Jurnal Geologi Indonesia, Vol. 2 No. 1 Maret 2007: 15-29

# Hydrothermal system of the Papandayan Volcano, West Java, Indonesia and its geochemistry evolution of thermal water after the November 2002 eruption

Agnès Mazot*, Alain Bernard*,
and Igan Supriatman Sutawidjaja**

* Department of Earth and Environmental Sciences, CP 160/02,
Université Libre de Bruxelles, 50 Ave. Roosevelt, 1050 Brussels, Belgium
** Center for Volcanology and Geological Hazard Mitigation,
Jalan Diponegoro 57, Bandung, Indonesia 40122

## Abstract

Papandayan is a strato volcano situated in West Java, Indonesia. After the last magmatic eruption in 1772, only few phreatic explosions have been occurring. At the present time, the activity is centered in the northeast crater manifested by the presence of fumaroles and hot springs. In November 2002 an explosive eruption occurred and ejected ash and altered rocks. Study of the altered rocks revealed that an advanced argillic alteration took place in the hydrothermal system by an interaction between acid fluids and rocks. Four zones of alteration have been formed as a limited extension along faults or across permeable structures at different levels beneath the active crater of the volcano.

Two types of acid fluids are distinguished in the crater of the Papandayan Volcano: (1) acid sulphate-chloride water with pH values between 1.6 and 4.6, and (2) acid sulphate water with pH values between 1.2 and 2.5. The samples collected after the eruption revealed an increase in the $SO_4$/ Cl and Mg / Cl ratios. This evolution is likely explained by an increase in the neutralization of acid fluids which tends to show that water-rock interactions were more significant after the eruption. The changes in chemistry observed in 2003 were the consequence of the opening of new fractures where unaltered or less altered volcanic rocks were in contact with the ascending acid water. The high $\delta^{34}S$ values (9-17‰) observed in the acid sulphate-chloride water before the November 2002 eruption suggest that dissolved sulphates were mainly formed by the disproportionation of magmatic $SO_2$. On the other hand, the low $\delta^{34}S$ values (-0.3-7 ‰) observed in acid sulphate-chloride water sampled after the eruption suggest that the origin of dissolved sulphates for these waters is the surficial oxidation of hydrogen sulphide.

**Keywords**: Papandayan Volcano, phreatic eruption, hydrothermal system, fluid geochemistry, advanced argillic alteration

## *Sari*

*Papandayan adalah gunung api strato yang terletak di Jawa Barat, Indonesia. Setelah erupsi magmatik terakhir pada 1772, letusan yang terjadi hanyalah bersifat freatik. Pada saat ini, kegiatan vulkanik terpusat pada kawah sebelah timur laut berupa fumarola dan mata air panas. Pada November 2002, terjadi letusan eksplosif yang memuntahkan abu dan batuan alterasi. Studi batuan alterasi menunjukkan bahwa perkembangan alterasi argilik yang terjadi dalam sistem hidrotermal merupakan interaksi antara cairan asam dengan batuan. Empat zona alterasi yang terbentuk terbatas pada rekahan sepanjang sesar, memotong struktur lapisan lolos air yang berbeda-beda lapisan di bawah kawah aktif gunung api ini.*

*Dua macam cairan asam yang berbeda pada kawah Gunung Api Papandayan, yaitu: (1) air asam sulfat-klorida dengan pH berkisar antara 1,6 dan 4,6, dan (2) air asam sulfat dengan pH* *antara 1,2 dan 2,5. Pengambilan percontoh setelah erupsi menunjukkan peningkatan pada rasio* $SO_4$*/Cl dan Mg/Cl. Evolusi ini tampaknya mencerminkan peningkatan dalam netralisasi cairan asam yang cenderung menunjukkan bahwa interaksi air-batuan adalah tipe kontak dengan meningkatnya air asam. Tingginya* $\delta^{34}S$ *(9-17‰) yang teramati di dalam air asam sulfat-klorida sebelum erupsi November 2002 menunjukkan bahwa larutan sulphate terutama terbentuk karena ketidak seimbangan* $SO_2$ *dalam magma. Sementara, rendahnya* $\delta^{34}S$ *(-0,3–7‰) yang teramati di dalam contoh air asam sulfat-klorida setelah erupsi menunjukkan bahwa larutan sulfat yang berasal dari air tersebut merupakan oksidasi permukaan hidrogen sulfida.*

***Kata kunci**: Gunung Api Papandayan, erupsi freatik, sistem hidrotermal, cairan kimia, alterasi argilik lanjut*

## INTRODUCTION

Papandayan Volcano produced a catastrophic debris avalanche during the brief magmatic eruption in 1772. Afterwards, only small phreatic eruptions had occurred prior to the more explosive eruption in November 2002 which has changed the crater morphology. Today, the volcano activity is reduced to be the presence of fumaroles with sulphur-mud pools and hot springs. The geochemical survey of fumaroles and thermal springs can provide useful information on the state of activity of the volcano, on the relationship between the hydrothermal and the structural systems of the volcano and on the activity evolution with time (Fischer, 1997; Taran, 1998; and Federico, 2002). Changes in the chemical composition of gases and/or hot springs may reflect an interaction more or less important between the deep fluid and the superficial aquifer (Ohsawa, 1993; Valentino, 1999; and Tassi, 2003). But, these evolutions may also be the consequence of an increase in the volcano activity that could generate a phreatic eruption (Nogami, 2000), or a magmatic one (Giggenbach, 1990; Takano and Watanuki, 1990; Arribas, 1995; and Fischer, 1997). The recent activity ejected ash and altered rocks coming from the inside of the hydrothermal system offers an opportunity to improve our knowledge on the alteration processes occurring at depth (Christenson and Wood, 1993). This paper presents the results of chemical and isotopic studies of hot-spring waters sampled from 1994 to 2002. After the phreatic eruption that occurred in November 2002, new hot-spring waters were collected for chemical and isotopic analyses, whilst volcanic ashes and altered rocks were also sampled for mineral analysis. The chemical and mineralogical data serve in having a better understanding about the alteration by the acid-fluids on the rocks in the hydrothermal system and allow to observe changes in the activity of the Papandayan Volcano which has already produced a catastrophic magmatic eruption in its historical time.

## VOLCANO SETTING AND THE NOVEMBER 2002 ERUPTION

The Papandayan Volcano is a stratovolcano (7°32’ S, 107°73’ E, 2665 m a.s.l.) located at 180 km to the southeast of the Jakarta (Figure 1). During its historic activity, the eruptive center moved to the northeast with the formation of successive new craters. The deposits in this area consist of Tertiary andesitic lava flows overlain by numerous alternating pyroclastic flows and falls with andesite basaltic lavas. The last magmatic eruption of the Papandayan Volcano occurred in 1772. A debris avalanche created a horseshoe-shaped crater open to the northeast and covered an area of about 250 km$^2$, resulted in the destruction of 40 villages and the death of 2957 inhabitants (van Padang, 1951). The last reported activity, during June 1998, consisted of increased seismicity and minor phreatic explosions (USGS, 1998). Until November 2002 eruption, the hydrothermal activity was centred in the crater (1 × 1.5 km) with multiple fumaroles, mud-pools and hot springs.

In Early October 2002, the seismicity of the volcano increased and small phreatic explosions occurred in the crater (USGS Volcanic Activity Report, 2002). On 11 November 2002, a phreatic eruption from the southeast of the crater caused a landslide that became a lahar. On 15 November 2002, a phreatic eruption ejected steam and an ash plume up to

4000 m above the crater. Earth Probe TOMS (Total Ozone Mapping Spectrometer) instrument detected small amount of $SO_2$ on November 13 (<1500 tons). On November 15, $SO_2$ was again detected, in a small plume extending west of Papandayan. The estimated $SO_2$ mass was 7000 tons. Between 16 and 20 November 2002, explosions ejected an ash plume up to 700 m high then followed by landslides and lahars. On 20 November, another major eruption took place at the northwest of the crater. Ash plume reached 1500 m above the vent and the cloud drifted to the northeast. The eruption also produced a directed blast as far as 2 km and left blocks and smaller fragments of altered rocks and 4-8 cm thick deposit of wet ashes. Bread crust bombs with maximum diameter of 50 cm were found. During the next month, the activity decreased and actually only fumarolic manifestations were present (USGS Volcanic activity report, 2003). New vents have been created with one containing a small lake, and another mud-pool and new hot springs appeared (Figure 1).

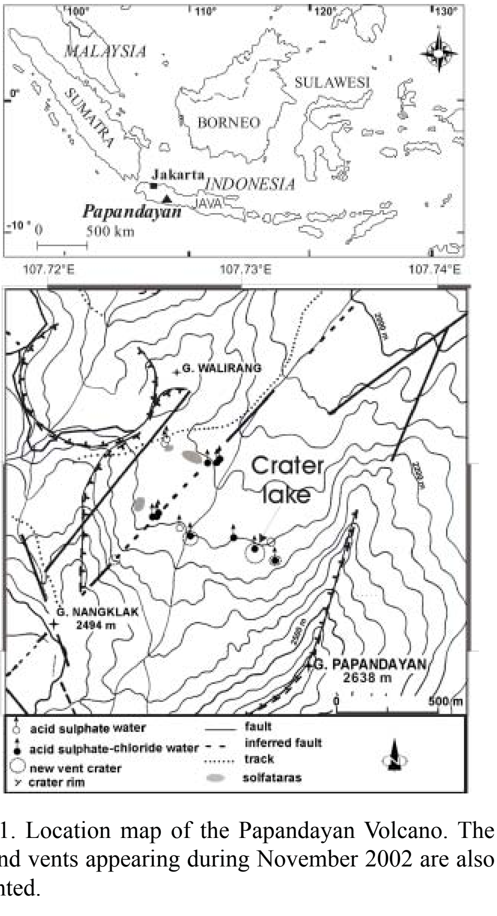

Figure 1. Location map of the Papandayan Volcano. The faults and vents appearing during November 2002 are also highlighted.

## Sampling and Analytical Methods

Water samples were collected from 1994 to 2005 in the crater (Figure 1). The pH was determined in the field after calibration with pH 1 and standard reference buffers. The concentrations of cations were measured by inductive coupled plasma optical emission spectroscopy (ICP-OES) whereas the anions $Cl^-$, $SO_4^{2-}$ and $F^-$ were analyzed by high performance liquid chromatography (HPLC). Furthermore, the $\delta^{34}S$ of sulphates were determined by mass spectrometry. Products of 2002 eruption collected around the new vents consist of grey ashes and altered rocks. Their mineralogy was determined by means of an X-ray micro diffraction instrument equipped with a HISTAR detector. A scanning electron microscopy (SEM) and an energy-dispersive X-ray spectrometer (EDS) were also used to study the ejecta. The EDS detector was equipped with a NORVAR window that enables the detection of elements with atomic number (Z) above 3.

## Result of Investigations

### Mineralogy of Erupted Products

The altered rocks are derived from highly altered lavas of andesitic compositions. Some samples show a complete silicification. Bread crust bombs come from the eruption of 20 November 2002, the most explosive of this period. Rock and ash alteration mineralogy is summarized in Table 1. The most abundant phases are cristobalite (XRD patterns on Figures 3a and 4a), quartz (XRD patterns on figures 3b and 4b), pyrite (Figures 2a and XRD patterns on Figures 3b and 4) or marcasite (XRD pattern on figure 4a), pyrophyllite (Figure 2b and XRD patterns on Figures 3b and 4b) and alunite (Figure 2c). The alunite phase identified is a natroalunite ($(Na_{0.5}, K_{0.5}) Al_3 (SO_4)_2 (OH)_6$), based on XRD analysis (Figure 4a). Sometimes some radiating pyrite or marcasite (Figure 2d) has been found in ejectas covered by small crystals of alunite. In experimental studies (Murowchick and Barnes, 1986), the occurrence of marcasite indicates: (1) a fluid relatively acid (pH<4-5), (2) a temperature of deposition below 240 °C and post-depositional temperatures that remain below 160°C and (3) the presence of polysulphides (*e.g.* $H_2S_2$) that are formed by partially oxidation

Table 1. Alteration Phases in Ejecta from the November 2002 Eruption

| Samples | Cristobalite | Opal-CT | Quartz | Pyrite | Marcasite | Native Sulfur | Pyrophyllite | Natroalunite | Kaolinite | Anhydrite | Gypsum |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Ejecta** | | | | | | | | | | | |
| PAP_01 | X | | X | | | | X | X | | | |
| PAP_02 | X | | X | | | | | | | | |
| PAP_03 | | X | X | X | X | | | | | | |
| PAP_04 | X | | | X | | | | X | | | |
| PAP_05 | X | | | X | | | | X | X | | |
| PAP_06 | X | | | X | X | | | X | | | |
| PAP_07 | | | X | X | X | | | | | | |
| PAP_08 | | | X | X | | | X | | | X | X |
| PAP_09 | X | | X | X | | X | X | | | | |
| PAP_10 | X | | X | | | | X | X | | | |
| PAP_11 | | | X | | | | X | X | | X | |
| PAP_12 | | X | X | X | | | | | | | |
| PAP_13 | | X | X | X | | | | | | | |
| **Ashes** | | | | | | | | | | | |
| Ash1 | X | | X | X | | X | X | X | X | X | |
| Ash2 | X | | X | X | | X | X | X | X | | X |
| Ash3 | X | | X | X | | X | X | X | X | | |
| Ash4 | X | | X | X | | | X | X | X | | |
| Ash5 | X | | X | X | | | X | X | X | | X |
| Ash6 | X | | X | X | | X | X | X | X | X | |
| Ash7 | X | | X | X | | X | X | X | X | X | |

of sulphides species (*e.g.* $H_2S$) close to the site of deposition. Marcasite has been found coexisting with pyrite, quartz and/or alunite in high altered rocks. Anhydrite (Figure 2e and XRD pattern on figure 3b) or gypsum and kaolinite (XRD pattern on Figure 4b) are sporadic phases. The accessory minerals are, in altered rocks, rare enargite, rutile or anatase inclusions in pyrite and muscovite. The bread crust bomb shows many phenocrysts of plagioclase, hypersthene and augite in a gangue of glass plus crystals of principally plagioclases and pyroxenes (Figure 2f). This bomb is not altered and is characterized by a fragment of lava without vesicles and contains many phenocrysts.

Four alteration assemblages have been determined in altered rocks. The first assemblage consists of pyrophyllite, quartz ± cristobalite ± natroalunite ± anhydrite ± pyrite ± native sulphur and gypsum (PAP-01, PAP-08, PAP-09, PAP-10 and PAP-11). The second assemblage contains kaolinite, quartz, cristobalite, natroalunite, anhydrite and pyrite (PAP-05). The third suite is composed of natroalunite, pyrite, cristobalite and ± marcasite (PAP-04 and PAP-06). The last assemblage consists of quartz ± cristobalite ± pyrite and ± marcasite (PAP-02, PAP-03, PAP-07, PAP-12, PAP-13).

## Composition of Volcanic Gases

Chemical compositions of volcanic gases from the crater of Papandayan Volcano (Figure 1) are presented in Table 2. The crater discharged gases up to 400°C in 1994-1996, and in 2004 after the eruption, the maximum temperature measured was 260°C. The gases collected in the fumaroles consist mostly of $H_2O$ with minor amount of $CO_2$ and $H_2S$ and very low $SO_2$ and HCl contents.

## Composition of Thermal Water

The analysis result of hot spring water collected since 1994 are shown in Table 4. Several hot springs are present on the west and south sides of the crater with mud pools close to solfataras (Figure 1). Considering the data on Table 3, two groups of springs can be distinguished: acid sulphate-chloride and acid sulphate water. Acid sulphate-chloride water have pH varying from 1.6 to 4.6, temperatures between 17 and 94°C and TDS concentrations between 506 to 8380 mg/l. A crater lake was formed during the November 2002 eruption and belongs to the same type of acid sulphate-chloride water. Acid sulphate (or steam condensates) water containing high sulphate concentration but low amounts of chloride, have pH values between 1.2 to 2.5, temperatures between 23

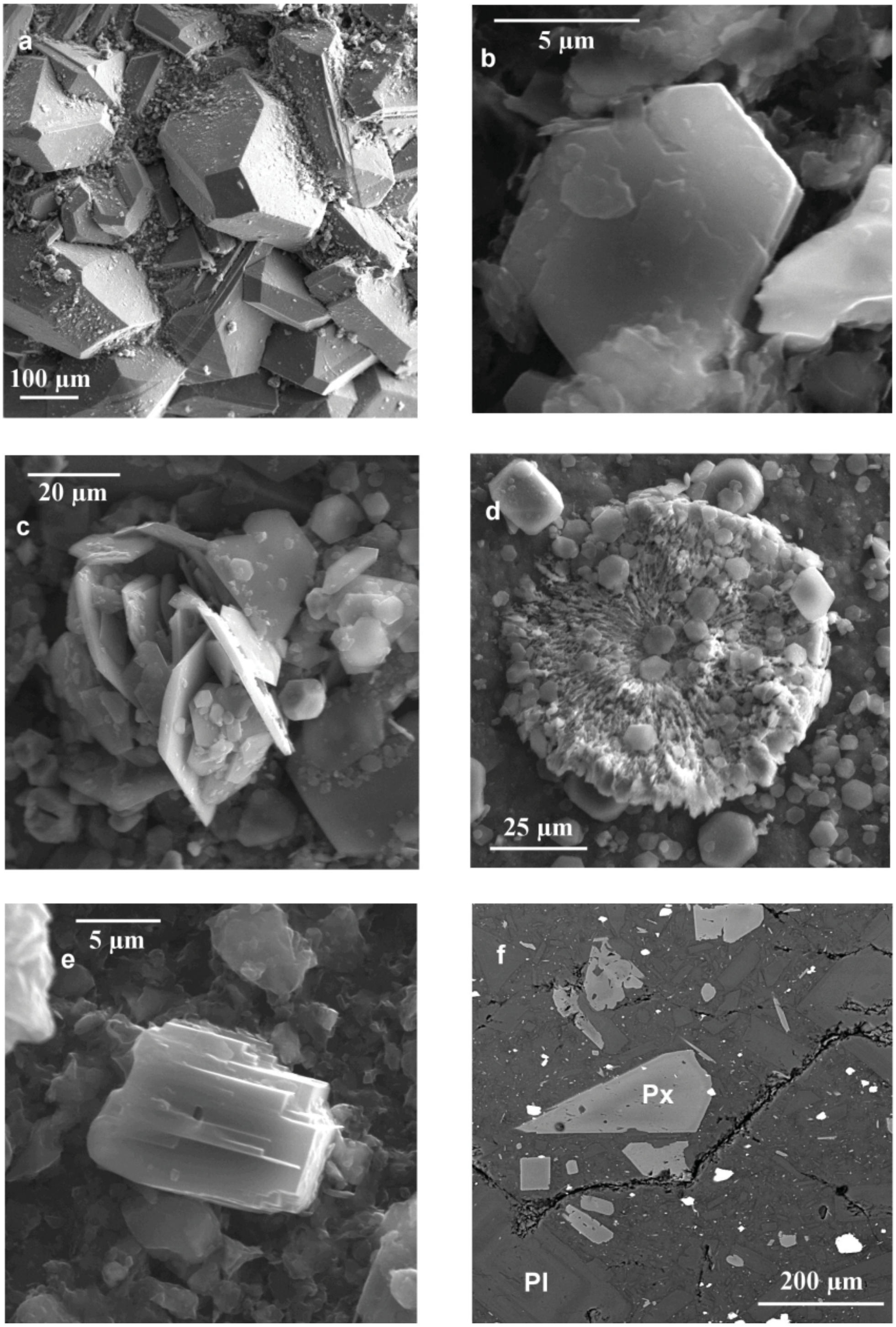

Figure 2. Secondary electron image (SEI) photomicrographs (a, b, c, and d) and back scattered electron image (BEI) photomicrograph (f) of altered minerals. (a) Octahedral pyrite in ejecta, (b) Crystal of clay (pyrophyllite or kaolinite) in ash, (c) Rhombohedral alunite in ejecta, (d) Radiating pyrite or marcasite covered by crystals of alunite in ejecta, (e) Crystal of anhydrite in ash, (f) Section in bread crust bomb: phenocrysts of plagioclase (Pl) and pyroxenes (Px) in glass with microlites of plagioclase.

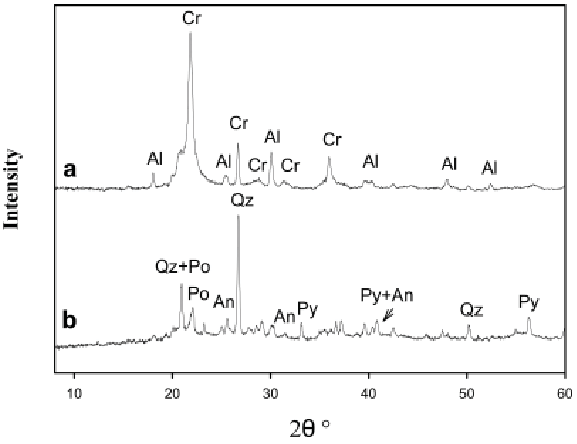

Figure 3. X-ray microdiffraction of (a) PAP-06 (assemblage 3) and (b) ash-1. Mineral abbreviation: Al= Natroalunite; An= Anhydrite; Cr= Cristobalite; Po= Pyrophyllite; Py= Pyrite; Qz= Quartz.

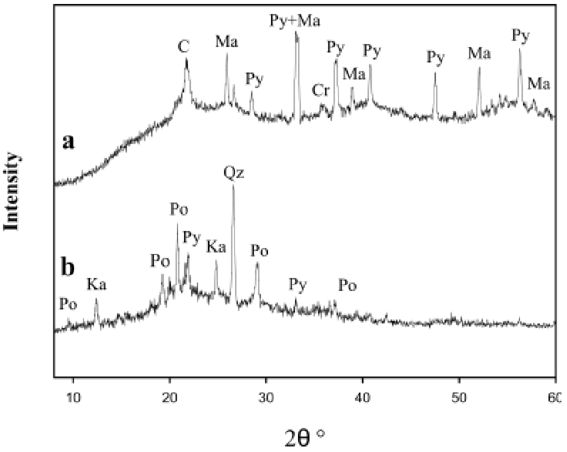

Figure 4. X-ray microdiffraction of (a) PAP-03 (assemblage 4) and (b) ash-2. Mineral abbreviations: C= Opal; Ka= Kaolinite; Ma= Marcasite.

to 91°C and TDS concentrations between 1350 to 5660 mg/l. Mud-pools differing greatly from the two groups of springs, have low pH (0.3 and 1.1), temperatures close to boiling (87 to 95°C) and high TDS concentration (2860 to 41610 mg/l). These types of water are highly enriched in Boron due to the strong evaporation of the pools.

## DISCUSSIONS

### Chemical Composition of Gases

Relative concentrations of HCl, St and $CO_2$ are shown on Figure 5. The St/HCl ratio of the gases vary, while the $CO_2$/St ratios remain constant. These variations are probably caused by a selective absorption of more soluble water species, $H_2S$, $SO_2$ and HCl, by the hydrothermal water and re-equilibration of magmatic gases at a low temperature (<400°C). To confirm the origin of the volcanic gases, the hydrogen (D/H) and oxygen ($^{18}O/^{16}O$) isotopic ratios for the Papandayan gases and hot springs (Tables 3 and 4) are compared (Figure 6) with the compositions of local meteoric water and high temperature gases from volcanic arc magmas (Taran *et al*., 1989; Giggenbach, 1992). The local meteoric water line

Table 2. Chemical Composition (μ.mol.mol$^{-1}$) and Isotopic ($^0/_{00}$) of Volcanic Gases and Temperature (C). (From (a) Giggenbach (1996), (b) Giggenbach *et al.* (2001), and (c) Fisher (pers.com))

| Sample | date | Temp. | $H_20$ | $CO_2$ | $H_2S$ | $SO_2$ | St | HCl | $H_2$ | HF | $N_2$ | $O_2$ | $CH_4$ | CO | $\delta^{18}O$ | δD | réf. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| gaz1 | - | 400 | 960000 | 29400 | 2900 | 6750 | 9650 | 1250 | 140 | 33 | 550 | <20 | 0.6 | 0.3 | - | - | (a) |
| gaz2 | 23/07/1994 | 282 | 965000 | 24900 | 7010 | 1490 | 9030 | - | - | - | - | - | - | - | - | - | (b) |
| gs1 | 12/07/1995 | 360 | 949530 | 36042 | 7935 | 2563 | 10498 | 1846 | 268 | 99 | 1687 | 28 | 0.9 | <0.04 | 4.6 | -31 | (c) |
| gs2 | 14/07/1995 | 148 | 971570 | 20560 | 5354 | 1029 | 6383 | 1073 | 72 | 13 | 324 | <7 | 0.4 | <0.02 | 2.8 | -35 | (c) |
| gs3 | 14/07/1995 | 170 | 969730 | 25398 | 4052 | 319 | 4371 | 15 | 17 | 14 | 440 | <9 | 2.3 | <0.003 | -3.5 | -54 | (c) |
| gs4 | 14/07/1995 | 99 | 989770 | 14406 | 2266 | <100 | 2070 | 317 | 22 | 0.7 | 415 | <5 | 0.7 | <0.001 | 0.1 | -41 | (c) |
| gs5 | 14/07/1995 | 150 | 971150 | 20734 | 4419 | 805 | 5224 | <2400 | 70 | 7.6 | 389 | <7 | 0.7 | <0.002 | 3.5 | -32 | (c) |
| gs6 | 16/07/1995 | 280 | 977170 | 16142 | 3931 | 1169 | 5100 | 1109 | 53 | 26 | 377 | <7 | 0.4 | <0.002 | 4.5 | -32 | (c) |
| gs7 | 16/07/1995 | 100 | 962400 | 29785 | 5570 | 1387 | 6957 | <280 | 17 | 2.8 | 543 | 12 | 0.4 | <0.004 | 1.3 | -41 | (c) |
| gs8 | 18/07/1996 | 300 | 967880 | 23469 | 5819 | 1198 | 7017 | 918 | 310 | 25 | 368 | <12 | 1.2 | 0.004 | 4 | -36 | (c) |
| gs9 | 18/07/1996 | 128 | 973900 | 18418 | 4647 | 1133 | 5780 | 1639 | 8.7 | 22 | 229 | <6 | 0.6 | 0.002 | 3.1 | -34 | (c) |
| gs10 | 18/07/1996 | 103 | 971620 | 23550 | 4034 | 401 | 4435 | 17 | 14 | 0.4 | 353 | <9 | 0.2 | <0.003 | -3.3 | -53 | (c) |
| gs11 | 22/07/1996 | 138 | 963230 | 28315 | 6058 | 1578 | 7636 | <370 | 76 | 5.1 | 357 | <10 | 3.0 | <0.004 | 2.5 | -35 | (c) |
| gs12 | 22/07/1996 | 160 | 964050 | 25666 | 6146 | 2032 | 8178 | 1466 | 270 | 4.9 | 361 | <13 | 1.1 | 0.004 | 3.2 | -39 | (c) |
| gs13 | 22/07/1996 | 96 | 969160 | 25041 | 4931 | 399 | 5330 | <16 | 9.2 | 0.9 | 432 | <10 | 1.0 | 0.003 | -0.7 | -49 | (c) |

Table 3. Chemical (mg.kg-1) and Isotopic Compositions of Waters from the Papandayan Volcano

| Sample | Date | Temp ($^0$C) | pH meas | Na | K | Ca | Mg | Si | B | Mn | Al | $Fe_{Tot}$ | $Fe^{2+}$ | F | Cl | $SO_4$ | $H_2S$ | TDS | $SO_4$/Cl | Mg/Cl | $\delta^{34}S_{SO4}$ (‰) | $\Delta^{18}O$ of Water (‰) | δD of Water (‰) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Acid sulphate-chloride waters** | | | | | | | | | | | | | | | | | | | | | | | |
| Pap1 | Jul.94 | 63 | 2.5 | 24 | 11 | 33 | 13 | 73 | 2.2 | 0.6 | 31 | 0.4 | - | 4 | 216 | 222 | - | 631 | 1.0 | 0.06 | - | - | - |
| Pap2 | Jul.94 | 55 | 2.5 | 21 | 10 | 35 | 12 | 108 | 1.2 | 0.5 | 49 | 2.8 | - | 4 | 183 | 404 | - | 830 | 2.2 | 0.07 | - | - | - |
| Pap3 | Jul.94 | 80 | 1.9 | 20 | 17 | 28 | 11 | 111 | 4.1 | 0.4 | 91 | 4.5 | - | 11 | 747 | 481 | - | 1526 | 0.6 | 0.01 | - | - | - |
| Pap5 | 23/08/1998 | 75 | 2.3 | 21 | 10 | 28 | 11 | 80 | 1.7 | 0.4 | 17 | 0.4 | - | 3 | 163 | 215 | - | 551 | 1.3 | 0.07 | - | - | - |
| Pap6 | 23/08/1998 | 93 | 1.6 | 28 | 21 | 32 | 11 | 145 | 4.0 | 0.4 | 141 | 8.7 | - | 13 | 1186 | 509 | - | 2099 | 0.4 | 0.01 | - | - | - |
| Pap7 | 23/08/1998 | 70 | 2.2 | 28 | 22 | 26 | 12 | 93 | 1.6 | 0.3 | 33 | 4.1 | - | 4 | 198 | 364 | - | 787 | 1.8 | 0.06 | - | - | - |
| Pap8 | 23/08/1998 | 71 | 2.5 | 16 | 9 | 23 | 9 | 76 | 1.5 | 0.3 | 16 | 0.8 | - | 4 | 159 | 191 | - | 506 | 1.2 | 0.06 | - | - | - |
| Pap9 | 05/02/2000 | 88 | 1.7 | 48 | 20 | 73 | 27 | 245 | 7.3 | 1.4 | 146 | 21 | 18 | 17 | 981 | 867 | - | 2453 | 0.9 | 0.03 | 9.5 | -7.3 | -56 |
| Pap10 | 05/02/2000 | 92 | 1.9 | 28 | 15 | 45 | 14 | 166 | 4.1 | 0.8 | 80 | 8.0 | 8 | 11 | 566 | 518 | - | 1457 | 0.9 | 0.03 | 10.3 | -7.1 | -53 |
| Pap11 | 05/02/2000 | 86 | 1.9 | 37 | 24 | 52 | 18 | 220 | 4.2 | 1.0 | 107 | 13 | 13 | 11 | 606 | 605 | - | 1698 | 1.0 | 0.03 | 8.7 | -7.2 | -54 |
| Pap12 | 05/02/2000 | 63 | 2.0 | 29 | 18 | 38 | 14 | 151 | 3.1 | 0.7 | 57 | 7.0 | - | 8 | 380 | 427 | - | 1122 | 1.1 | 0.04 | 9 | - | - |
| Pap9 | 31/07/2001 | 94 | 1.7 | 26 | 22 | 37 | 13 | 169 | 4.7 | 0.6 | 114 | 6.5 | 8 | 11 | 919 | 417 | - | 1741 | 0.5 | 0.01 | 14.5 | -6.7 | -56.5 |
| Pap13 | 31/07/2001 | 66 | 2.4 | 14 | 11 | 25 | 10 | 70 | 1.7 | 0.3 | 21 | 0.2 | - | 3.4 | 190 | 200 | - | 547 | 1.1 | 0.05 | - | - | - |
| Pap12 | 31/07/2001 | 69 | 2.1 | 26 | 18 | 31 | 12 | 136 | 2.1 | 0.4 | 45 | 3.3 | - | 5 | 364 | 291 | - | 935 | 0.8 | 0.03 | 9.5 | -7.6 | -55.5 |
| Pap14 | 14/09/2002 | 91 | 1.5 | 22 | 19 | 33 | 14 | 112 | 7.2 | 0.5 | 86 | 10 | 9 | 8 | 1420 | 531 | - | 2263 | 0.4 | 0.01 | - | - | - |
| Pap13 | 14/09/2002 | 64 | 2.4 | 14 | 8 | 25 | 9 | 115 | 1.9 | 0.3 | 25 | 0.3 | 0.3 | 3.9 | 213 | 174 | - | 590 | 0.8 | 0.04 | - | - | - |
| Pap12 | 14/09/2002 | 66 | 2.2 | 22 | 21 | 26 | 11 | 105 | 2.4 | 0.3 | 53 | 2.8 | - | 6 | 384 | 295 | - | 928 | 0.8 | 0.03 | - | - | - |
| Pap13 | 14/09/2002 | 90 | 1.7 | 24 | 25 | 33 | 10 | 154 | 5.3 | 0.4 | 160 | 7.3 | 8 | <10 | 1422 | 790 | - | 2630 | 0.6 | 0.01 | 17 | - | - |
| Pap15 | 29/01/2003 | 45 | 2.6 | 74 | 17 | 550 | 134 | 99 | 3.8 | 21.8 | 396 | 854 | - | 8 | 679 | 5544 | - | 8380 | 8 | 0.2 | - | - | - |
| Pap16 | 29/01/2003 | 17 | 3.1 | 42 | 16 | 498 | 44 | 180 | 1.2 | 11.0 | 7.2 | 22 | 6 | <8 | 198 | 1449 | - | 2469 | 7 | 0.2 | - | - | - |
| Pap17 | 31/01/2003 | 40 | 3.8 | 30 | 7 | 99 | 20 | 51 | 1.1 | 2.3 | 6.5 | 1.0 | - | <4 | 46 | 359 | - | 623 | 8 | 0.4 | - | - | - |
| Pap18 | 29/06/2003 | 75 | 3.3 | 56 | 20 | 97 | 38 | 77 | 7.4 | 1.6 | 10 | 28 | - | <10 | 185 | 393 | - | 835 | 2 | 0.2 | - | - | - |
| Pap19 | 30/06/2003 | 88 | 1.9 | 84 | 26 | 209 | 92 | 162 | 17.1 | 6.3 | 172 | 561 | - | 4.5 | 1192 | 2769 | - | 5134 | 2 | 0.1 | 1.4 | - | - |
| Pap20 | 23/07/2004 | 48 | 2.6 | 86 | 19 | 338 | 112 | 104 | - | 1.5 | 211 | 473 | - | <20 | 298 | 2962 | 0 | 4513 | 10 | 0.4 | - | - | - |
| Pap18 | 23/07/2004 | 82 | 3.2 | 56 | 22 | 101 | 41 | 86 | - | 2 | 4 | 44 | - | <5 | 149 | 433 | 3 | 852 | 3 | 0.3 | 7.3 | - | - |
| Pap19 | 23/07/2004 | 85 | 1.9 | 120 | 20 | 234 | 122 | 147 | - | 9 | 79 | 798 | - | <10 | 639 | 3090 | 0 | 5111 | 5 | 0.2 | 0.4 | - | - |
| Pap21 | 24/07/2004 | 49 | 2.4 | 80 | 22 | 437 | 123 | 97 | - | 2.2 | 131 | 427 | - | 6.9 | 308 | 3042 | 0.2 | 4599 | 10 | 0.4 | - | - | - |
| Pap22 | 24/07/2004 | 92 | 2.6 | 47 | 10 | 336 | 122 | 75 | - | 6.1 | 153 | 668 | - | <10 | 539 | 3123 | - | 5058 | 6 | 0.2 | 2.0 | - | - |
| Pap17 | 16/08/2004 | 36 | 4.6 | 17 | 6 | 84 | 22 | 41 | - | 3 | 0.22 | 0.32 | - | <5 | 25 | 286 | - | 443 | 11 | 0.9 | - | - | - |
| Pap23 | 30/07/2005 | 86 | 2.3 | 113 | 15 | 134 | 48 | 178 | - | - | 16 | 62 | - | 9 | 93 | 1187 | - | 1676 | 13 | 0.5 | 3.5 | - | - |
| Pap18 | 30/07/2005 | 86 | 3.2 | 55 | 20 | 111 | 46 | 97 | - | - | 4 | 60 | - | 4 | 142 | 513 | - | 954 | 4 | 0.3 | 6.4 | - | - |
| Pap19 | 30/07/2005 | 84 | 1.9 | 140 | 23 | 284 | 170 | 155 | - | - | 106 | 1010 | - | 20 | 631 | 4386 | - | 6750 | 7 | 0.3 | -0.3 | - | - |
| **Crater lake** | | | | | | | | | | | | | | | | | | | | | | | |
| Pap24 | 27/06/2003 | 50 | 3.2 | 98 | 35 | 645 | 125 | 116 | 7.4 | 19.4 | 44 | 44 | 49 | <10 | 580 | 2241 | - | 3839 | 4 | 0.2 | 6.0 | - | - |
| Pap24 | 23/07/2004 | 42 | 2.7 | 26 | 8 | 481 | 60 | 40 | - | 9 | 67 | 176 | - | <10 | 108 | 2142 | 16 | 3078 | 20 | 0.6 | 4.8 | - | - |
| Pap24 | 30/07/2005 | 37 | 2.7 | 13 | 4 | 367 | 38 | 30 | - | - | 85 | 219 | - | <10 | 60 | 2086 | - | 2873 | 35 | 0.6 | 2.9 | - | - |
| **Acid sulphate waters** | | | | | | | | | | | | | | | | | | | | | | | |
| Pap25 | 05/02/2000 | 23 | 1.2 | 34 | 23 | 70 | 31 | 75 | 0.3 | 1.7 | 313 | 248 | - | 5.3 | 27 | 4905 | - | 5658 | 182 | 1.2 | -0.99 | - | - |
| Pap26 | 27/06/2003 | 92 | 2.5 | 41 | 8 | 177 | 77 | 161 | 1.6 | 4.0 | 81 | 556 | - | <10 | 14 | 2886 | - | 3845 | 206 | 5.5 | 1.8 | - | - |
| Pap27 | 27/06/2003 | 45 | 2.4 | 47 | 22 | 550 | 84 | 193 | 0.6 | 2.9 | 249 | 220 | - | <16 | 15 | 4012 | - | 5202 | 269 | 5.6 | 4.5 | - | - |
| Pap26 | 2307/2004 | 91 | 1.7 | 28 | 7 | 79 | 52 | 154 | - | 2 | 241 | 204 | - | <10 | 24 | 3839 | 45 | 4575 | 161 | 2.2 | 1.8 | - | - |
| Pap27 | 23/07/2004 | 52 | 1.8 | 18 | 8 | 85 | 29 | 138 | - | 0.89 | 160 | 69 | - | 0 | <5 | 2201 | 18 | 2570 | - | - | 3.4 | - | - |
| Pap26 | 30/07/2005 | 82 | 2.1 | 19 | 6 | 76 | 42 | 152 | - | - | 234 | 250 | - | 3 | 10 | 2656 | - | 3296 | 263 | 4.2 | - | - | - |
| Pap27 | 30/07/2005 | 79 | 1.9 | 14 | 5 | 62 | 16 | 150 | - | - | 93 | 19 | - | 2 | 4 | 1579 | - | 1794 | 367 | 3.7 | - | - | - |
| Pap28 | 3007/2005 | 94 | 2.6 | 43 | 9 | 96 | 28 | 153 | - | - | 23 | 130 | - | <5 | 8 | 1011 | - | 1347 | 135 | 3.7 | - | - | - |
| **Sulfur-mud pools** | | | | | | | | | | | | | | | | | | | | | | | |
| Pap29 | 05/02/2000 | 88 | 0.4 | 35 | 22 | 77 | 32 | 177 | 500 | 2.3 | 250 | 110 | - | 212 | 26797 | 1107 | - | 29145 | 0.04 | 0.001 | - | - | - |
| Pap30 | 05/02/2000 | 87 | 1.1 | 3 | 3 | 7 | 4 | 169 | 3.6 | 0.2 | 63 | 33 | - | 6.5 | 1520 | 1215 | - | 2857 | 0.08 | 0.003 | - | - | - |
| Pap31 | 31/07/2001 | 95 | 0.3 | 26 | 16 | 54 | 24 | 140 | 100 | 1.1 | 99 | 36 | - | 45 | 26771 | 1256 | - | 28428 | 0.05 | 0.001 | - | - | - |
| Pap30 | 31/07/2001 | 89 | 0.8 | 4 | 8 | 7 | 5 | 165 | 8.4 | 0.2 | 80 | 37 | - | 9.4 | 2858 | 1644 | - | 4661 | 0.58 | 0.002 | - | - | - |
| Pap30 | 14/09/2002 | - | 0.9 | 6 | 6 | 12 | 6 | 150 | 11.4 | 0.3 | 89 | 36 | - | 1.2 | 4443 | 2272 | - | 6883 | 0.51 | 0.001 | - | - | - |
| Pap32 | 24/07/2004 | 90 | 0.6 | 362 | 141 | 1432 | 643 | 214 | - | 26 | 5020 | 1871 | - | 21 | 26963 | 5134 | 12 | 41613 | 0.19 | 0.024 | - | - | - |

(LMWL) was constructed from the GNIP data covering the period 1962-1997 for Indonesia (Jakarta station). The isotopic compositions of the Papandayan fumaroles lie on a mixing line between "magmatic end member" and local meteoric water. The water discharges are dominated by meteoric waters with a minor magmatic contribution. The $\delta^{18}O$ values of gases close to the local meteoric waterline are shifted by ~4 ‰ from the hot springs $\delta^{18}O$ values. A similar shift has been observed in fumaroles from Kudryavy volcano (Taran *et al*., 1995) and Galeras (Fischer *et al*., 1997). These autors attributed this shift to an interaction between meteoric water and magmatic gases leading to enrichment in $\delta^{18}O$ of the vapor phase. The same process may be present at the Papandayan Volcano.

## Changes in the Chemistry of Thermal Water after the Eruption

Different processes which can occur between the cooling magma at depth and the hot springs at the surface are as follows: injection of magmatic gases into the hydrothermal system, dissolution of rock by the acid fluids and dilution of acid fluids by meteoric water. On Figure 7, a positive correlation between Cl and hydrogen ion activity ($10^{-pH}$) is shown. The increase in $Cl^-$ is concomitant with the more $H^+$ value. The correlation indicates that the Cl in the springs was supplied in the form of HCl solution or vapor. Furthermore, the concentrations in F, Cl and $SO_4$ in the acid chloride-sulphate water reflect an injection of magmatic gases ($SO_2$, $H_2S$, HCl, HF) in to the hydrothermal system.

Table 4. Average Chemical Composition of Andesite

| $SiO_2$ (wt%) | $Al_2O_3$ (wt%) | $Fe_2O_3$ (wt%) | MnO (wt%) | MgO (wt%) | CaO (wt%) | $Na_2O$ (wt%) | $K_2O$ (wt%) |
|---|---|---|---|---|---|---|---|
| 57.27 | 18.52 | 7.49 | 0.13 | 3.03 | 7.10 | 2.80 | 1.38 |

The chemistry of samples collected two months before the November 2002 eruption show no detectable changes, suggesting that no significant modification occurred in the pre-eruptive degassing. The chemistry of samples collected after the eruption reveals however notable changes. The most significant changes are an increase in $SO_4$/Cl and Mg/Cl ratios (Figure 8, Table 3). This could be due to the intrusion of a fresh magma at shallow depth (Giggenbach, 1974; Pasternack and Varekamp, 1994). The acid sulphate water that are likely to have been generated at subsurface show the same increase in Mg/Cl ratio than the acid chloride-sulphate water. A more likely explanation for the changes observed in the 2003 data is the opening of new fractures where unaltered or less altered volcanic rocks were brought in contact with the ascending acid water. To confirm this hypothesis, we evaluated the degree of water-rock interaction was evaluated by calculating the percentage of residual acidity (PRA) recently introduced by Varekamp and Kreulen (2000) for crater lake studies. The PRA is defined as the residual acidity left after the neutralization of a fluid by water-rock (WR) interaction. Since acidity is consumed by hydrolysis reaction during WR interaction, PRA is independent of dilution or boiling. The pure acid or initial acidity was computed for each sample from their Cl and $SO_4$ concentrations with PHREEQC. The graph 100 × Mg / (∑ RFE) versus residual acidity is shown on Figure 9, corresponds to the easily leached element Mg on a molar basis relative to the sum of major rock forming elements (RFE = Na + K + Mg + Ca + Al). The data show a net decrease in the residual acidity for the sampled collected in 2003-2005 accompanied by an increase in the relative Mg concentration. This trend reflects an increase in the neutralization of the acid springs and show that the WR interactions were more significant after the eruption.

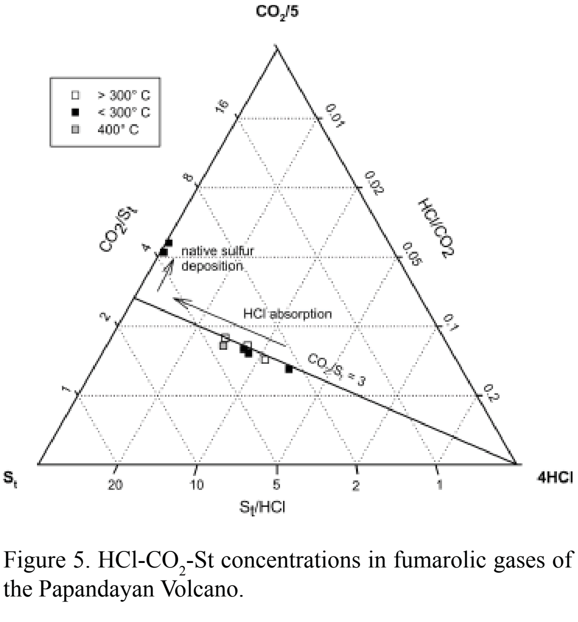

Figure 5. HCl-$CO_2$-St concentrations in fumarolic gases of the Papandayan Volcano.

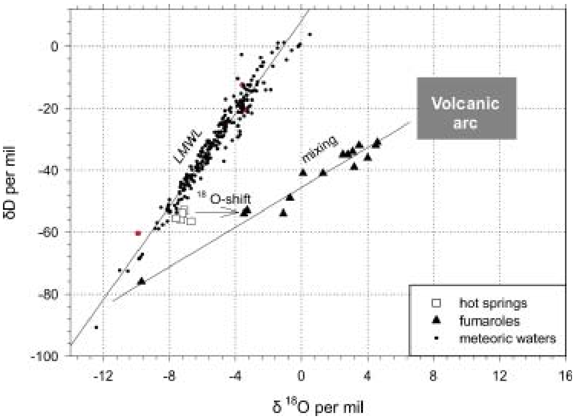

Figure 6. Oxygen and hydrogen isotopic compositions of the Papandayan gases, hot springs and meteoric water. LMWL is local meteoric line.

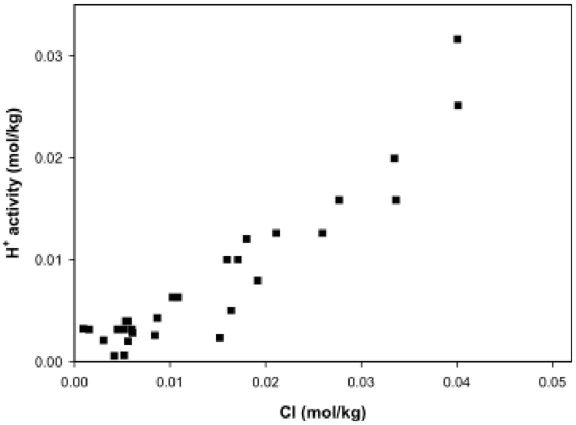

Figure 7. Cl versus $H^+$ activity of the Papandayan hot springs.

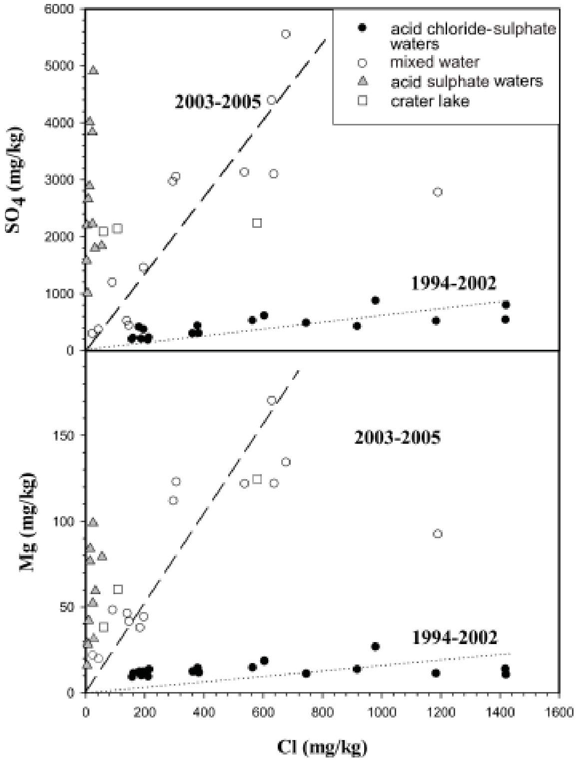

Figure 8. Cl concentration versus $SO_4$ and Mg concentrations of water sampled before (1994-2002) and after the eruption (2003-2005).

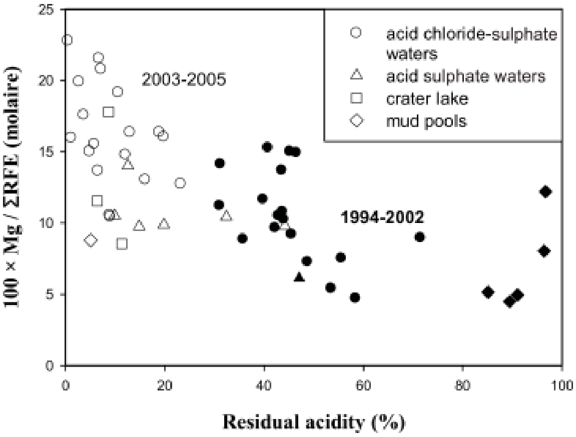

Figure 9. Plot of the percentage of residual acidity versus 100 x Mg/ERFE (Sum of major rock-forming elements)= Na+Ca+Mg+K+Al+Fe.

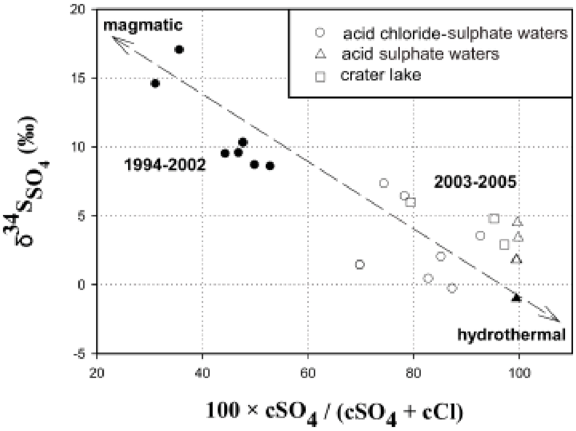

Figure 10. Plot of $\delta^{34}S$ $SO_4$ versus $100xcSO_4/(cSO_4+cCl)$ of hotsprings from the Papandayan Volcano. Ci= Concentration of element I in mg/kg.

## Sulphur Isotopic Composition

Figure 10 shows $\delta^{34}S$ of sulphates versus the SO4 weight fraction $100 \times cSO_4 / (cSO_4 + cCl)$. The high $\delta^{34}S$ values (9-17 ‰) observed in acid sulphate-chloride water before the November 2002 eruption strongly indicates that dissolve sulphates are mainly formed from the disproportionation of magmatic $SO_2$ (Ohmoto and Goldhaber, 1997; Kusakabe *et al.,* 2000) according to the reaction of: $4SO_2 + 4H_2O \rightarrow 3HSO_4 + H_2S + 3H^+$ or $3SO_2 + 3H_2O \rightarrow 2HSO_4 + S^0 + 2H$. Kusakabe *et al.* (1992) show that the disproportionation of $SO_2$ leads to a large isotopic fractionation between dissolved sulphates and $H_2S$ or elemental sulphur. The low $\delta^{34}S$ of sulphates in the chloride-depleted water collected before the eruption indicates that the origin of sulphates for this water is the surficial oxydation of hydrogen sulphide (Kiyosu and Kurahashi, 1983). This Cl-depleted water has been formed from the condensation of steam rising from the boiling hydrothermal system to the subsurface above the water table (Reed and Spycher, 1985). The water samples collected after the eruption show low values of $\delta^{34}S$ of dissolved sulphates (7 to -0.3‰). This indicates that there was no increase in the contribution of magmatic fluids in the upper part of the hydrothermal system.

## Crater Lake

Water from the new crater lake have been collected since 2003. An evolution in the $SO_4$/Cl ratio is observed during 2003-2005 showing a decrease in Cl content, whereas $SO_4$ value remains stable (Table

4). The low values of $\delta^{34}S$ (3-6 ‰) for sulphates of the lake water indicates that the origin of these sulphates may be the result of $H_2S$ surficial oxidation and not the disproportionation of $SO_2$. The lake water reflects the hydrothermal fluids present at depth with a magmatic contribution less important with time. Cation concentrations have decreased since 2003, but the residual acidity increased slightly (Figure 9). This indicates a decrease in water-rock interaction or a contact between acid waters and wall rock has already completely leached.

## Water-rock Interaction

A relationship between rock forming elements (RFE) concentrations and their abundance in volcanic rocks from sample data collected before the November 2002 eruption is presented in Figure 11. An average composition of 4 samples of andesite reported is used for the comparison (Table 4). A congruent dissolution is observed with thermal water and corresponds to 1g of andesite per kg of acid waters. This water is depleted in Si, Al, and Fe compared to their rock abundance. The solubility of Si decreases with a decrease in temperature (Nicholson, 1993). Aluminium is strongly negatively correlated with the pH, where solubility of Al decrease with an increase in pH and can co-precipitates with Si. The iron is highly depleted compared to its rock abundance. Fe solubility is pH dependent but this can not explain the very low concentrations in water. However, abundant pyrites have been found in the ashes and altered rocks. Therefore, Fe could be consumed in the reaction that formed pyrite. In experimental studies (Schoonen and Barnes, 1991) two steps of formation of pyrite and marcasite has been described. The first step is the precipitation of iron monosulphide (FeS) by the reaction:

$$Fe^{2+} + H_2S\,(aq) \rightarrow FeS\,(s) + 2\,H^+$$

In the second step, iron monosulphide is converted to an iron disulphide either

(1) Fe loss:

$$2FeS(s) + 2H^+ \rightarrow FeS_2(s) + Fe^{2+} + H_2(g)$$

or

(2) sulphidation:

$$FeS(s) + H_2S(aq) \rightarrow FeS_2(s) + H_2(g)$$

or

$$FeS(s) + HS^-(aq) + H_2O(l) \rightarrow FeS_2(s) + H_2(g) + OH^-$$

Iron disulphides are formed most readily if the solutions contain an excess of thiosulphates, poly-

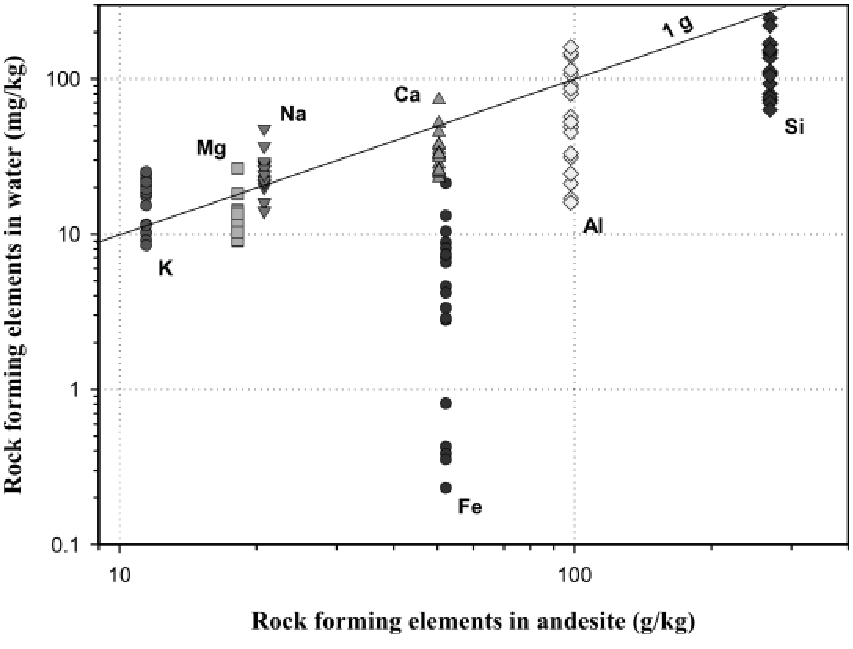

Figure 11. Concentration of rock forming elements (RFE) in lake water compared to the Papandayan andesite.

thionates and/or polysulphides.

Congruent dissolution of rock has been reported by Bernard *et al.* (2004) for Santa-Ana Crater Lake and by Ohba (1994) for Yugama Crater Lake as the main source of RFE in water. However, other processes can affect the concentration of RFE in crater lakes. The dissolution of lava rock by magmatic volatiles leads to leaching different rates for the RFE (Christenson and Wood, 1993; Varekamp and Kreulen, 2000). The incongruent dissolution can be explained also by the precipitation or dissolution of minerals in lake water or in the hydrothermal system depending on the temperature and chemical fluctuations of acid fluids injected in to the system (Delmelle and Bernard, 1994; Christenson and Wood, 1993). The congruent dissolution of RFE at the Papandayan Volcano may be explained by a large circulation of thermal water in the subsurface system. However, the assemblages of alteration minerals found in the ejectas show that an interaction between acid fluids and non-altered lava rocks (or less altered) occurs. So, a precipitation of minerals and neutralization of fluids took place in the hydrothermal system (Giggenbach, 1992; Hedenquist *et al.*, 1994; Reyes, 1990).

To improve our knowledge about the water-rock interaction in the system, a model is used on the basis of the stability of pyrophyllite, kaolinite and alunite as a function of log $SiO_2$, aq and pH (figure 12). The code SUPCRT92 (Johnson *et al.*, 1992) was used to compute the thermodynamic constant needed to build the stability field diagram. Quartz is assumed to be oversaturated in the model, because this phase is largely present in the altered rocks. The limits of stability reported on Figures 12a, b, c, and d correspond to the fluids Pap-2 (higher pH = 2.5)

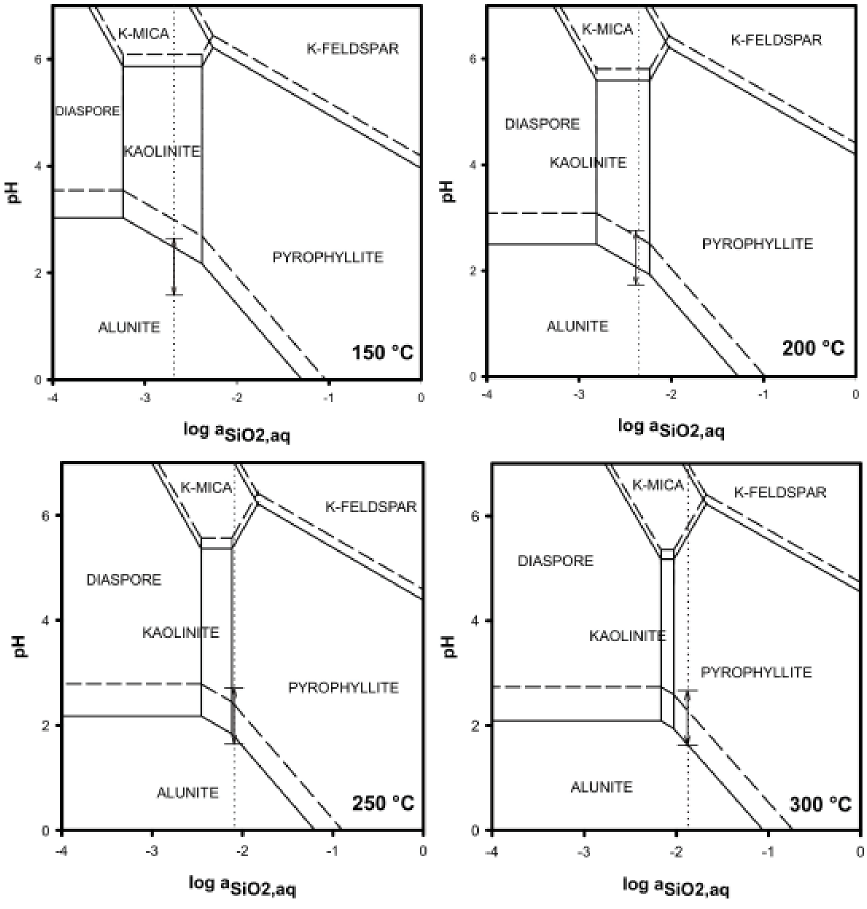

Figure 12. Stability diagram of pH versus log $^aSiO_2$, aq of the acid sulphate-chloride alteration phases from 150°C to 300°C. The dotted line corresponds to the saturation of silica.

and Pap-14 (lower pH=1.5) at different temperature and computed with PHREEQC (Parkhurst and Appelo, 1999) by using the thermodynamic database Wateq4f (Ball and Nordstrom, 1991). In Figure 12, the range in pH measured in the fluids and calculated at different temperatures is also indicated by arrows on the diagram. In the stability diagrams (Figures 12c and d), pyrophyllite and kaolinite coexist at 250°C. Experimental studies by Hemley *et al.*(1980) show that kaolinite and pyrophyllite can coexist at temperature about 270°C at quartz saturation. The presence of kaolinite is pH dependent and for water with pH below 2 and temperature of 250°C, kaolinite is no more stable. Pyrophyllite is a mineral that may form at high temperature in geothermal systems (Reyes, 1990; Nogami *et al.*, 2000; Hedenquist *et al.*, 1998), in many ore deposits districts (Marumo, 1989; Hedenquist *et al.*, 1994; Yilmaz, 2003) and on active volcanic sites (Christenson and Wood, 1993; Nogami *et al.*, 2000). Alunite can also coexist with kaolinite and pyrophyllite between 250-300°C (Hedenquist *et al.*, 1998). For the fluids studied, alunite is a stable phase between 200 and 150°C.

To specify the temperature of formation of alunite, another stability diagram was used (Stoffregen *et al.*, 2000; Figure 13). In this diagram, stabilities of alunite, kaolinite/pyrophyllite and muscovite were plotted versus $H^+$-$SO_4^{2-}$ activities and $K^+SO_4^{2-}$ activities. Silica is fixed by the quartz saturation. On Figure 13, equilibrium compositions of fluids calculated at different temperatures are also plotted. Alunite appears at temperatures below 300°C and this is the Al-bearing phase stable at temperatures below 150 °C (Figure 13).

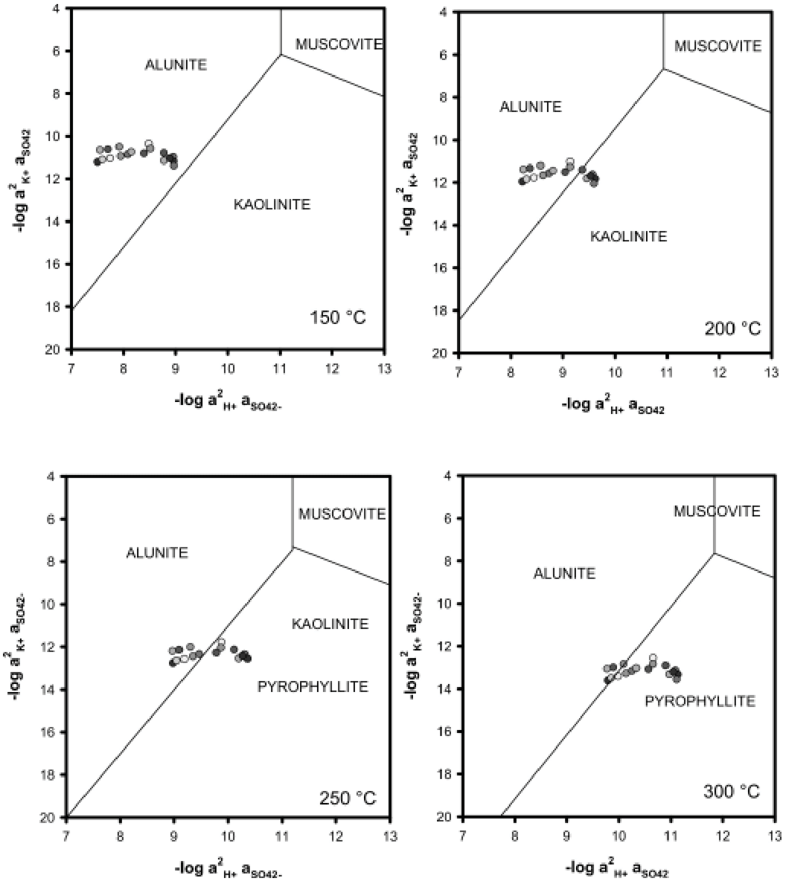

Figure 13. Stability diagram of log ($a^2H^+$ x $aSO_4^{2-}$) versus -log ($a^2K^+$ x $aSO_4^{2-}$) of the muscovite, pyrophyllite, and alunite phases from 150°C to 300°C. Data from the Papandayan water is also reported on the diagram.

## CONCLUSIONS

The chemical and isotopic compositions of acid hot springs from the crater of THE Papandayan Volcano sampled since 1994 indicate that a contribution of magmatic volatiles (HCl, $SO_2$, $H_2S$, HF) to the hydrothermal system is likely present and that interaction between acid fluids and rocks took place. The altered mineral assemblages identified in the rocks ejected during the November 2002 eruption and coming from the hydrothermal system is a typical of an advanced argillic alteration.

The eruption produced notable changes in the chemistry of the hot springs. Most of these chemical changes can be related to a modification in the dynamic circulation of these fluids to the surface by the opening of new fractures. Furthermore, no evidence of intrusion of fresh magma in the upper part of the hydrothermal system has been found. The hydrothermal zones are likely restrained to faults or permeability structure (Reyes, 1990; Stoffregen, 1987). The acid fluids could ascend to the surface and lead to the formation of hot springs or descend along the structures to deep level and react with the host rock. This interpretation may explain why closely different fluids can cause different type of advanced argillic alterations.

The chemical monitoring at the Papandayan Volcano is a useful tool for understanding the processes in the hydrothermal system and to survey the level of activity, especially after the phreatic eruption like that in November 2002 which was able to be follow by a magmatic eruption.

**Acknowledgments—**This work was financially supported by the "Centre de Recherches Volcanologiques" (CRV-OPGC, University Blaise Pascal), in France and the Comunauté Française in Belgium. We are very grateful to the directors of the Volcanology and Geological Hazard Mitigation (DVGHM), in Indonesia, Wirakusumah and Siagian to their cooperation. We thank also our colleagues of DVGHM for their participation in field campaigns.

## REFERENCES

Arribas, A.J., 1995. Geology, geochronology, fluid inclusions, and isotope geochemistry of the Rodalquilar gold alunite deposit, Spain. *Economic Geology*, 90, p. 795-822.

Ball, J.W. and Nordstrom, D.K., 1991. WATEQ4f-User's manual with revised thermodynamic database and test cases for calculating speciation of major, trace and redox elements in natural waters. *U.S. Geological Survey Open-File Report*, 90-129:185p.

Bernard, A., Escobar, C.D., Mazot, A., and Guttierres, R.E., 2004. The acid crater lake of Santa Ana volcano, El Salvador. *Geological Society of America Special Paper*, 375, p. 121-133.

Christenson, B. and Wood, C.P., 1993. Evolution of a vent-hosted hydrothermal system beneath Ruapehu Crater Lake, New Zealand. *Bulletin of Volcanology*, 55, p. 547-565.

Delmelle, P. and Bernard, A., 1994. Geochemistry, mineralogy, and chemical modeling of the acid crater lake of Kawah Ijen Volcano, Indonesia. *Geochemica et Cosmochimica Acta*, 58(11), p. 2445-2460.

Federico, C., 2002. Magma-derived gas influx and water-rock interactions in the volcanic aquifer of Mt. Vesuvius, Italy. *Geochemica et Cosmochimica Acta,* 66(6), p. 963-981.

Fischer, T.P., 1997. The chemical and isotopic composition of fumarolic gases and spring discharges from Galeras Volcano, Colombia. *Journal of Volcanology and Geothermal Research*, 77, p. 229-253.

Giggenbach, W.F., 1974. The chemistry of Crater Lake, Mt Ruapehu (New Zealand) during and after the 1971 active period. *New Zealand Journal of Science*, 17, p. 33-45.

Giggenbach, W.F., 1992. Magma degassing and mineral deposition in hydrothermal systems along convergent plate boundaries. *Economic Geology*, 87, p. 1927-1944.

Giggenbach, W.F., 1996. Chemical composition of volcanic gases. In: Scarpa, R.W. and Tilling, R.I. (Editors), *Monitoring and Mitigation of Volcano Hazards*, Berlin, p. 221-256.

Giggenbach, W.F., García, N. Londoño, A. Rodríguez, L. Rojas, N., and Calvache, M.L., 1990. The chemistry of fumarolic vapor and thermal-spring discharges from the Nevado del Ruiz volcanic-magmatic-hydrothermal system, Colombia. *Journal of Volcanology and Geothermal Research*, 42, p. 13

Giggenbach, W.F., Tedesco, D., Sulistiyo, Y., Caprai, A., Cioni, R., Favara, R., Fischer, T.P., Hirabayashi, J.-I., Korzhinsky, M., Martini, M., Menyailovk, I., and Shinohara, H., 2001. Evaluation of results from the fourth and fifth IAVCEI field workshops on volcanic gases, Vulcano island, Italy and Java, Indonesia. *Journal of Volcanology and Geothermal Research*, 108, p. 157-172.

Hedenquist, J.W., Arribas, A.J., and Reynolds, T.J., 1998. Evolution of an intrusion-centered hydrothermal system: Far Southeast-Lepanto porphyry and epithermal Cu-Au deposits, Philippines. *Economic Geology*, 93(4): 373-404.

Hedenquist, J.W., 1994. Geology, geochemistry, and origin of high sulfidation Cu-Au mineralization in the Nansatsu District, Japan. *Economic Geology*, 89(1), p. 1-30.

Hemley, J.J., Montoya, J.W., Marinenko, J.W., and Luce, R.W., 1980. Equilibria in the system $Al_2O_3$-$SiO_2$-$H_2O$ and some general implications for alteration/ mineralization processes. *Economic Geology*, 75, p. 210-228.

Johnson, J.W., Oelkers, E.H., and Helgeson, H.C., 1992. SUPCRT92: a software package for calculating the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions from 1 to 5000 bar and 0 to 1000°C. *Computers & Geosciences*, 18(7), p. 899-947.

Kiyosu, Y. and Kurahashi, M., 1983. Origin of sulfur species in acid sulphate-chloride thermal waters, northeastern Japan. *Geochemica et Cosmochimica Acta*, 47, p. 1237-1245.

Kusakabe, M. and Komoda, Y., 1992. Sulfur isotopic effects in the disproportionation reaction of sulfur dioxide at hydrothermal temperatures. *Report, Geological Survey of Japan*, 279, p. 93-96.

Kusakabe, M., Komoda, Y., Takano, B., and Abiko, T., 2000. Sulfur isotopic effects in the disproportionation reaction of sulfur dioxide in hydrothermal fluids: implications for the $\delta^{34}$S variations of dissolved bisulfate and elemental sulfur from active crater lakes. *Journal of Volcanology and Geothermal Research*, 97, p. 287-307.

Marumo, K., 1989. Genesis of kaolin minerals and pyrophyllite in Kuroko deposits of Japan: implications for the origins of the hydrothermal fluids from mineralogical and stable isotope data. *Geochemica et Cosmochimica Acta*, 53, p. 2915-2924.

Murowchick, J.B. and Barnes, H.L., 1986. Marcasite precipitation from hydrothermal solutions. *Geochemica et Cosmochimica Acta*, 50, p. 2615-2629.

Nicholson, K., 1993. *Geothermal fluids: Chemistry and Exploration Techniques*. Springer-Verlag, Berlin, 268 pp.

Nogami, K., Hirabayashi, J.-I., Ohba, T., and Yoshiike, Y., 2000. The 1997 phreatic eruption of Akita-Yakeyama volcano, northeast Japan: Insight into the hydrothermal processes. *Earth Planets Space*, 52, p. 229-236.

Ohba, T., Hirabayashi, J.-I. and Nogami, K., 1994. Water, heat and chloride budgets of the crater lake, Yugama at Kusatsu-Shirane volcano, Japan. *Geochemical Journal*, 28, p. 217-231.

Ohmoto, H. and Goldhaber, M.B., 1997. Sulfur and carbon isotopes. In: H.L. Barnes (Editor), *Geochemistry of hydrothermal ore deposits (third edition)*. Wiley &Sons, New York, p. 517-611.

Ohsawa, S., Takano, B., Kusakabe, M. and Watanuki, K., 1993. Variation in volcanic activity of Kusatsu-Shirane volcano as inferred from $\delta^{34}$S in sulfate from the Yugama crater lake. *Bulletin of the Volcanological Society of Japan*, 38, p. 95.

Parkhurst, D.L. and Appelo, C.A.J., 1999. User's guide to PHREEQC-- A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *U.S. Geological Survey Water-Resources Investigations Report*, 99-4259: 312 p.

Pasternack, G.B. and Varekamp, J.C., 1994. The geochemistry of Keli Mutu volcanic lakes Flores, Indonesia. *Geochemica et Cosmochimica Acta*, 28, p. 243-262.

Reed, M.H. and Spycher, N.F., 1985. Boiling, cooling and oxidation in epithermal systems : A numerical modeling approach. *Geology and Geochemistry of epithermal systems*, p. 249-272.

Reyes, A.G., 1990. Petrology of Philippine geothermal systems and the application of alteration mineralogy to their assessment. *Journal of Volcanology and Geothermal Research*, 43, p. 279-309.

Schoonen, M.A.A. and Barnes, H.L., 1991. Mechanisms of pyrite and marcasite formation from solution:III. Hydrothermal processes. *Geochemica et Cosmochimica Acta*, 55, p. 3491-3504.

Stoffregen, R., 1987. Genesis of acid-sulfate alteration and Au-Cu-Ag mineralization at Summitville, Colorado. *Economic Geology*, 82, p. 1575-1591.

Stoffregen, R., Alpers, C.N., and Jambor, J.L., 2000. Alunite-Jarosite Crisatllography, Thermodynamics, and Geochronology. In: Alpers, C.N., Jambor, J.L., and Nordstrom, D.K. (Editors), Sulfate minerals-Crystallography, Geochemistry, and Environmental Significance. *Reviews in Mineralogy & Geochemistry. The Mineralogical Society of America*, Washington, p. 453-480.

Takano, B. and Watanuki, K., 1990. Monitoring of volcanic eruptions at Yugama crater lake by aqueous sulfur oxyanions. *Journal of Volcanology and Geothermal Research*, 40, p. 71-87.

Taran, Y., 1998. Geochemistry of the volcano-hydrothermal system of El Chichon Volcano, Chiapas, Mexico. *Bulletin of Volcanology*, 59, p. 436-449.

Taran, Y., Pokrovsky, B., and Dubik, Y.M., 1989. Isotopic composition and origin of water from andesitic magmas. *Doklady (Translations) Academy of Science USSR*, 304, p. 401-404.

Taran, Y.A., Hedenquist, J.W., Korzhinsky, M.A., Tkachenko, S.I., and Shmulovich, K.I., 1995. Geochemistry of magmatic gases from Kudryavy volcano, Iturup, Kuril Islands. *Geochemica et Cosmochimica Acta*, 59(9), p. 1749-1761.

Tassi, F., 2003. Chemical composition of fumarolic gases and spring discharges from El Chichon volcano, Mexico: causes and implications of the changes detected over the period 1998-2000. *Journal of Volcanology and Geothermal Research*, 123, p. 105-121.

USGS, 1998. *Bulletin of Global Volcanism Network*, 23:07: http:// volcano.si.edu/reports/usgs.

USGS, 2002. *Bulletin of Global Volcanism Network*, 27:11: http:// volcano.si.edu/reports/usgs.

USGS, 2003. *Bulletin of Global Volcanism Network*, 28:07: http:// volcano.si.edu/reports/usgs.

Valentino, G.M., Cortecci, G., Franco, E., and Stanzione, D., 1999. Chemical and isotopic compositions of minerals and waters from the Campi Flegrei volcanic system, Naples, Italy. *Journal of Volcanology and Geothermal Research*, 91, p. 329-344.

van Padang, N.M., 1951. Indonesia. Catalogue of the Active

Volcanoes of the World,Rome: *IAVCEI*, 1, p. 1-271.

Varekamp, J.C. and Kreulen, R., 2000. The stable isotope geochemistry of volcanic lakes, with examples from Indonesia. *Journal of Volcanology and Geothermal Research*, 97, p. 309-327.

Yilmaz, H., 2003. Exploration at the Kuscaryiri Au (Cu) prospect and its implications 3 for porphyry-related mineralization in western Turkey. *Journal of Geochemical Exploration*, 77, p. 133-150.