak, Mahagnao, Palinpinon, and Bacon-Manito. Eleven other wells at Palinpinon, Bacon-Manito, Daklan, Natib, Mt Apo and Alto Peak, as suggested by alteration mineralogy and fluid inclusion features, may have harbored magmatic-hydrothermal fluids in the past. Other systems under exploration, such as those near Mt Canlaon and parts of Mt Apo which have not yet been drilled, show surface evidences for the influx of active magmatic-hydrothermal fluids at depth.

There are indications for deep magmatic-hydrothermal fluid input even during early surface exploration stages. They are: proximity to Pleistocene to Recent silicic andesite to dacite domes, most of which have erupted within the last 1 ka, eg Pinatubo (1991), Cagua (1860), Canlaon (1993), Biliran (?1939), and Mahagnao (1895); the occurrence of solfataras discharging high Cl and/or F vapors as at Biliran (Ruaya, 1981; Ramos-Candelaria et al, 1994), Pinatubo (Ruaya et al, 1992; Clemente, 1984), and Mt. Apo (Delfin et al, 1984) and highly acid Cl-SO_4 springs at high elevations as at Pinatubo, Cagua, and Saray. Wells are sited to avoid faults that may channel magmatic fluids.

Rock formations penetrated by wells with considerable magmatic input have generally low permeabilities which lead to rapid pressure drawdown, the drying up of wells and the subsequent discharge of super-heated steam. Measured temperatures are >330°C. Gas and water discharges of wells with active magmatic components are characterized by $^3He/^4He$ ratios $> 7\ R_A$ (Giggenbach and Poreda, 1993). The waters generally have high SO_4 contents and show an ^{18}O- and a distinct D-shift (Reyes and Giggenbach, 1992). The latter may be ascribed to the addition of varying proportions of D-enriched "andesitic" water (Giggenbach, 1992a), which in Philippine magmatic-hydrothermal systems ranges from 45% at Alto Peak to 85% at Mahagnao. The relative contents of N_2, He and Ar provide indications for the presence of magmatic vapors. Exceptionally high H_2 and CO contents in the vapors point to the existence of high temperature, possibly magmatic environments nearby (Reyes and Giggenbach, 1992). The wells often discharge acid waters, eg at Pinatubo (Ruaya et al, 1992), Biliran (Ramos-Candelaria et al, 1994) and Cagua.

Reyes A G (1994)

Apart from the geochemistry of discharges from surface geothermal manifestations and wells, valuable evidence for the influx of magmatic fluids is provided by a range of geological and petrological characteristics of altered reservoir rocks encountered during drilling. Except for the Mahagnao wells, which were partly drilled through serpentinites, most Philippine "magmatic wells" penetrated andesitic volcanics, volcaniclastics, and sedimentary rocks. Young quartz dioritic dikes in all the wells induced contact metamorphism that grades into high temperature hydrothermal alteration. Thus for "magmatic wells", high temperature minerals like allanite, actinolite-tremolite, hornblende, diopside, wollastonite, vesuvianite, biotite and staurolite are associated with hydrothermal minerals like anhydrite, quartz, epidote, and garnet. Instead of adularia, orthoclase forms with these minerals. In the serpentinites, a different set of contact metamorphic and magmatic-hydrothermal assemblages occur, consisting of forsterite, merwinite, chondrodite, and monticellite, again associated with quartz, anhydrite, epidote and garnet.

The presence of minerals indicating deep acid sulfate alteration at depth >500m such as alunite, native sulfur, diaspore, pyrophyllite, dickite, anhydrite, quartz and sulfides is a harbinger of magmatic input at depth. Three wells, located in Palinpinon and Bacon-Manito, intersected sulfur lenses at depths of 1200-1800 m, where temperatures of 240-280°C rendered the sulfur molten. About half of the discharge of one of these wells consisted of native sulfur. Albeit present in minor quantities, pneumatolytic-type minerals, often bearing Cl, B, PO_4, and F, are relatively common in "magmatic wells". These minerals, occuring at temperatures >280°C may be associated with acid alteration assemblages and commonly include lazulite, zunyite, and apatite, with rare danburite, ralstonite, gadolinite and fluorite. Apatite-infested anhydrite is a typical component of magmatic-hydrothermal assemblages, found in both "magmatic wells" and in the pumice of the 1991 Mt Pinatubo eruption. Other minerals found in these assemblages are andalusite and rare cordierite. Associated opaque minerals consist of pyrite, chalcopyrite, bornite, cubanite, pyrrhotite, pentlandite, sphalerite, galena, magnetite, and rare enargite and clausthalite.

Fluid inclusions in these wells typically homogenize at temperatures >350°C, to a liquid or vapor phase, or to a critical point. They may contain abundant halite and sylvite and other isotropic and anisotropic daughter minerals, some of which appear to be Cu compounds. Liquid sulfur is sometimes present. Equivalent salinities of inclusions are often >10% b.w. NaCl. At times, a second immiscible liquid appears at temperatures <10°C. In Alto Peak for example, high temperature (>360°C) and highly saline fluid inclusions containing daughter minerals are associated with vapor-rich fluid inclusions and melt inclusions, and are confined to micron-thick zones. The fluid and melt inclusions are found in quartz and anhydrite and are closely associated with high temperature minerals like biotite, diopside, vesuvianite, tremolite-actinolite, hornblende, topaz, wollastonite and B-bearing minerals (Reyes et al, 1993).

Drilling in Philippine systems shows that magmatic-hydrothermal environments occupy comparatively minor proportions of a system. The imprints of magmatic fluids are ephemeral, probably due to the relatively short duration of volcanic-magmatic episodes and the low fluid/rock ratios accompanying alteration during a "magmatic" stage. Often, "immature" magmatic systems appear to evolve into a "mature" hydrothermal system with time, when invading groundwaters mix with residual liquids and interact with the rock at lower temperatures, leading to the formation of neutral Cl waters. There are numerous examples of this process in the Philippines, foremost of which are Palinpinon, Bacon-Manito, and Tongonan. However, there are systems like Alto Peak, wherein a dying neutral Cl geothermal system is rejuvenated by renewed volcanism and the input of magmatic fluids within a confined space (Reyes et al, 1993).

Eruptions, like that of Mt. Pinatubo can unearth portions of a hydrothermal system, and like drilling, can provide information on the magmatic-hydrothermal interface. The hydrothermal components expelled by the eruptions, which commenced in April 1991, consisted of biotite, actinolite-tremolite, epidote, quartz, anhydrite, calcite, albite, illite, chlorite, rutile, sphene, chalcopyrite and pyrite. With time, the hydrothermal fragments in the ash and pumice decreased from about 12% in April to <1% in June, indicating the small proportion of the hydrothermal system in comparison to the magmatic materials, and its depletion as the eruption went on. In June, based on the hydrothermal mineral assemblage and comparisons with well data, the released materials originated from deeper within the hydrothermal system than those of April.

The magmatic-hydrothermal interphase during the eruption of the volcano is illustrated by the presence of melt and fluid inclusions in plagioclase, quartz, and anhydrite. Fluid inclusions in the plagioclase record temperatures of 400-430°C and salinities of 1-7% NaCl b.w. Clochiatti et al (1994) reported the coexistence of melt and fluid inclusions in quartz from the Pinatubo extrusives. The fluid inclusions homogenized to the vapor phase at 358-370°C and contained 0.9 to 3.4% NaCl b.w., CO_2 and trace H_2S. Secondary quartz, from drillhole samples of the Pinatubo well (Pin-3D) nearest the eruptive vents, contain fluid inclusions that record temperatures of 290 to 470°C, and salinities of 1.9 to 10% NaCl b.w., to as high as >40% NaCl b.w. The reservoir Cl concentration in Well Pin-3D is 1.7% NaCl b.w. and the H_2-Ar geothermometer (Giggenbach, 1992b) indicates temperatures of 365°C. Fluid inclusion salinities and temperatures of the eruptive minerals are comparable to those measured in the secondary minerals recovered from the magmatic-hydrothermal interphase intersected by Pin-3D. The lower salinity and temperature ranges in all the fluid inclusions are similar to the measured Cl concentrations and temperatures of the well reservoir. Melt inclusions in the eruptive minerals presumably originated below the drilled depths where temperatures were higher than recorded by well data. Preliminary sulfur isotopes measured on the Pinatubo anhydrite and chalcopyrite indicate origins other than hydrothermal (McKibbin et al, 1994). Exhumation of a hydrothermal system may provide information on deeper parts of the system, but the ejecta consist of relatively chaotic material compared to drillhole cores and cuttings.

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APPENDIX III

Water-Rock Interaction, Kharaka & Maest (eds) © 1992 Balkema, Rotterdam. ISBN 90 5410 075 3

Petrology and fluid chemistry of magmatic-hydrothermal systems in the Philippines

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ABSTRACT: Early warning signs of the likely presence of volcanic-magmatic fluids, within hydrothermal systems closely associated with andesitic magmatism, consist of the discharge of highly "immature", predominantly Cl, but SO_4-rich, frequently acid waters, enriched in both ^{18}O and D with respect to local groundwater. Relative N_2 contents of associated vapors are much higher than those in air-saturated groundwater, $N_2/Ar > 200$. More detailed information on the underground distribution of such fluids, whether relict or active, is obtained from the alteration mineralogy and fluid inclusion data. Contact minerals are present, pneumatolytic-type minerals may be associated with acid alteration assemblages. Fluid inclusions homogenize to the liquid and/or vapor phase at $t > 350^{\circ}C$, or sometimes to a critical point. Equivalent salinities are >10% NaCl and daughter minerals, including salts and anisotropic minerals, are abundant; some contain elemental S or exhibit two or three immiscible fluids at low temperatures. The comparative rarity of well developed magmatic-hydrothermal systems suggests that their temporal and spatial extents are limited to comparatively short periods and to small rock volumes.

1 INTRODUCTION

With 894 MWe installed, geothermal energy provides 21 to 26% of the power needs of the Philippines. An additional 1010 MWe of steam-field capacity is planned to be developed by 1996 (Javellana, 1992). Most of the explored and developed geothermal systems are associated with Late Pliocene to Recent andesitic volcanic complexes and/or dacite to silicic andesite domes (Reyes 1990). A typical well, from top to bottom, penetrates: a sequence of andesitic, basaltic and dacitic lava flows and pyroclastics; andesitic hyaloclastites grading into a sedimentary sequence of limestone, breccias, sandstones, siltstones, claystones and shales; an intrusive complex that predates the sedimentary formations; and a series of young dikes that cross-cut the older intrusives and the sedimentary rocks. The sedimentary formations are usually late Miocene to Pliocene in age. Aquifers are largely associated with faults and fractures, occasionally with lithological contacts and primary porosity.

2 MAGMATIC HYDROTHERMAL SYSTEMS

Based on fluid discharge chemistry and isotopic compositions, alteration mineralogy and fluid inclusion characteristics, about ten of the more than 400 geothermal wells drilled in the Philippines show strong indications for the presence of an active magmatic component. They are, or were encountered at Biliran, Mt Pinatubo, Mt Cagua, Alto Peak, Mahagnao, Palinpinon, and Bacon-Manito. Alteration mineralogy and fluid inclusion studies suggest that ten other wells may have harbored magmatic-hydrothermal fluids in the past, as at Palinpinon, Bacon-Manito, Daklan, Natib and Alto Peak.

3 SURFACE INDICATIONS FOR POSSIBLE ACTIVE MAGMATIC INPUT

In most cases there are good indications that wells may encounter active magmatic input at depth, even during the early surface exploration stages. Such wells are usually found close to Pleistocene-Recent silicic andesite to dacite domes, often associated with an active solfatara, substantial sulfur flows, and/or kaipohans. Some of these volcanoes have erupted within the last 1 ka., e. g. Pinatubo (1991), Cagua (1860), Canlaon (1988), Biliran (1939?) and Mahagnao (1895). Carbonized wood in sulfur flows from Biliran was dated 500 a b.p. (NZ Geol. Survey). Active solfataras in such areas sometimes discharge high Cl vapors suach as at Biliran (Ruaya, 1981), Pinatubo (Clemente 1984) and Mt Apo (Delfin et al. 1984). The presence of highly acid Cl-SO_4 springs at high elevations at Pinatubo and Cagua were used as indications for possible influx of magmatic volatiles (Clemente, 1984; and pers. commun. 1992). Wells are sited to avoid faults that may act as conduits for magmatic fluids. Otherwise the wells are drilled away from the upflow of magmatic fluids.

4 EVIDENCE OF MAGMATIC INPUT FROM DRILLHOLES

The main thrust of this study is to establish, in addition to chemical, petrological criteria useful as an "early warning device" for the occurrence of active magmatic components at depth while a well is being drilled. Such information is required for safety reasons, to assist in the assessment of the suitability af a system for power production, and in the location of future wells.

4.1 Fluid discharges

Strong evidence for the input of an active magmatic input is gleaned from the chemical and isotopic composition of well discharges. All the discharges have $^3He/^4He$-ratios >7 R_A. (R. J. Poreda, pers. comm.). The waters, associated with andesitic magmatism, generally have elevated SO_4 contents and show, in addition to the more common ^{18}O-shift, a distinct deuterium shift (Matsuhisa 1991). It may be ascribed to the addition of varying proportions of D-enriched, "andesitic" water (Giggenbach 1992a). Fig. 1 shows the total discharge isotopic compositions of wells drilled recently into four "magmatic-hydrothermal" systems.

According to this evaluation, the proportions of andesitic water ranges from 45% at Alto Peak to 85% at Mahagnao. Another good indicator for the presence of magmatic components are relative N_2, He and Ar contents (Giggenbach 1992b), as shown in Fig. 2. All indicators point to the presence of considerable proportions of magmatic fluids.

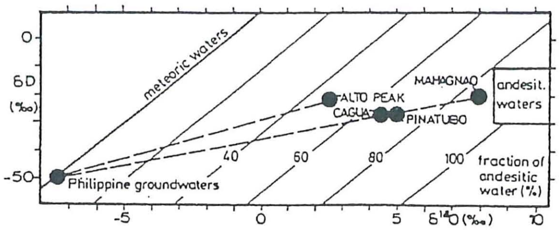

Fig. 1 Isotopic composition of waters

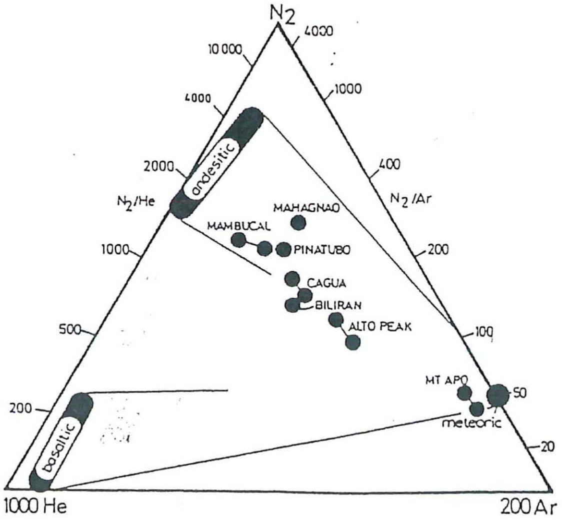

Fig. 2 Relative N_2, He and Ar contents

Other common features of vapors produced in volcanic-magmatic-hydrothermal systems are their exceptionally high H_2 and CO contents, pointing to the existence of high temperature, possibly magmatic, environments "nearby".

Fluid discharges are acid in wells from Pinatubo, Biliran, and initially, from Cagua. Cagua like Mahagnao subsequently produced only steam. A well at Palinpinon, OK-11D, did not sustain discharge, but eventually produced molten sulfur inside the casing.

4.2 Reservoir characteristics

Except for well AP-2D at Alto Peak, most wells with high magmatic contributions have low permeabilities and eventually produce super-heated steam, some show large pressure drops. Measured downhole temperatures range from 330° to >400°C.

4.3 Petrological characteristics

Most "magmatic" wells are drilled into andesitic volcanics or derived clastics. The wells at Mahagnao encountered serpentinites and basic rocks and thus also a different set of alteration minerals. In all wells, young dikes induced contact metamorphism grading into high temperature hydrothermal alteration. The degree of alteration depends on permeability and "water/rock" ratios at the time of intrusion. Fig. 3 provides a list of minerals found in these magmatic-hydrothermal wells. The temperatures indicated are based on measured and fluid inclusion homogenization temperatures. The upper limit of 700°C is imposed by the capabilities of the heating stage used. The alteration suite encompasses both neutral Al-silicate and acid sulfate mineral associations grading into contact metamorphism.

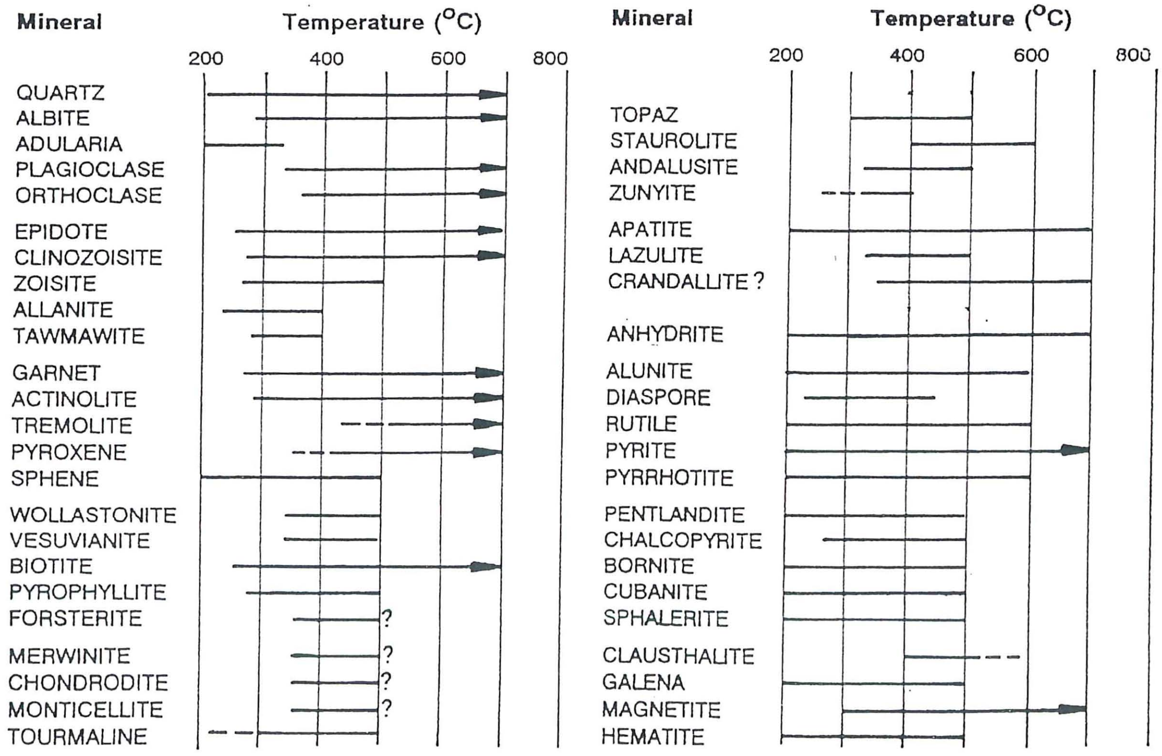

Fig. 3 Distribution of alteration minerals

Albeit present in only small quantities, Cl, B, PO_4 and F bearing minerals are relatively common in wells that encounter magmatic-hydrothermal fluids. Opaque minerals are mainly sulfides and oxides such as pyrite, chalcopyrite, bornite, cubanite, pyrrhotite, pentlandite, sphalerite, magnetite and rare enargite and clausthalite. Clay deterioration, especially of muscovite and illite, to an interlayered type clay is common when temperatures exceed 350°C.

4.4 Fluid inclusions

Fluid inclusion homogenization and melting temperatures were measured in quartz, orthoclase, anhydrite and plagioclase. Homogenization temperatures range from 350° to >700°C, with the upper limit for most between 450 to 500°C. The inclusions may homogenize to a critical point or to the liquid and/or vapor phase at >350°C. Salt crystals and anisotropic daughter minerals are common, equivalent salinities are frequently >10% NaCl. Some inclusions show the presence of elemental S; two or three immiscible fluids may appear at low temperatures.

5 DISCUSSION AND CONCLUSIONS

Since most of the geothermal systems in the Philippines are closely associated with Recent volcanism, there is always the danger of encountering highly immature fluids, unsuitable for geothermal power production with existing technology. In combination, pre-, syn- and post- drilling observations can provide unequivocal evidence for the presence of sub-magmatic fluids within or close to a geothermal well, allowing evasive action to be taken.

The comparatively rare occurrence of wells with distinct magmatic inputs, however, suggests that the extents of the primary magmatic environments are spatially quite limited, as compared to those of the "geothermal" zones proper, or that imprints left by the incursion of "immature" magmatic fluids are quickly erased. The major reasons for the ephemeral nature of imprints left by magmatic fluids are probably the comparatively short duration of volcanic-magmatic episodes and the low fluid/rock ratios accompanying alteration during a "magmatic" stage, leaving a considerable proportion of the wall rock unaltered. Later mixing of invading groundwaters with residual fluids and interaction with the unaltered rock, at lower temperatures, is likely to give rise to the formation of the neutral Cl waters typical of "mature" hydrothermal systems.

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APPENDIX IV

DISTRIBUTION OF LITHIUM, BORON AND CHLORIDE BETWEEN FRESH AND ALTERED ROCKS IN THE KAWERAU GEOTHERMAL SYSTEM, NEW ZEALAND

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SUMMARY - The partitioning of Li, B and Cl between altered rock and thermal waters in Kawerau is dependent primarily on their ability to be incorporated into the structure of secondary minerals. Chloride rarely finds a niche in alteration minerals below 320°C and is thus highly depleted in altered rock, but enriched in the waters. Boron and Li participate in hydrothermal mineral formation. At elevated temperatures, the mass distribution coefficient (K_{W-R}) between water and rock of B is 0.2 and that of Li is <0.06, showing that B has a high tendency to be leached, while Li stays in the rock. However, at temperatures <100°C, the K_{W-R} of B and Li is the same at 0.1, indicating that both have a similar tendency to partition into rock at low temperatures. The redistribution of other elements during alteration is affected by the chemical composition of the altering fluids and the original rock, and by permeability and temperature.

1. INTRODUCTION

In a series of studies on the partitioning of elements between rock and thermal waters in New Zealand, Ellis and Sewell (1963), Ellis and Mahon (1964), Mahon (1967) and Ellis and Mahon (1967) showed that (1) Li, B, Cl and F contents vary among basalt, andesite, rhyolite and greywacke, (2) certain ratios, such as B/Cl, in thermal waters are inherited from the parent rock, (3) rock components are increasingly leached with increasing temperatures and (4) that most constituents in thermal waters are likely to be derived by leaching of rock at >400°C. Goguel (1983) showed that Ca and Na are removed from rocks during alteration of volcanics by neutral Cl waters at temperatures of 200-300°C in Wairakei and Broadlands, whilst K, Rb, Cs and Li are added. Potassium and Rb are lodged in adularia, although clays and zeolites can also take in Rb; and Li is taken up by quartz and chlorite.

The primary processes in the partitioning of elements between rock and waters in the Taupo Volcanic Zone (TVZ) during hydrothermal alteration is leaching of rock at >400°C, followed by re-equilibration in response to boiling and dilution, at lower temperatures and shallower depths (Goguel, 1983).

This paper has two main objectives: (1) to determine the mobility of Li, B and Cl in rocks, minerals and waters during hydrothermal alteration in a water-dominated system, such as Kawerau, where temperatures are <320°C and (2) to compare Li, B and Cl with other elements as a function of the degree, intensity and type of hydrothermal alteration in volcanics and greywackes.

2. RESULTS

2.1 Analytical Methods

The determination of light elements, such as Li and B, in powdered rocks, and in individual minerals in polished thin sections, was made possible by the recent development of an ion beam technique at the Institute of Geological and Nuclear Sciences (Vickridge et al., 1994). Major and trace elements including Cl and S were analysed by X-ray fluorescence at Victoria University of Wellington.

2.2 Study Area

Kawerau is an arc-type geothermal system in the TVZ characterized by discharges high in CO_2, a CO_2/Cl ratio of 3.9±1.5, high B/Cl (0.06) and high Li/Cs (0.55). Ratios among B, Cl, Li and Cs suggest that they are derived from leaching of associated andesitic rock (Giggenbach, 1995). The wells intersect a thick sequence, >1000 m, of andesitic and rhyolitic lava flows, ignimbrites and volcaniclastics overlying the Mesozoic greywacke basement (Browne, 1978; Nairn, 1982; Allis et al., 1993). Within the main borefield, measured temperatures range from 260-290°C at production depths, although in the southern wells drilled towards Mt Edgecumbe, where thermal fluids are believed to upwell, temperatures are as high 315°C (Christenson, 1987, 1989).

Table 1- The Li, B and Cl contents, in mg/kg, of core samples from Kawerau wells, including typical TVZ basalt, andesite, rhyolite and greywacke. Also shown are depths (m) and measured temperatures (°C) at sampling points.

No.	Sample/ Well No.	Depth	Temp.	Rock Type	Li	B	Cl
1	KA-17	1038	250	Alt. Andesite	75	14.7	140
2	KA-26	521	236	Alt. Andesite	48	18.2	80
3	KA-26	641	261	Alt. Andesite	31	29.7	90
4	Onepu Spr	–	–	Alt. Rhyolite	22	9.0	10
5	KA-4	275	198	Alt. Rhyolite	85	22.0	–
6	KA-8	870	281	Alt. Rhyolite	59	7.2	200
7	KA-26	189	86	Alt. Rhyolite	20	11.1	<10
8	KA-26	345	86	Alt. Rhyolite	17	–	360
9	KA-26	396	120	Alt. Rhyolite	37	11.8	310
10	KA-26	459	180	Alt. Rhyolite	48	17.9	190
11	KA-26	577	250	Alt. Rhyolite	46	22.0	160
12	KA-38	164	200	Alt. Rhyolite	439	3.0	<10
13	KAM-3	131	160	Alt. Rhyolite	65	20.0	10
14	KAM-4	109	150	Alt. Rhyolite	109	9.8	10
15	KA-21	1027	285	Greywacke	–	18.2	50
16	KA-23	1170	285	Greywacke	–	13.2	20
17	KA-24	1069	253	Greywacke	–	15.0	10
18	KA-29	687	200	Greywacke	–	6.0	60
19	KA-34	1545	300	Greywacke	–	14.9	10
[a]Bs	K-Trig	–	–	Basalt	10	3.0	90
[b]Ad	Edgecumbe	–	–	Andesite	39	15.0	230
[c]Ry	TVZ ave.	–	–	Rhyolite	40	12.5	560
[d]Gw	TVZ recons.	–	–	Greywacke	60	30.0	12

Notes

[a] Reconstructed K-Trig basalt: this study, Ewart et al. (1968)

[b] Edgecumbe andesite: this study except for U, from Ewart et al. (1968)

[c] Average rhyolite from six TVZ fresh samples, this study

[d] Reconstructed Hauhungaroa Range surface greywacke from Reid (1982), Ellis and Sewell (1963) and Ellis and Mahon (1964).

A composite Kawerau well, shown in Fig. 1, was drawn up from samples selected from Table 1. Altered volcanics are represented by rhyolites from KA-4, 8, 26, 38, KAM-3 and 4; and andesites from KA-17 and 26. Greywacke is exemplified by KA-23 and 24. Typical TVZ rock compositions were selected for comparison with altered rocks (Tables 1, 2 and 3).

2.3 Alteration Patterns

The deep, >310°C, slightly alkaline waters in Kawerau have a Cl concentration of 925 mg/kg and a CO_2 content of 2.8% by weight. (Christenson, 1987, 1989; Giggenbach, 1995). As the deep fluids rise and cool, their acidity increases (Giggenbach, 1983). There are three major alteration assemblages in Kawerau, distinguished by key minerals:

1) semi-argillic alteration characterized by the presence of kandites, silica polymorphs, marcasite and pyrite, (Fig. 1) typical of the shallow weakly acid condensate layer where temperatures are <200°C,

2) phyllic alteration, consisting of illite, illite-smectite, quartz and pyrite found at the margins of the upflow and associated with >200°C, weakly acid Cl waters, and

3) neutral pH alteration, characterized by the presence of chlorite, illite or illite-smectite, quartz, sphene, sulfides, calcite, adularia, epidote and wairakite, associated with >200°C neutral Cl waters. Differences in CO_2 contents of the deep fluids are reflected in the presence or absence of wairakite, epidote or calcite (Giggenbach, 1983).

3. DISCUSSION

3.1 Variations in Li, B, Cl and other Trace Elements in Rocks

The distribution of Li, B and Cl with depth, alteration and lithology is shown in Fig. 1. Typical rhyolite and greywacke compositions are plotted on the top and bottom of the graph, respectively, for comparison with hydrothermally altered rock.

The Li contents of volcanics altered by neutral pH waters at >180°C, are low and nearly uniform, ranging from 17 to 75 mg/kg, with most values clustering between 50 to 60 mg/kg. Lithium is probably accomodated in the structures of quartz, chlorite (Goguel, 1983), illite-smectite and pyrite (Table 4). At shallow depths and temperatures <200°C within the acid altered zone, Li is enriched in the rock where quartz is more abundant than clays. Here its concentration ranges from 65 to 440 mg/kg, with the highest value found in KA-38 (164 m), a sample altered to >75% quartz.

Boron contents in altered volcanics do not deviate significantly from those in fresh rocks (Table 1, Fig. 1). Most samples contain 7 to 30 mg/kg B, with the exception of KA-38 (164 m) which contains only 3 mg/kg B, but has the highest Li content (440 mg/kg). Slight increases in the B contents of volcanics are associated with the abundance of open-lattice minerals, such as smectite, vermiculite, kaolinite-smectite, illite-smectite, chlorite-vermiculite, rectorite and even leucoxene (Fig. 1). In the greywackes however, B is significantly higher in the surface, than the well samples. The more permeable a formation, the lower is its B content (Fig. 1), indicating that B in greywackes is loosely held in the clay structures and thus easily washed out by hydrothermal solutions.

The higher the alteration intensity, the more depleted is a volcanic rock in Cl. The highest Cl of 360 mg/kg occurs in the least altered core of this study, KA-26 (345 m), where 60% fresh glass is still extant. Only in one sample, a greywacke from KA-29, is Cl enriched relative to fresh rock.

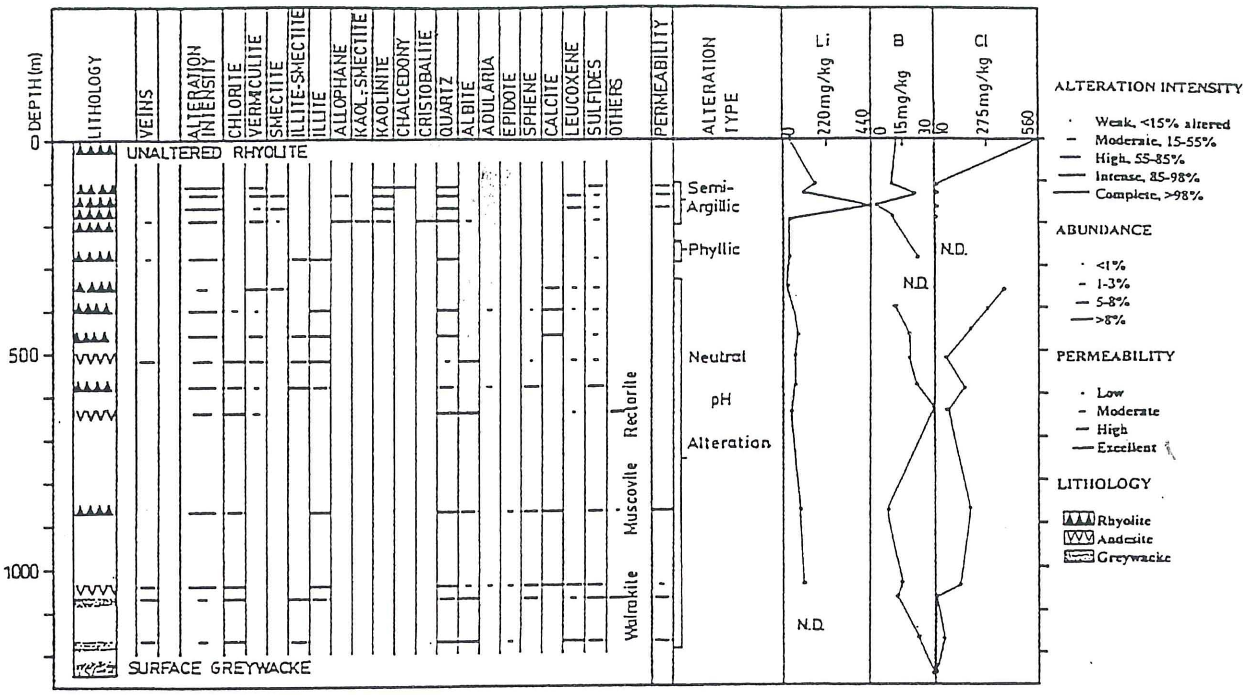

Figure 1- The lithology, alteration intensity, measured permeability, abundance of veins and various secondary minerals, types of alteration and the Li, B and Cl contents of rocks, in mg/kg, in a composite Kawerau well.

In order to account for compositional changes in the rock during alteration, the element concentrations in fresh (C_F) and altered (C_A) rock are plotted in Fig. 2. A 45° isocon line (Grant, 1982) is drawn through those components that show least relative gain or loss of mass. These are the immobile elements. The equation for the isocon, modified from Grant (1982), is:

$$\log C_A = \log C_F + \log (M_F/M_A) \qquad (1)$$

where M_F/M_A is the ratio of the mass of fresh to altered rock. Lines showing relative gains and losses are drawn parallel to the isocon line in Figs. 2A-D.

The mobility of elements during alteration is influenced by several factors: chemical compositions of the altering waters and original rocks, formation permeability and temperature. These factors in turn affect alteration intensity and the type of mineral assemblages formed. During hydrothermal alteration, whether by acid or neutral pH waters, Si, Al, Ga, Nb, La, Ce, Th and U are effectively immobile; Ti and Zr often are.

In rhyolites and andesites affected by neutral Cl waters (Figs. 2A and B), the total water in the rock, S and As are increasingly enriched and Ti, Fe, Mn, Ca, Li, B, Cl, Sc, Cu, Pb, Zn, Y and Sr are depleted as alteration intensifies. Where alteration is most intense, S in the rock, existing mainly as sulfides, is augmented by as much as a factor of 500, while B is reduced to 10% of its original concentration. The main difference in the mobility of elements between andesite and rhyolite is that Mg (Fig. 2A) tends to be enriched in altered rhyolite, but is depleted or immobile in andesite.

For subsurface greywackes, alteration by neutral Cl waters results in enrichment in the rock by Cl, but depletion in Na, Sr, Ti, P, B and Cu. The remaining elements are immobile (Fig. 2C).

Table 2- Major element composition, in weight %, of selected Kawerau cores and typical TVZ basalt, andesite, rhyolite and greywacke. Sample numbers are the same as in Table 1.

No.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	H_2O	CO_2	Total
1	56.01	0.81	17.89	6.71	–	0.09	3.39	5.42	2.42	2.13	0.13	–	3.40	1.60	100.00
6	69.87	0.32	14.97	1.77	–	0.04	0.42	2.06	4.30	2.33	0.06	–	2.07	1.60	99.81
8	70.72	0.21	12.23	1.42	–	0.06	0.25	1.74	3.13	1.92	0.02	–	8.00	0.60	100.30
12	83.36	0.14	11.46	0.51	–	0	0.01	0.04	0.01	0.02	0.05	–	4.10	0.20	99.90
14	83.89	0.18	5.66	3.89	–	0	0	0.02	0.07	0.04	–	–	2.92	0.18	96.85
15	68.55	0.49	12.20	5.47	–	0.10	2.77	2.61	0.31	2.34	0.10	–	3.70	1.90	100.54
16	64.65	0.76	15.21	5.76	–	0.07	1.50	2.38	3.05	2.37	0.19	3.71	–	–	99.65
18	59.44	0.84	18.28	5.68	–	0.07	1.53	2.99	1.94	3.71	0.14	5.15	–	–	99.77
[a]Bs	50.07	1.15	16.40	4.70	5.79	0.19	6.26	10.6	3.92	0.40	0.19	0.10	–	–	99.77
[b]Ad	61.01	0.69	16.5	6.86	–	0.13	3.30	6.70	2.77	1.64	0.10	0.22	–	–	99.92
[c]Ry	74.40	0.26	13.20	1.42	0.77	0.03	0.27	1.55	3.75	3.25	0.04	0.41	–	–	99.35
[d]Gw	63.12	0.83	16.17	6.23	–	0.07	2.02	2.27	5.33	1.63	0.21	2.60	–	–	100.48

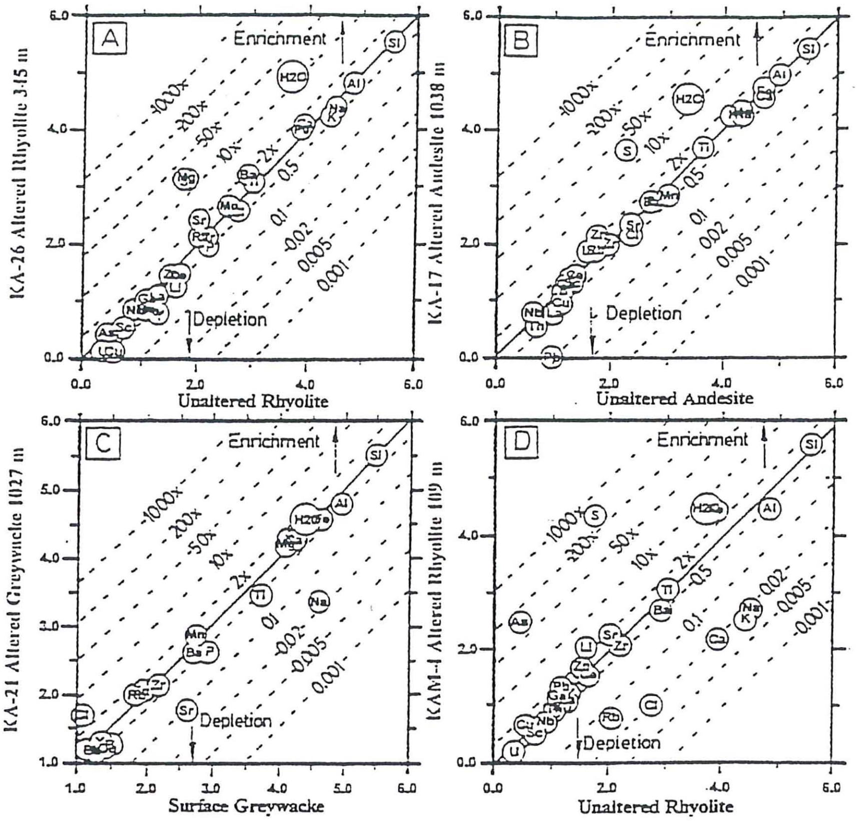

Figure 2- Log-log plots of element compositions of altered against fresh rock, showing isocon lines (——) and the amount of enrichment and depletion (- - -).

(A) Neutral pH altered vs fresh rhyolite from KA-26 (345 m),

(B) Neutral pH altered vs fresh andesite from KA-17 (1038 m),

(C) Neutral pH altered vs surface greywacke from KA-21 (1027 m) and

(D) Acid altered rock vs fresh rhyolite from KAM-4 (109 m).

In rhyolites affected by weakly acid waters, within the shallow condensate layer (Fig. 1), primary feldspars, ferromagnesians, magnetite and glass are replaced mainly by kandites and silica; and only zircon, apatite and quartz are left of the primary minerals. A majority of the elements, including Ca, Na, K, Fe, Mg, Mn, Cl, Zn and Rb are mobile and are depleted down to as low as <0.3% of the original rock content; total water, Fe, As, S, Li and Sr are enriched by as much as a factor of 500 in the case of S (Fig. 2D). Thus changes in elemental abundances between fresh and altered rock affected by weakly acid waters are >10 times higher than those affected by neutral pH Cl ones.

Table 3- Trace elements, in mg/kg, in selected Kawerau cores and typical TVZ basalt, andesite, rhyolite and greywacke. Sample numbers are the same as in Table 1. Trace elements were not analysed for Sample 5.

No.	S	Sc	Cu	Zn	Ga	As	Rb	Sr	Y	Zr	Nb	Ba	La	Ce	Pb	Th	U
1	4170	20.0	9.0	145.0	19	<0.5	77	208	25.0	99	6.0	535	6	28	1.0	3.5	<1
2	2130	17.3	26.2	81.9	19	8.8	61.4	474	19.8	176	6.7	383	16	42	14.1	7.5	2.0
3	5110	15.9	3.7	54.4	28	15.5	119.7	378	25.6	388	13.2	989	19	73	17.0	20.0	1.2
4	4680	6.0	5.6	14.1	10	0.5	9.8	65	8.8	114	5.8	4441	4	9	5.7	6.9	1.1
6	2820	10.0	4.0	52.0	17	<0.5	84	169	26.0	211	11.0	611	9	52	5.0	7.5	2.2
7	12850	3.2	0.6	30.5	12	101.6	77.7	69	12.4	133	5.4	784	13	29	9.0	7.4	1.7
8	1240	3.4	1.3	29.3	11	2.8	133.0	260	5.5	129	6.8	1632	12	28	6.7	7.3	1.3
9	11090	9.1	3.8	49.5	14	6.9	84	239	22.5	187	8.8	529	17	37	12.7	8.2	2.0
10	7900	5.2	1.4	15.9	14	60.2	122.3	35	12.7	124	7.3	888	13	32	14.2	8.6	2.1
11	28500	8.9	45.7	209.9	18	215.6	172.7	29	37.4	8	–	838	35	62	12.7	12.7	3.1
12	2765	3.2	1.5	0.6	7	8.7	2.0	296	2.5	108	4.9	357	6	13	10.7	7.6	1.2
13	6360	5.9	2.7	14.5	12	78.9	28.9	160	10.6	116	5.6	259	16	42	8.1	6.3	2.3
14	22240	3.3	4.6	50.4	15	302.5	6.3	177	16.2	113	5.3	484	13	36	22.1	8.9	1.5
15	9470	10.3	16.1	113.4	15	20.3	98.4	58	20.0	139	7.2	423	14	32	15.4	6.7	0.9
16	1690	11.1	29.7	74.9	17	5.5	76.1	545	18.9	201	8.3	456	18	45	20.6	8.7	2.5
17	410	12.3	8.9	104.2	22	3.0	91.5	294	29.6	214	10.3	558	21	44	18.0	10.6	2.9
18	310	14.5	33.9	87.1	21	2.1	101.6	128	26.6	216	10.9	768	22	56	20.7	12.3	1.5
19	4220	14.0	26.9	80.1	18	11.1	75.9	430	22.7	198	8.9	693	20	44	27.0	9.7	1.5
[a]Bs	100	39.0	35.0	88.0	13.0	–	9.6	328	19.0	120.0	4.0	115.0	10	19.0	1.7	1.1	0.2
[b]Ad	180	21.6	13.7	61.8	16.3	2.9	55.2	237	19.7	94.9	4.4	493.3	11	23.7	9.6	5.0	1.3
[c]Ry	55	5.1	3.5	34.1	12.6	2.7	113	106	21.0	162.0	7.9	825.0	19	44.5	14.8	11.2	2.3
[d]Gw	–	–	28	82	17	–	71	392	22	145	–	511	–	–	17	–	–

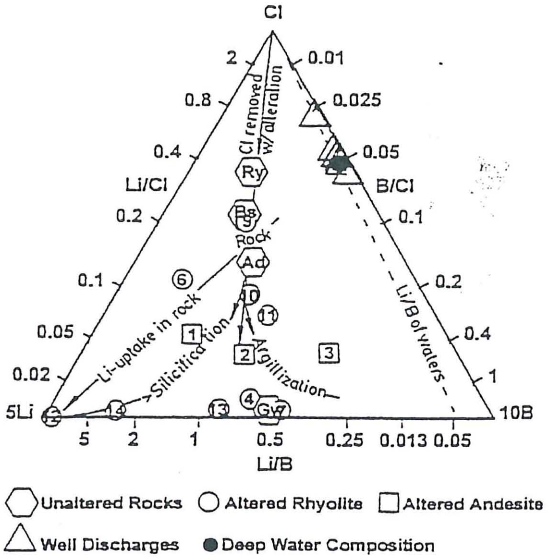

Figure 3- Relative Li, Cl and B contents of fresh and altered TVZ rocks and Kawerau thermal waters.

3.2 Partitioning of Li, B And Cl Between Rocks and Waters

The Li/B ratio of fresh volcanic rocks of the TVZ, as shown in Fig. 3, is nearly constant at 0.75; for greywacke it is 0.5 and for well discharge waters, 0.05. The Li/Cl ratio of fresh TVZ volcanics ranges from 0.07 to 0.2. It is lower in the thermal waters (<0.01), but higher in the altered rocks (>0.2). The more intense the alteration and silicification, the higher the Li/Cl ratio of the altered rock.

Boron is taken up by expanding clays (Table 4), but its concentration in the rock and its behaviour with rising well temperatures are affected by permeability. For example, the B/Cl ratio of 0.05 of a core (6) adjacent to a highly permeable horizon (870 m) in KA-8, is the same as that of the deep thermal waters. In impermeable formations, such as in KA-26 (9-11), the B/Cl ratio of the rock increases to higher values as temperatures increase from 120 to 250°C (Table 1, Fig. 3), possibly due to proximity to the magmatic source.

Table 4- Average Li and B contents, in mg/kg, of alteration minerals in rhyolite from KA-26 (396 m).

Alteration Mineral	Li	B
Illite-Smectite	11.0 ± 9.0	21.0 ± 5.7
Chlorite-Vermiculite	6.0	5.0
Calcite	<1.0	3.7 ± 1.3
Quartz	8.3	<0.1
Pyrite	6.0	0.4

The mass distribution coefficient $K_{W\text{-}R}$ of B and Li between water and rock, as determined from Fig. 4 and listed in Table 5, is defined by

$$K_{W\text{-}R} = C_W / C_R \qquad (2)$$

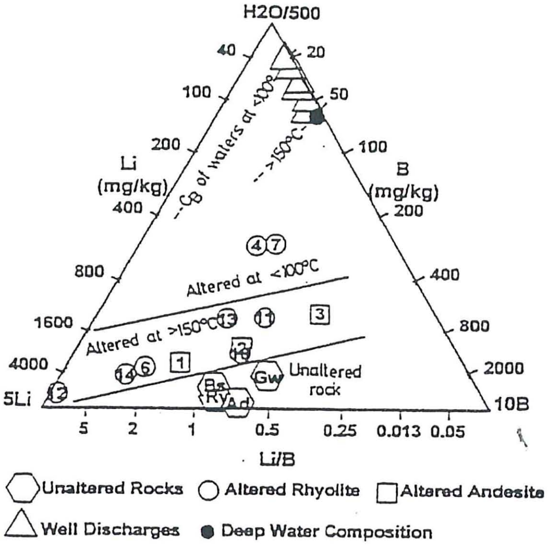

Figure 4- Relative Li, H_2O and B contents of fresh and altered TVZ rocks and thermal waters.

where C_W is the concentration of the component in thermal waters and C_R its concentration in the rock. Where temperatures are >150°C, the mass distribution coefficient $K_{W\text{-}R}$ of B is 0.2, higher than that of <0.06 for Li, indicating that B preferentially enters the solution while Li stays in the rock. However, at temperatures <100°C, the $K_{W\text{-}R}$ of B and Li become 0.1, suggesting that they have similar tendencies with regard to water-rock interaction.

Table 5- Concentrations (C) of B and Li in water and rock in, mg/kg, and their distribution coefficients K_B and K_{Li} with temperature, in °C.

Temp. of Alteration	Water		Rock		$K_{W\text{-}R}$	
	C_B	C_{Li}	C_B	C_{Li}	K_B	K_{Li}
<100°C	15	30	145	295	0.10	0.10
>150°C	50	30	250	520-9000	0.20	<0.06

4. CONCLUSIONS

The partitioning of Li, B and Cl between altered rock and thermal waters at Kawerau is dependent primarily on their ability to be incorporated into the structure of secondary minerals. Chloride, ranging from 12 to 560 mg/kg in unaltered volcanics and greywacke, rarely finds a niche in alteration minerals below 320°C and is thus highly depleted in altered rock, but enriched in the waters. Lithium and B participate in hydrothermal mineral formation. The former is generally incorporated into quartz, chlorite and pyrite; the latter enters the interlayers of expanding clays such as smectite, vermiculite, rectorite and interlayered illite-smectite, chlorite-vermiculite or kaolinite-smectite or is adsorbed onto the surface of leucoxene. The mass distribution coefficient $K_{W\text{-}R}$ of B at >150°C is >70% higher than that of Li suggesting that B preferentially goes into solution whilst Li stays in the rock. Below 100°C, they have the same K_{W-R} and thus have a similar affinity for rock.

The redistribution of other elements during alteration is affected by the chemical composition of the altering fluids and of the original rock, permeability and temperature. The maximum changes in elemental concentration occur in acid altered rhyolites where S may be enriched 500-fold and nearly all of the original Mg and Mn washed out. The least affected by thermal waters are greywackes sampled from impermeable wells. Here, <20% of Na and B are lost, and Cl is augmented by a factor of five.

The behaviour of rock components during hydrothermal alteration in a water-dominated hydrothermal system whose temperatures are <320°C, such as Kawerau, is different from that of a vapor-cored magmatic-hydrothermal system, as occurs in the Philippines, where temperatures are >350°C. Here, trace elements such as B and Cl appear to be introduced directly from the crystallizing magma and take part in the formation of secondary minerals such as gadolinite and zunyite at temperatures >350°C (Reyes, 1992; Reyes et al, 1993). Lithium, on the other hand, is nearly zero in altered rocks at these high temperatures and apparently is quantitatively leached (Reyes and Vickridge, 1996 unpublished data).

5. ACKNOWLEDGMENT

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APPENDIX V

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Lithium and boron distributions in geological samples

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Abstract

The concentration of elements in whole rocks and maps of their distribution in petrographic thin sections were determined using ion beam microprobe analysis. Lithium and B contents in rocks and minerals are measured using the ^{7}Li(p, α)^{4}He and ^{11}B(p, α)^{8}Be reactions. X-rays are simultaneously detected for elements heavier than Na, including Cl, to corroborate microscopic mineral identification. The ion beam analysis data are integrated with observations under the petrographic and scanning electron microscopes, as well as analysis using X-ray fluorescence and the electron microprobe.

Lithium, B and Cl can be used to assess volcanic and hydrothermal processes. In a study of 62 samples, Li, B and Cl increase proportionally with increasing silica content in fresh volcanic rocks from the Taupo Volcanic Zone in New Zealand. The median values for Li, B and Cl in rhyolites ($SiO_2\% = 70–76\%$) are 35, 20 and 800 ppm (wt), respectively, and 19, 11 and 340 ppm (wt), respectively, for andesites ($SiO_2 = 56–62\%$). Boron and Cl preferentially partition into the glassy matrix of rhyolite and andesite. In rhyolites, Li occurs mainly in minerals such as hornblende and biotite but resides in the glassy matrix of andesites. During hydrothermal alteration of volcanic rocks, Cl always partitions into hydrothermal solutions while Li and B are preferentially redistributed in the rock. As hydrothermal alteration proceeds, Cl in the rock decreases and B and Li increase proportionally, depending on the type of mineralization present and the temperature of alteration. © 1999 Elsevier Science B.V. All rights reserved.

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Keywords: Boron; Lithium; Ion beam analysis; Ion microprobe; Geothermal; Water–rock interaction

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1. Introduction

The Taupo Volcanic Zone (TVZ) in the North Island of New Zealand is characterized by exceptionally high heat flow [1] and the close association of two tectonic environments: crustal extension (rifting) associated with mostly rhyolitic volcanism and subduction, or the sliding under, of the Pacific beneath the Indian Plate [2] associated with arc-type volcanism. Active volcanism and geothermal systems abound in this region, where rock and mineral samples for this study were collected.

The interest in light element analysis of geological samples in New Zealand resulted from intense geothermal exploration activities initiated in the 1960's and continuing up to the present. Lithium, B and Cl were routinely analyzed in thermal waters from hot springs and well

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discharges [3], but seldom in rocks, mainly because of their low concentrations and the unavailability of routine techniques.

In the chemical analysis of rocks and minerals, elements with atomic weights heavier than F are often analyzed using electron beam techniques. The determination of light elements, such as B and Li in geological samples, traditionally employed laborious methods and involved wet chemical techniques requiring a large amount of material [4]. Although measurements by (n,γ) and (n,α) reactions are very sensitive for B and Li contents [5], they require access to a suitably equipped reactor facility. With the introduction of ion beam analysis (IBA), light element measurements can be performed on milligram-weighted rock powders or micron-sized (> 20 μm) spots on minerals in petrographic thin sections. This is a straightforward technique that does not require an additional preparation process, in general. Aside from single point analyses of B and Li, X-ray detection of elements heavier than Na provide relative concentrations that can be used to map their distribution in polished rock sections. To verify the concentrations of heavier-Z elements, the samples are also analyzed using a scanning electron microscope (SEM), X-ray fluorescence (XRF) and an electron microprobe (EPMA). Prior to IBA, all rocks and minerals were identified under a petrographic microscope.

The objectives of this report are to describe the IBA analytical techniques employed in the analysis of rock and mineral chemical compositions and to discuss two resulting geological applications: (i) the distribution of light elements in various phases of a volcanic rock and (ii) the redistribution of Li, B and Cl during hydrothermal alteration of volcanics.

2. Previous boron and lithium IBA measurements

Boron and Li can be detected using a variety of techniques such as (p,α) and (n,α) reactions, and particle induced γ-ray emission (PIGE). Comparisons among these techniques have been made by a number of authors, e.g. Raisanen [6], and Moncoffre [5]. In a recent review of light element analysis using a nuclear microprobe, Demortier [7] describes various methods previously used to measure B and Li. Rio et al. [8] compared a range of nuclear methods such as (p,α)reactions and PIGE, and achieved a minimum detection limit of 10 ppm for B (^{11}B(p,α)^{8}Be reaction at $E_p = 700$ keV), and 20 ppm for Li (PIGE reaction at $E_p = 1.8$ MeV). Rio et al. also listed possible interferences for B determination with ^{18}O and ^{19}F, which may affect the analysis, if their concentration is above a certain level, e.g. 2000 ppm. Lappalainen et al. [9] used the ^{11}B(p,α)^{8}Be reaction at $E_p = 700$ keV to obtain a B detection limit below 1 ppm in biological samples. Furthermore they showed that it is possible to measure α particle yields of B, Li, F, and N, simultaneously [9].

For geological materials, Rio et al. [8] investigated Li, B and Be in volcanic glasses and minerals, and Toulhoat et al. [10] studied the stability and distribution of Li and B in minerals. In our laboratory, B was recently studied successfully in rocks, coal and coal ash [11–15]. It should be mentioned that the B detection in standards corresponds well with several conventional techniques [15].

Based on these recently published reviews and papers, the (p,α) reactions appear to be the most frequently used in determining B and Li concentrations, mainly due to fewer interferences compared to other nuclear reaction analysis (NRA) methods, higher sensitivity, and superior detection limits. IBA methods also have the major advantages of relative speed, cost savings, comparable accuracy to conventional techniques and ability to use a microbeam on small samples. Although microbeam diameters of 1 μm can be produced today, geological IBA often requires much 'larger' ion beam spots to achieve results in a reasonable time without destroying the sample by radiation damage.

3. Method of analysis

An incident proton beam of 750 keV is used in the experimental set-up in order to exploit the ^{11}B(p,α)^{8}Be ($E_\alpha \approx 2.3$ and 4.6 MeV) and the ^{7}Li(p,α)^{4}He ($E_\alpha \approx 7.4$ MeV) reactions [8]. The B and Li concentrations in the target are inferred from the yield of α particles as detected with a silicon surface barrier detector placed at 150° to the incident beam direction. The high flux of elastically scattered protons is kept out of the detector by a 10 μm Mylar film, which is thick enough to fully stop the scattered protons, but thin enough to allow the energetic alpha particles to pass through. In this study the samples were sputter-coated with C prior to the analysis to avoid charging up of the specimen during analysis, especially when analyzing highly insulating specimens, such as quartz.

When analyzing B there is an interference from ^{18}O (natural abundance 0.20%) via the reaction ^{18}O(p,α)^{15}N ($E_\alpha \approx 1.6$ MeV) in the lower energy region of the ^{11}B(p,α)^{8}Be spectrum which restricts the analysis to the high energy region of the spectrum. A further possible interference originates from the ^{15}N(p,αγ)^{12}C reaction (^{15}N has 0.37% natural abundance), however none of the samples used in the present work contained high N contents. An interference also occurs between Li and F ($E_\alpha \approx 5.3$ MeV), but only significantly when the F content in the specimen is higher than 2000 ppm.

To quantify results, sample analyses were calibrated against the United States Geological Survey (USGS) SD01 standard containing 128 ppm (wt) B, taking into account the matrix effects of stopping power and the average atomic mass of the 'unknown' sample, whose major element composition is therefore required. For uniform samples it may be shown [15] that the weight concentration, W_u, of B or Li atoms or of their oxides is given by the following equation:

$$W_u = W_{std}\left[\frac{Y_u}{Y_{std}}\right]\left[\frac{S_u/A_u}{S_{std}/A_{std}}\right], \qquad (1)$$

where Y is the yield of measured α particles at the detector per incident proton, S the stopping power of the matrix for protons, and A is the average atomic mass of the sample. The relative effects of the 'S/A' correction in the case of 750 keV protons are given for the following materials, where S/A for SiO_2 is defined as 1.0: (i) USGS SD01: $S/A =$ 1.01; (ii) USGS Granite: $S/A =$ 0.99; (iii) C: $S/A =$ 1.16; (iv) CaO: $S/A =$ 0.93; (v) Fe: $S/A =$ 0.66; (vi) Fe_2O_3: $S/A =$ 0.79.

In our experimental set-up, X-rays originating from the proton excitation are simultaneously collected during the measurements, additionally. At a proton energy of 750 keV, X-rays are measured starting from Na. Especially, Cl X-rays are of special interest in geothermal studies and are conveniently measured this way. X-rays from other important constituent elements, such as Si, S, K, Ti, and Fe, may assist with the identification of the minerals, since the mineral fluorescence induced by the ion beam can be used either as an initial mineral identification method or to supplement other analytical techniques. For example, glass, plagioclase and potassium-feldspar emit blue colors of varying intensity; quartz has a pinkish-orange fluorescence whilst magnetite sometimes emits yellow hues; biotite and other ferromagnesians such as hypersthene and hornblende, especially those high in Fe, do not fluoresce at all. The glassy matrix turns brown under the beam due to radiation damage with virtually no change in the Li and B concentrations.

To produce a 2D map of the elements of interest, the beam was focused to 40 μm diameter beam spot, scanning a 3×3 mm area over the sample. The current density was low enough to minimize beam damage, resulting in reproducible measurements, but high enough to generate reasonable count rates for the B and Li. The elemental maps shown in Fig. 1 were collected over several hours using the Oxford microbeam data acquisition system [16], connected to the microprobe focussing and scanning system [17,18], which collects 256×256 mapping points from both the particle detector, and the X-ray detector, simultaneously.

4. Light elements in rocks and minerals from New Zealand

To identify the phases where light elements reside in fresh volcanics, a polished thin-section of a rhyolite from the TVZ was scanned using the ion beam microprobe. In Fig. 1 a SEM back-scattered image shows phenocrysts of quartz (Q), plagioclase (Plg), potassium-feldspar (Kf), biotite

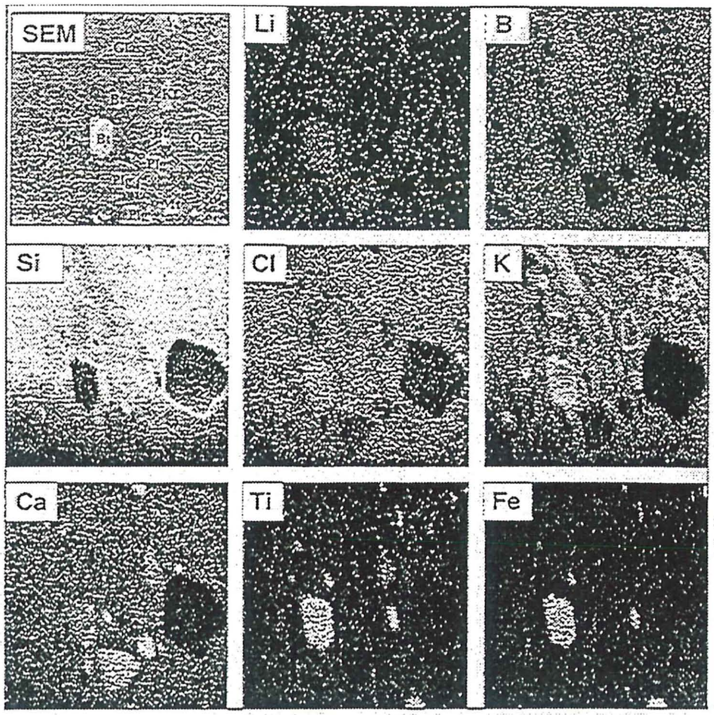

Fig. 1. Backscattered image and elemental maps for Li, B, Si, Cl, K, Ca, Ti and Fe over a 3×3 mm^2 area of a polished petrographic thin section of a biotite rhyolite from the Taupo Volcanic Zone, New Zealand. Q = quartz; Plg = plagioclase; Kf = K-feldspar; Bt = Biotite; Mt = Magnetite. Gray values in the elemental maps indicate the concentration (e.g. 'white' for highest concentration).

(Bt) and magnetite (Mt) set in a glassy matrix (Glass). The distribution of Li, B, Si, Cl, K, Ca, Ti and Fe in these various rock components are depicted in the following panels. Boron and Cl, as presented in Fig. 1, are concentrated in the glass. Chlorine is also incorporated in biotite together with high amounts of Li. Among the minerals, quartz has the lowest concentrations of Li, B and Cl. Also shown in the figure are lighter-shaded lenticles rich in Si and K, cutting across the uniformly gray glassy matrix. These lenticles are enriched in B but depleted in Cl relative to the main glass matrix.

Apart from the rhyolite above, minerals from an andesite were also point-analyzed. In total, 45 points in both rocks were measured for B and Li contents. Table 1 shows the range of B and Li contents in minerals from rhyolite and andesite. The silica content of the volcanic rock affects the partitioning of B and Li between minerals and the glassy matrix. For example, in the rhyolite of Fig. 2, B contents in the silicate minerals generally increase with decreasing Li while in the glassy matrix B proportionally increases with Li. In the andesite, however, a volcanic with lower SiO_2 contents than rhyolite, B increases with Li in all rock components [19]. The variations in light element distribution between these two rocks may be caused by different sources for B and Li in the TVZ volcanics.

Silicate crystal structures limit the amount of B and Li accommodated by a volcanic material, thus the more amorphous or open structure of glass allows it to be a sink for both elements. This difference in behavior of trace elements in glass and minerals led to the concept of the distribution coefficient K_D as defined in Eq. (2) where C_{min} is the concentration of an element in a mineral and

Table 1
Range of B and Li contents (ppm) in various minerals in the TVZ rhyolite shown in Fig. 2

Mineral	Rhyolite		Andesite	
	B	Li	B	Li
Glass	9–11	8–19	5–13	3–22
Plagioclase	1–9	11–67	0.2–3	3–19
Quartz	0.2–2	17–42	MNP	MNP
K-feldspar	1–3	42–61	MNP	MNP
Augite	18	14	0.4–5	<1–14
Hypersthene	0.2–33	14–67	MNP	MNP
Hornblende	2–4	116–177	MNP	MNP
Biotite	2–4	150–427	MNP	MNP
Olivine	MNP	MNP	2–3	<1–3

(MNP = mineral not present).

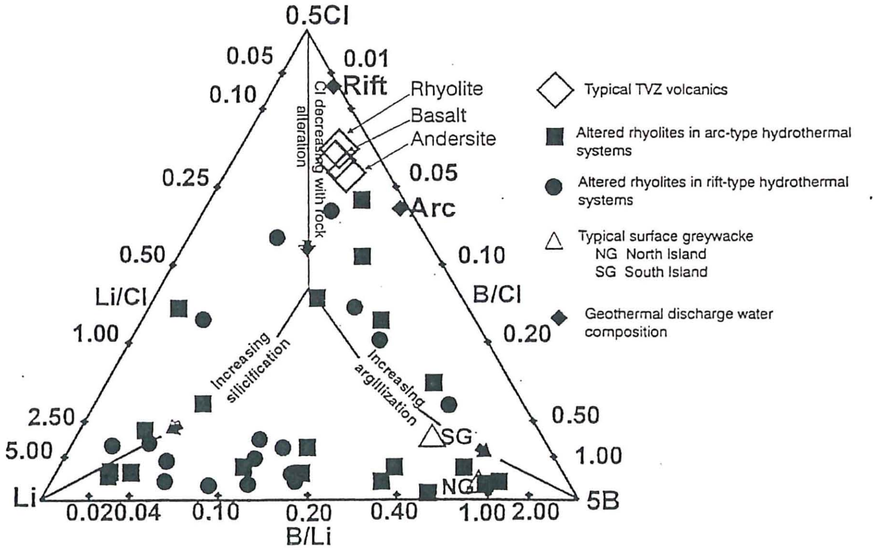

Fig. 2. A ternary diagram showing the distribution of Cl, Li and B in fresh basalt, rhyolite and andesite, hydrothermally altered rhyolites in arc-and rift-type hydrothermal systems in the Taupo Volcanic Zone and graywacke compositions from the North Island (NG) and the South Island (SG). Arc- and rift-type discharge waters from geothermal wells plot along the Cl–B axis. Arrows point to changes in relative elemental contents as volcanics are altered.

C_m is its concentration in the melt or equilibrium glass:

$$K_D = C_{min}/C_m. \qquad (2)$$

Boron, with a K_D of 0.2 for both rhyolite and andesite, occurs mainly in the glass matrix. On the other hand, Li preferentially resides in the rhyolitic minerals, especially hornblende and biotite (Fig. 2); while it is found mainly in the glassy matrix of andesite. Thus during magmatic or volcanic processes B preferentially partitions into the glassy mesostasis of rhyolite and andesite, while Li occurrences vary with the silica content of the rock. On the basis of whole rock analysis, Li, B and Cl increase with increasing silica content in the volcanic rock. The median values, in a study of 62 rocks, for Li, B and Cl for rhyolites are 35, 20 and 800 ppm (wt), respectively, while in andesites the contents are much lower at 19, 11 and 340 ppm (wt), respectively [19]. The same study [19] shows the various ratios among these three elements in andesites of the TVZ appear to reflect the nature of the underlying crust, the dip of the subducting slab and hence the depth and temperature of magma generation. Because of the proximity in the TVZ of the rhyolite-dominated rift-type setting, to the andesitic arc, trace elements in rhyolites are probably also affected by the subducting slab. This may be the reason why the relative Li, B and Cl contents of rhyolites overlap those of andesite.

During hydrothermal alteration of rhyolite, in the TVZ, Cl always partitions into solution while Li and B preferentially go into the rock. Thus as alteration proceeds Cl in the rock decreases and B and Li increase, depending on the type of mineralization present (ref. to Fig. 2) which in turn is affected by alteration temperatures. Changes in the B/Li ratio with temperature in altered rhyolites are associated with alteration intensity and types. Above 220°C, the B/Li ratio is lower than that of the original unaltered rhyolite (ref. to Fig. 2) due to trapping of Li into quartz (silicification) and chlorite and the preferential partitioning of B into solution. The increase in the B/Li ratio when the temperature decreases from 220°C to 100°C is related to the release of Li from the ferromagnesian minerals as alteration intensifies, leading to the formation of clays (argillization) such as smectite, interlayered illite-smectite and rectorite, and oxides such as leucoxene where B in turn may be adsorbed. As the temperature decreases from 100°C to 80°C the ratio decreases as B is released from the rhyolitic glass and Li stays constant because hornblende and biotite are only weakly affected by hydrothermal waters. Thus variations in B/Li ratios with temperature in altered rhyolites are the result of the dissolution of primary minerals followed by the formation of secondary ones. The lowering of the B/Cl ratio of altered rocks with temperature may be related to a decrease in phyllic and argillic alteration coupled with an increase in propylitization. The latter involves recrystallization and a mere reshuffling of chemical compounds into, mainly, hydrothermal Ca-silicates while the former is associated with the destruction of the rock or parts of it and the subsequent formation of clays. Again, B is largely adsorbed onto the open structures of clays hence the high B/Cl ratio at low temperatures. In general more Li partitions into the rock than B at any given temperature.

The tectonic setting of a hydrothermal system, because of its effect on the composition of the thermal fluids [20], also influences the partitioning of these light elements between water and rock. Boron contents in altered rocks are, in general, much higher than Li in rift-than in arc-type hydrothermal systems in the TVZ.

5. Conclusions

The (p,α) reactions at 750 keV are the most suitable IBA methods of determining B and Li concentrations, mainly due to fewer interferences compared to other NRA methods, higher sensitivity, and superior detection limits. Chlorine is also measured simultaneously by collecting X-rays. Li, B and Cl can be used as tracers for source components and to delineate volcanic, and hydrothermal alteration metamorphic processes [20] that may have affected a rock suite.

During volcanic processes B and, in general, Cl preferentially partitions into the glassy mesostasis of rhyolite and andesite. When biotite is present, Cl is incorporated in this mineral and into the glass. The behavior of Li varies with the silica content of the rock, residing in hornblende and biotite in rhyolite and staying in the glassy matrix in andesite. Lithium, B and Cl increase proportionally with the silica concentration of volcanic rocks. Their relative proportions in andesites of the TVZ appear to reflect the nature of the underlying crust, the dip of the subducting and hence the depth and temperature of magma generation. The unusual tectonic geometry of the TVZ, characterized by the proximity of the rhyolite-dominated rift-type setting to the andesitic arc, may be the reason why the various ratios among the Li, B and Cl contents of rhyolites overlap those of andesite.

Variations in the concentrations of Li, B and Cl with temperature in altered rhyolites are the result of the dissolution of primary minerals followed by the formation of secondary ones. The type and abundance of secondary minerals formed are dictated by the composition of the altering fluid, formation permeability and temperatures. Boron has a higher tendency to go into solution in rift- than in arc-type hydrothermal systems. Thus the redistribution of Li, B and Cl during water–rock interaction in hydrothermal systems is affected by: (i) temperature, (ii) the presence of secondary minerals (that may incorporate these light elements), (iii) the tectonic setting, and (iv) the composition of altering waters.

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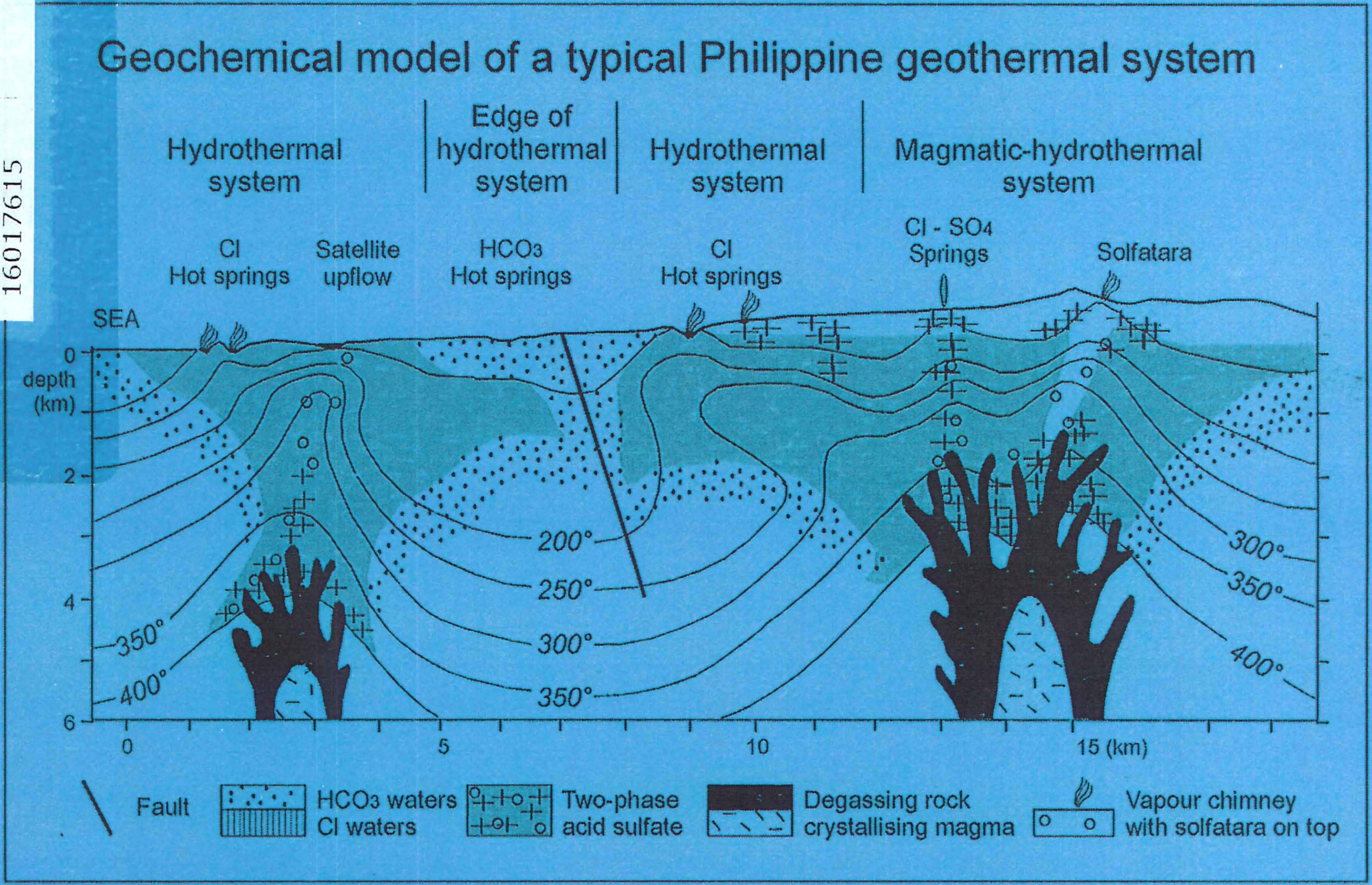

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