

## GEOCHEMICAL CHARACTERISTICS OF ACID FLUIDS IN MT PINATUBO, PHILIPPINES

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### ABSTRACT

The surface geochemical characteristics of Mt Pinatubo indicate widespread deep acid fluids as shown by the following : presence of solfataras or sulphur-depositing fumaroles near or at the summit, and recent or active volcanism ; discharge of mixed fluids with significant chloride at middle elevations ; significant amounts of sulphate found in spring discharges at almost all levels (except at lowest levels or near sea level) ; springs with neutral pH and have high amounts of chloride and significant amounts of magnesium and boron ; low Cl/Mg values accompanied by significant amounts of Mg observed at various elevations ; higher proportions of gases, especially CO<sub>2</sub> and significant N<sub>2</sub> ; widespread occurrence of iron hydroxide deposits at almost all elevations ; and all springs discharge immature waters.

A new mixing model is proposed, the Cl-B-Mg ternary diagram, to differentiate the effects on well and spring water chemistry of the following processes: seawater mixing, groundwater dilution and magmatic input.

Seawater mixing is not indicated for Mt Pinatubo springs as shown by crossplots of chloride versus other chemical constituents and the Cl-B-Mg ternary diagram. Neutral alkali chloride waters are present in the area. This is supported by the chemical crossplots, and the Cl-B-Mg plots. In the Cl-B-Mg plot, springs that discharge low pH waters are shown to be manifestations of acid fluids that are localized within a shallow or deep fault zone.

### INTRODUCTION

The Mt Pinatubo geothermal area is located in the main northern Philippine island, Luzon. It is approximately 90 kms northwest of Manila.

A preliminary assessment of geothermal energy potential was done through a detailed exploration programme by the Philippine National Oil Company-Energy Development Corporation (PNOC-EDC) from 1982 to 1983 at Mt Pinatubo. The exploration programme involved semi-detailed geologic mapping,

geochemical and geophysical surveys.

A three-well deep exploration drilling programme was carried out starting late 1988 at Mt Pinatubo (Fig. 1). All three wells were characterized by low pH values (2.4-3.8), excess enthalpy and low permeability.

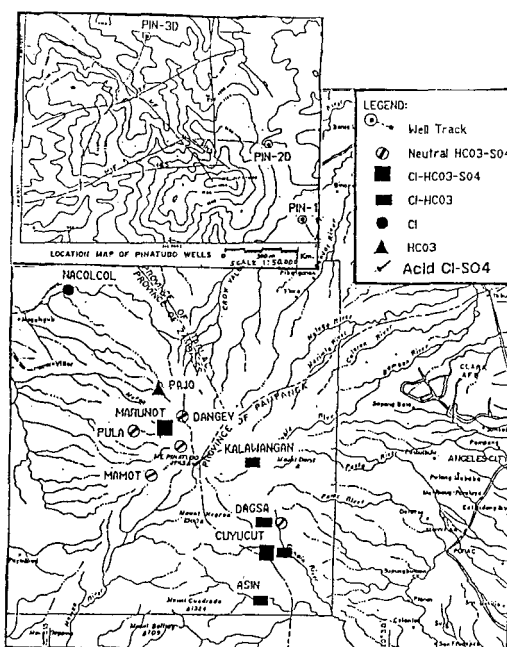


FIG.1 THERMAL MANIFESTATIONS AND WELL  
LOCATION MAP OF MT. PINATUBO  
SCALE 1:250,000

### BACKGROUND : RESULTS OF GEOCHEMICAL INVESTIGATIONS AT MT PINATUBO

Mt Pinatubo is an andesitic strato-volcano. It is the youngest and highest peak (1745 mASL) on a late Tertiary to Quaternary volcanic arc in west Luzon. A breached oval-shaped caldera is enclosing the peak of Mt Pinatubo, an andesitic dome. The caldera is formed by piece-meal subsidence due to the eruption of voluminous pyroclastic materials. The latest activity probably culminated in the growth of the dome. Structures control the location of the thermal features in this area.

The most significant geochemical characteristics of the spring and well fluids in Mt Pinatubo are summarised as follows:

Classification of springs are based on the relative Cl, HCO<sub>3</sub> and SO<sub>4</sub> contents of the water samples (Table 1). Mixed fluids with significant Cl (>20%) are found at middle elevations. Significant bicarbonate contents are found at almost all elevations. Sulphate-rich fluids are found at higher elevations i.e. discharges at greater than 1000 mASL at Mt Pinatubo.

All springs have very low to medium discharge flow rates and are below boiling temperatures. There are solfataras or sulphur-depositing fumaroles near the summit.

Chloride-rich springs such as Dagsa and Cuyucut have significant SO<sub>4</sub>, HCO<sub>3</sub>, and Mg. This could be due to mixing of chloride-rich fluids from depths with steam condensate fluids flowing along the flanks of the volcano. Such enrichment could also be due to mixing of acid Cl + SO<sub>4</sub> - rich fluids with groundwater.

The only acid spring sample is from the Pinatubo solfataras pool. The latest samples indicate that sampling points are different and show greater meteoric water contribution (M.N.Ramos, pers. comm.). Dilution with meteoric water, as indicated by lower chloride values, is observed for the most recent samples of Dangey, Lower Marunot, Kalawangan and Dagsa springs.

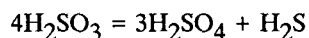
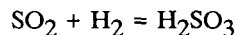
Iron hydroxide deposits are noted in most of the springs at Mt Pinatubo. They are normally thought of as products of weathering (P.R.L. Browne, pers. comm.). Their widespread occurrence in Mt Pinatubo are taken to be significant. Inaccuracies in sampling could account for the higher values of iron in a few samples. Acid added to unfiltered water samples would dissolve the iron hydroxide precipitates.

Higher concentrations of iron observed for the three Pinatubo wells are mainly due to acid corrosion of the wellhead assembly in drill pipes. The prevalence of iron hydroxide deposits in the surface could be linked to a significant amount of dissolved iron at depth, however.

Gas samples from the solfataras show significant amounts of H<sub>2</sub>S but is predominantly CO<sub>2</sub> with some F, S<sub>2</sub> and Cl.

The origin of the gases discharged from wells and solfataras or fumaroles may be deduced from their chemistry. This is made possible by use of ternary diagrams - plotting relative amounts of N<sub>2</sub>, Ar and He or CO<sub>2</sub> (Giggenbach and Goguel, 1989). Higher proportions of N<sub>2</sub> and CO<sub>2</sub> are indicative of magmatic origin (Figs. 2a and 2b). All the Pinatubo well discharge gases are of magmatic or volcanic origin. The solfataras or fumarole gas samples show significant air contamination.

The neutral pH of springs is due to the interaction of acid fluids with the host rocks as it travels to the surface. The very high SO<sub>4</sub> concentration is due to disproportionation of SO<sub>2</sub> into sulphuric acid and hydrogen sulphide, and the oxidation of H<sub>2</sub>S in the vadose zone, as shown by the following reactions:



Low Cl/Mg values and high Mg values are indicators for acid fluids. Lowest Cl/Mg values are found in Pajo and Upper Marunot.

#### NEAR SURFACE MIXING RELATIONSHIPS

A series of chemical crossplots (Figs. 3a-3f) of chloride versus other chemical constituents

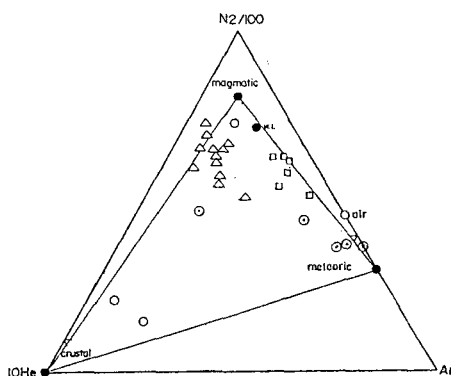


FIG. 2.a RELATIVE N<sub>2</sub>, He, Ar CONTENTS OF MT. PINATUBO INDICATING MAGMATIC ORIGIN OF GASES

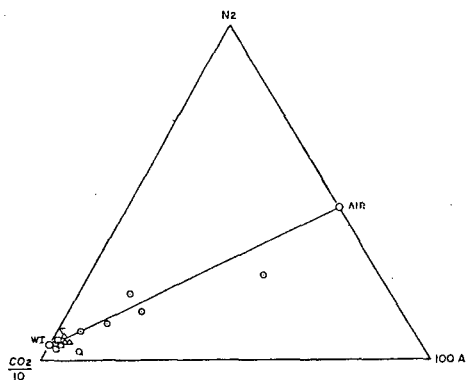


FIG. 2.b RELATIVE N<sub>2</sub>, CO<sub>2</sub> AND Ar CONTENTS OF MT. PINATUBO GAS DISCHARGES

#### LEGEND:

- PIN-1
- PIN-20
- △ PIN-30
- PINATUBO SOLFATARAS
- WI WHITE ISLAND, N.Z.

Fig 3a Plot of chloride vs sulphate of Mt Pinatubo springs

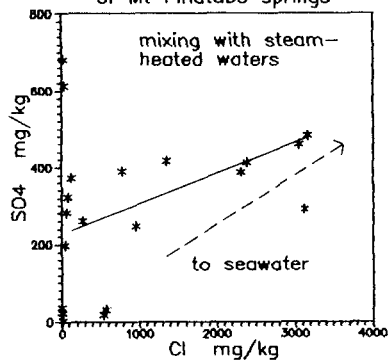


Fig.3b Plot of chloride vs sulphate of Mt Pinatubo springs

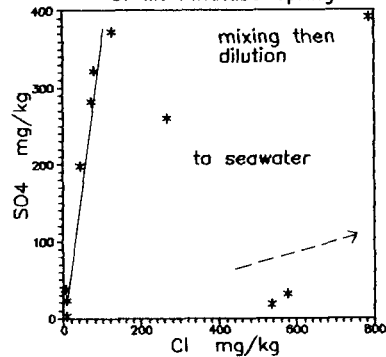


Fig 3c Plot of chloride vs magnesium of Mt Pinatubo springs

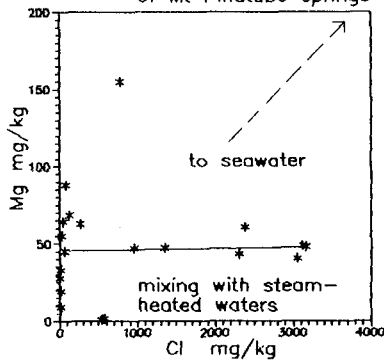


Fig. 3d Plot of chloride vs boron of Mt Pinatubo springs

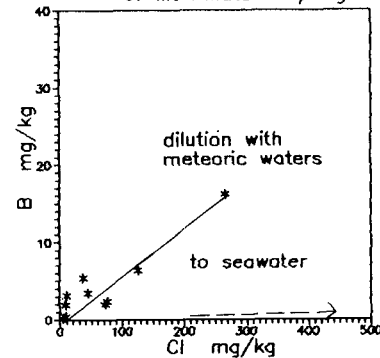


Fig. 3e Plot of chloride vs silica of Mt Pinatubo springs

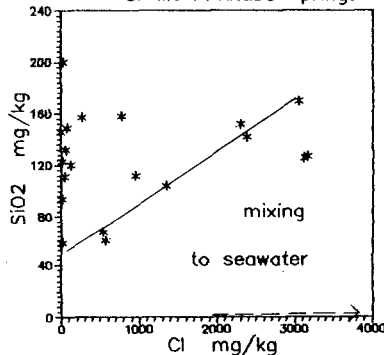
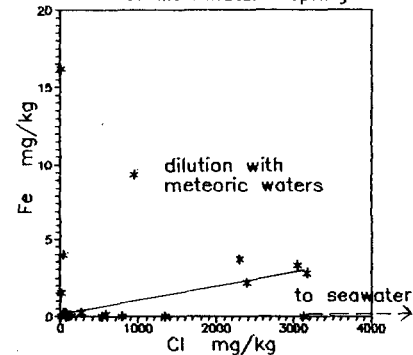


Fig. 3f Plot of chloride vs iron of Mt Pinatubo springs



(Arnorrson, 1985) confirm mixing of alkali-chloride fluids with various thermal waters and dilution with meteoric waters in the Mt Pinatubo area. Springs at higher elevations show mixing of steam-heated groundwaters and thermal fluids followed by dilution with meteoric waters (Fig. 3b). Springs at different elevations show mixing of thermal fluids (including steam-heated groundwaters) (Figs. 3a,3c and 3e) or just plain dilution with meteoric waters (Figs. 3d and 3f). Lines to indicate mixing with seawater is precisely drawn in every diagram. Seawater mixing is not indicated for springs since the mixing and dilution lines do not coincide with the line for seawater mixing.

Alkali chloride waters in Mt Pinatubo are diluted and appear at Nacolcol springs. They are mixed with other thermal waters and appear at Asin, Cuycut and possibly at Dagsa springs. They are diluted and appear at Lower Marunot and Mamot springs.

#### ORIGIN OF FLUIDS AND DEEP PROCESSES

Very high temperatures allow for the leaching of boron from rocks and boron is volatilized into ascending steam. The Cl-Li-B ternary diagram (Giggenbach and Goguel, 1989) shows that Mt Pinatubo well fluids reflect the deep processes and a dilution line can be drawn towards Pinatubo springs

(Fig. 4). Other Philippine wells have variable chloride and boron values (Table 2).

The relative Cl, Li and B contents of the springs, with the exception of Upper Marunot and Dagsa springs, plot them near the chloride corner but no clear distinction is made for seawater mixing from magmatic input.

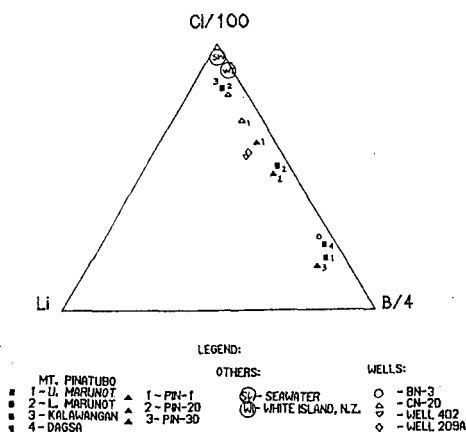


FIG. 4 RELATIVE CL, LI AND B CONTENTS OF MPGP WATERS

As fluids start to ascend, water-rock interaction occurs, the intensity being dependent on the volume of fluid reacting with the rocks. Most of the spring and well discharge data points plot in areas of geothermal waters (Fig. 5). Surprisingly, the highly acidic Pinatubo well fluids do not plot near the Rb corner, which is supposed to imply initial dissolution of crustal rocks in acid waters formed through absorption of magmatic vapour into the deeply circulating ground water (Giggenbach and Goguel, 1989). Most of the fluids show equilibration with rocks either at depth (from well chemistry data points) or at the surface (from spring chemistry data points).

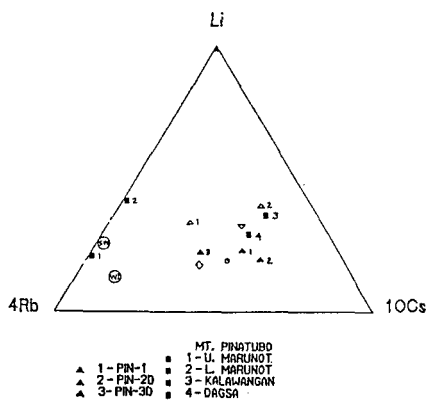


FIG. 5 RELATIVE LI, Rb AND Cs OF MPGP WATERS

## RESERVOIR CONDITIONS

When fluids at reservoir depths have equilibrated then the corresponding spring chemistry could be used to determine the minimum temperatures at that depth. This is done by plotting relative Na, K and Mg contents of various spring and well discharges in the area (Fig. 6) (Giggenbach, 1988). PIN-1 (acidic NaCl-SO<sub>4</sub> fluid) and PIN-3D (acidic NaCl fluid) plot in the partial equilibrium area together with the acidic well CN-2D, and near neutral pH well 402. The neutral pH surface springs at Mt Pinatubo plot along a mixing line and yield a minimum reservoir temperature estimate of 210°C which is way below the maximum measured downhole temperature of 336°C at PIN-2D. Acidic wells PIN-2D (Na+K-Cl+SO<sub>4</sub> fluids) and BN-3 plot near the rock dissolution line in the area for immature waters (Giggenbach, 1988).

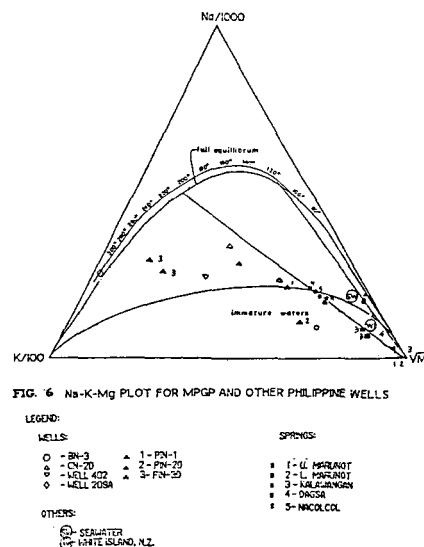


FIG. 6 Na-K-Mg PLOT FOR MPGP AND OTHER PHILIPPINE WELLS

An attempt was made to differentiate the effects on well and spring water chemistry of the following processes: seawater mixing, groundwater dilution and magmatic input. Relative Cl, B and Mg contents of various springs and well waters were plotted along with seawater and solfatara spring samples (Fig. 7). Seawater has significant amounts of Cl and Mg but low boron concentration (Table 1). Volcanic springs have similar levels of Cl and Mg but contain more boron, e.g Pinatubo solfatara spring. High temperature volcanic steam volatilizes boron from rocks and deposits it into shallow aquifers that feed springs.

Neutral pH geothermal systems (Wairakei and Tongonan wells) plot along the common Cl and B axis since their deep well fluids contain trace amount of Mg (Table 2). Brine fluids, (Salton Sea well) plot near the Cl corner along this same axis. Sedimentary-hosted geothermal systems (Ngawha well) (K. Nicholson, pers. comm.) plot near the B corner along

this same axis. Vapour-dominated systems (Kamojang well) also plot near the B corner but has significant Mg due to acidic steam leaching .

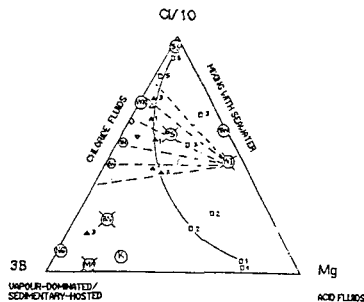


FIG. 7 RELATIVE Cl, B AND Mg CONTENTS IN WATERS OF MPPG AND OTHER GEOTHERMAL AREAS

- LEGEND:
- |                           |                              |
|---------------------------|------------------------------|
| <b>SPRINGS:</b>           | <b>WELLS:</b>                |
| 01 UPPER MARUNOT          | A PIN-1                      |
| 02 LOWER MARUNOT          | ▲ PIN-2D                     |
| 03 KALAWANGAN             | ▲ PIN-2D                     |
| 04 DAGSA                  | ▲ SALTOM SEA                 |
| 05 NACOLCOL               | ○ NOLAN                      |
| <b>OTHERS:</b>            | ○ NEUTRAL PH BILIRAN WELL    |
| ○ SEAWATER                | ○ BUN-2 ACID WELL, BILIRAN   |
| ○ WHITE ISLAND SPRING     | ○ KANULAN                    |
| ○ PINATUBO SOLFATARA POOL | ○ CH-2D BCO-NPH              |
| — 1000' level of Atoll    | ○ WELL ACC. TONGONAH         |
| — 2000' level             | ○ WELL ZONA, TONGONAH        |
| — 4000' level             | ○ MATSUKAWA ACID WELL, JAPAN |

Increasingly acidic geothermal wells plot away from the common Cl and B axis towards the Mg corner. BN-3 and Matsukawa wells plot quite near the B corner and have low amounts of Cl and Mg. Their acidity may be due to the presence of a higher proportion of gases and downward percolating acid fluids formed in steam-heated near surface aquifers. Pinatubo wells and the Bacman II well CN-2D have relatively greater proportions of Cl and variable amounts of B and Mg. Their chemistry implies deep seated acidity. Their high Cl contents are not due to seawater mixing as they contain significant amounts of boron.

"Path lines" are drawn from the neutral alkali chloride systems in the common Cl-B axis towards the volcanic systems data points. The nearer the well data points to the volcanic systems, the greater the magmatic input. A neutral alkali chloride reservoir possibly exists at the Mt Pinatubo geothermal area as deduced from the position of the well and Pinatubo solfatara data points. This is supported by the presence of a group of neutral pH springs at the lowest elevation, namely, Nacolcol springs.

The rest of the Mt Pinatubo springs show greater Mg concentration at higher elevations. Significant meteoric water component is implied for Upper Marunot and Dagsa springs. Lower Marunot spring waters come from the dilution of PIN-2D type fluids with meteoric water. Kalawangan spring waters lie along a potential "path-line" and together with Cuyucut springs (Fig. 7) are the only indicators for widespread deep acid fluids at Mt Pinatubo.

Curves are drawn between the waters near the Mg corner and the Cl-corner. These curves may represent mixing of alkali chloride waters that feed Nacolcol spring and acid (but have undergone neutralisation due to water-rock interaction) waters that feed Upper Marunot and Dagsa. The Pinatubo wells represent the dominantly acidic waters that have not yet undergone neutralisation by water-rock interactions at depth (Fig. 7).

Springs that discharge acidic waters are shown to be manifestations of acid fluids that are not widespread within the reservoir (Fig. 8). This is well illustrated by the springs of Biliran geothermal project, where, out of 3 wells drilled, one well discharged acidic fluids. Though magmatic input is invoked it is mostly due to acidic steam-heated groundwaters percolating downwards through fault zones.

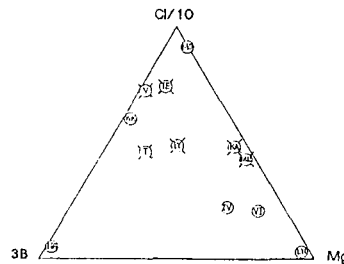


FIG. 8 Cl-B-Mg PLOT FOR ACID AND NEUTRAL pH SPRINGS OF VARIOUS GEOTHERMAL AND VOLCANIC AREAS

- LEGEND:
- |                        |                         |
|------------------------|-------------------------|
| <b>ACID SPRINGS:</b>   | <b>NEUTRAL SPRINGS:</b> |
| ○ BILIRAN, BILIRAN IS. | ○ MORERE, N.Z.          |
| ○ TONGONAH, BILIRAN    | ○ NOLAN, N.Z.           |
| ○ BUNO-2, BILIRAN      | ○ ZONE, QUATEMALA       |
| ○ MATSUKAWA, JAPAN     | ○ BILIRAN, BILIRAN IS.  |
| ○ TATUN 1 & 2, TAIWAN  | ○ WAPAKELI, N.Z.        |

The Lake Nyos sample has been used to represent slightly acid CO<sub>2</sub>-rich waters in a volcanic setting (Giggenbach and Goguel, 1989) and seawater mixing is exemplified by Morere spring, New Zealand.

The trends discussed above are summarised below (Fig. 9). The uncertainties of the mixing model come basically from assuming "representative" data points from various hydrothermal systems.

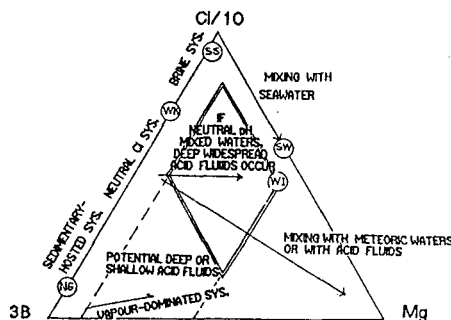


FIG. 9 OBSERVED TRENDS IN THE PROPOSED Cl-B-Mg TERNARY DIAGRAM

### **CONCLUSIONS: Geochemical Signatures of Widespread Deep Acid Fluids in Mt Pinatubo**

The surface geochemical characteristics of widespread deep acid fluids at Mt Pinatubo are summarised as follows:

1. Presence of solfataras or sulphur-depositing fumaroles near or at the summit and recent or active volcanism.
2. Discharge of mixed fluids with significant chloride at elevated grounds.
3. Significant amounts of sulphate found in spring discharges at almost all levels (except at lowest levels or near sea level).
4. Springs with neutral pH and have high amounts of chloride (that is not due to seawater mixing ) and significant amounts of magnesium and boron.
5. Low Cl/Mg values accompanied by significant amounts of Mg observed at various elevations.
6. Higher proportions of gases, especially N<sub>2</sub> and CO<sub>2</sub>.
7. Widespread occurrence of iron hydroxide deposits at almost all levels.
8. Most of the springs are immature waters and a few are partially equilibrated.

Using a Cl-B-Mg diagram, Kalawangan and Cuyucut springs are seen to indicate deep acid fluids at Mt Pinatubo. Mixing lines or curves indicate that neutral alkali waters that feed Nacolcol spring have mixed with widespread acid fluids that have neutralised and are feeding Upper Marunot and Dagsa springs. Acidic springs from other hydrothermal areas are shown to be manifestations of acid fluids that are localized within a shallow or deep fault zone.

### **ACKNOWLEDGEMENTS**

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- Giggenbach, W.F. and R.L. Goguel (1989): "Collection and analysis of geothermal and volcanic water and gas discharges", Report No. CD 2401, 4th ed, DSIR, New Zealand, 81 pp.

TABLE 1 : CHEMISTRY OF MT PINATUBO  
SPRINGS AND SEAWATER

SOURCE	ELEV. mASL	SAMPLE DATE (yyymmdd)	FIELD TEMP. (C)	LAB. pH (25 C)	Li	Na	K	Rb	Cs	(in mg/kg)									
										Ca	Mg	Fe	Cl	SO4	F	B	SiO2	HCO3	
PINATUBO	1150	830515	58	1.00	10.5	10134	2276	5.84	2.02	69	1056.0	ND	34053	40600	ND	423.0	605	ND	
U. MARUNOT	1075	821012	.76	7.75	0.12	58	13.9	0.11	ND	186	55.1	0.25	37	613	ND	5.4	200	259	
DANGEY	965	830514	41	7.97	0.41	113	8.3	0.04	0.47	139	88.1	ND	77	322	ND	2.4	149	603	
L. MARUNOT	965	900326	39	7.99	0.27	68	6.1	ND	ND	133	64.3	3.95	44	198	0.39	3.5	111	562	
	900	821012	47	7.60	0.46	369	27.6	0.16	ND	82	155.0	ND	787	391	ND	23.3	158	64	
MAMOT	900	900403	50	7.94	0.38	157	14.8	0.06	ND	62	62.7	0.27	265	260	0.47	16.2	157	165	
	900	821007	48	7.77	0.22	74	6.8	ND	ND	163	45.2	0.22	72	282	ND	2.0	132	445	
KALAWANGAN	675	830511	38	7.87	1.34	785	63.5	0.15	0.17	86	68.5	0.07	127	373	0.86	6.4	120	382	
	675	900523	40	7.64	1.09	570	49.2	0.13	0.03	114	47.2	9.38	950	417	ND	5.4	104	537	
PULA	600	821014	21	7.27	ND	8	3.8	ND	ND	13	9.2	1.55	9	23	ND	0.4	94	71	
PAJO	518	821028	27	7.66	ND	21	4.9	ND	ND	45	27.7	ND	5	37	ND	0.2	146	288	
	495	821028	25	8.03	ND	17	5.3	ND	ND	34	19.4	ND	9	3	ND	1.9	123	225	
CUYUCUT	325	830313	44	7.99	2.70	1687	123	0.58	0.43	197	43.5	3.65	2304	388	ND	27.7	152	1334	
	380	900329	57	8.30	3.19	1720	184	0.51	0.37	26	60.8	2.21	2387	413	0.21	33.5	142	481	
DAGSA	300	830314	48	8.10	3.45	2170	148	0.70	0.55	223	40.6	3.29	3049	460	ND	348.0	170	938	
	300	900327	44	7.83	0.09	19	3	ND	ND	241	33.1	16.2	10	681	0.32	3.1	58	66	
ASIN	295	830513	51	7.81	3.00	2169	158	0.45	0.43	123	48.9	ND	3123	291	ND	16.4	126	1416	
	295	900328	54	8.03	3.96	2180	229	0.63	0.46	287	48.3	2.82	3167	483	0.27	8.7	127	1549	
NACOLCOL	220	821006	30	6.43	ND	212	2.9	ND	ND	129	0.9	ND	535	18	ND	1.3	67	16	
	220	900404	49	7.20	ND	232	3.3	ND	ND	138	1.6	0.13	576	31	0.50	3.2	60	28	
SEAWATER	1	831206	29	8.17	0.14	10613	369	0.19	0.09	387	1221.0	0.21	19206	2460	ND	4.6	5	121	

TABLE 2: SELECTED WEIRBOX CHEMISTRY OF MT PINATUBO  
AND OTHER PHILIPPINE WELLS

SOURCE	DATE (yyymmdd)	WHP (MPa)	Hd (J/g)	pH (25 C)	Li	Na	K	Ca	Mg	Fe	(in mg/kg)						
											Cl	F	SO4	HCO3	B	SiO2	H2S
PIN-1	891010	0.51	1835	3.61	12.6	7930	889	112	142	80	13300	1.73	1260	ND	186	731	ND
	891014	0.47	1876	3.77	13.0	8036	859	102	177	92	13211	1.66	1367	ND	175	747	ND
	891024	0.34	2231	3.96	10.2	6584	690	109	231	119	10900	2.57	1743	3.9	190	662	ND
PIN-2D	890211	0.97	1531	2.46	5.1	2989	582	34	243	421	5531	2.78	2836	ND	152	1248	6.1
	890212	0.72	1907	2.38	6.7	3302	603	47	283	541	5566	3.32	3143	ND	175	1326	21.8
PIN-3D	900225	0.39	2494	3.23	23.5	17220	3290	2260	170	212	35450	ND	335	ND	331	1883	NA
	900301	0.29	2519	3.25	60.2	30500	10820	6525	451	1340	73740	ND	254	ND	797	1810	0.6
	900313	0.27	2562	3.77	38.3	34550	6780	3640	255	1200	7130	3.19	225	ND	1113	1033	3.8
BN-3	821230	-	1872	3.3	2.1	1246	278	9	84.5	ND	2127	ND	2089	ND	222	1140	ND
CN-2D	820421	-	-	3.78	2.5	2007	173	20	18.2	ND	2553	ND	1416	ND	27	585	ND
	820715	-	1002	3.7	3.2	2601	231	11	8.73	ND	3758	ND	1710	ND	22	651	ND
402	810507	-	-	4.44	17.2	5350	860	119	53	-	9109	-	1340	-	197	612	-
209A	831222	-	-	6.75	24.4	7955	2197	215	0.31	-	14861	-	22	-	292	963	-

- = NOT ANALYSED  
ND= NOT DETECTED