

Modeling Mineral Equilibrium in the Pinatubo Geothermal System

Ma. Ines Rosana, D. Balangu and Ma. Gracia C. Collantes

National Institute of Geological Sciences, University of the Philippines, Diliman, Quezon City, Philippines

rbalangu@nigs.upd.edu.ph

Keywords: Pinatubo, mineral equilibrium, SOLVEQ, geochemical modeling

ABSTRACT

The equilibrium state between present-day geothermal fluids and hydrothermal mineral phases was tested for the Pinatubo geothermal field. Observed hydrothermal minerals in Pinatubo are typical of neutral to alkaline fluids. Important hydrothermal minerals found in the field include clay minerals (montmorillonite, kaolinite/dickite, interlayered clays, illite), chlorite, epidote, quartz, pyrite, with minor actinolite, calcite and sphene. Calculated mineral saturation indices for the well discharges in the Pinatubo geothermal system showed that the reservoir fluids are oversaturated with actinolite, anhydrite, chlorite, epidote, hematite, magnetite, and pyrite. Chemical equilibrium between the present day fluids and hydrothermal minerals was not attained as indicated by a spread of temperature in log (Q/K) plot and appearances of some minerals that have not been reported.

1. INTRODUCTION

No historic eruptions had occurred at Mount Pinatubo, but the volcano was known to be thermally active and had been explored as a potential geothermal energy source by the Philippine National Oil Company. Prior to its eruption in 1991, three exploratory geothermal drilling at Mount Pinatubo in 1988-90, revealed its igneous character as being governed by high-temperature (261-336°C), highly acidic fluids and low permeability (Delfin et al., 1996). A research

study aimed to continue the prior investigation on Mt. Pinatubo as a geothermal system can lead to the understanding of its behavioral characteristics as an active volcano and as a geothermal system with significant magmatic contribution.

As part of this on-going research, a geochemical modeling exercise designed to examine whether the pre-1991 geothermal fluids were in equilibrium with the hydrothermal mineral phases observed in well cores and cuttings was undertaken. The partial results of which are presented in this paper.

2. PINATUBO AS A GEOTHERMAL SYSTEM

Prior to the 1991 eruption of Mt. Pinatubo, an active hydrothermal system manifested at the surface by thermal springs and solfataras was observed. Most of the springs were concentrated along a narrow, ~25-km-long belt north-northwest of the summit at altitudes of 900 to 1180 m (Delfin, 1984). This pre-eruption hydrothermal system was a source of elemental sulfur and had attracted geothermal exploration, including the drilling of three deep wells (Figure 1).

Drilling encountered acidified reservoir fluids (pH to 2.3 for well PIN-3D, temperatures to 336°C measured for PIN-2D) (PNOC, 1990). Chemical and isotopic (helium, oxygen and carbon) analyses of well fluids indicate the presence of magmatic components such as carbon and sulfur gases, as well as heat in the Pinatubo reservoir (Figure 2)(Ruaya and others, 1992).

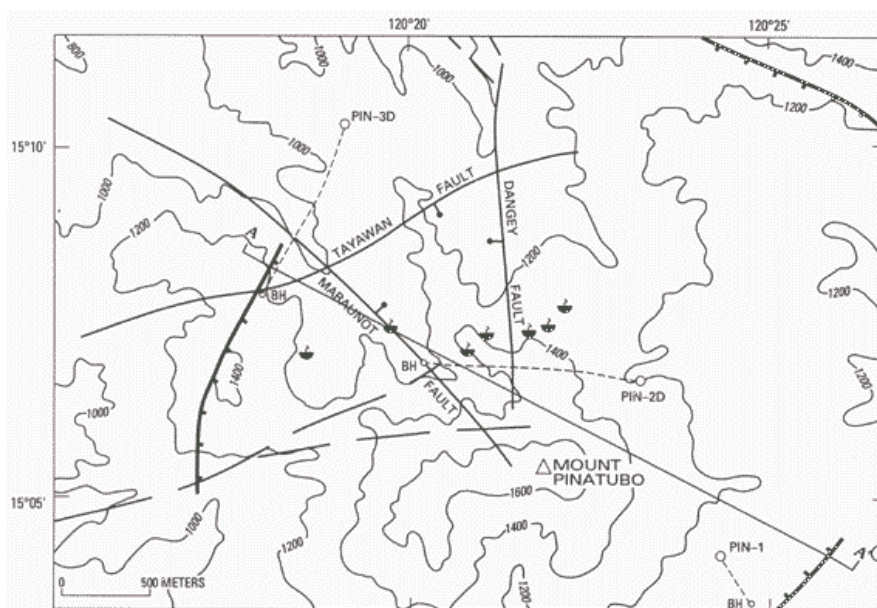


Figure 1: Well location map of Mount Pinatubo exploratory Well PIN-1 had a total vertical depth of 2,733 m; well PIN-2D, 2,216 m; well PIN-3D, 2,190 m. (Delfin et al., 1996)

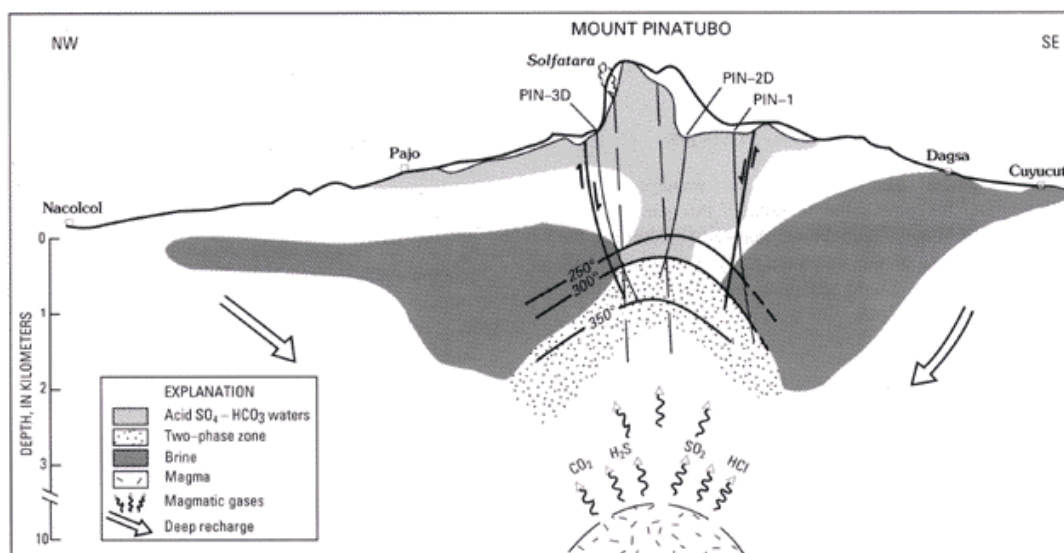


Figure 2 Conceptual model of the pre-1991 Mount Pinatubo hydrothermal system (modified from Ruaya and others, 1992).

Drilling of three deeps wells revealed a pile of andesitic to dacitic volcanic rocks, 1,300 to more than 2,000 m thick underlying the area. The upper few hundred meters of this unit are largely dacite and andesite breccias and tuffs believed to be erupted from the modern Pinatubo. This sequence is underlain by dacitic lava flows and by a thicker sequence of waterlaid (?) pyroclastics presumed to be deposits of the ancestral Pinatubo. Dioritic dikes of uncertain affinity crosscut the volcanics generally below 200 m in altitude (Delfin et al., 1996)

Hydrothermal alteration in the Pinatubo geothermal field results mainly from the reaction between the reservoir rock and neutral pH chloride fluids. The observed clay zonation in other Philippine geothermal areas was not found at Mount Pinatubo (Reyes, 1990). Persistence of the smectite and illite-smectite zones to depths where temperatures are over 300°C has been interpreted to suggest existence of several regimes of hydrothermal activity. Both smectite and illite-smectite zones are stable only up to temperatures of 180° and 230°C, respectively (Reyes, 1990). Despite the acidic fluids discharged by the wells (pH = 2.18 – 3.18, weirbox, PIN-2D (Pagado and Villarosa, 1989)), acid alteration assemblages are restricted to major permeable zones associated with fault intersections. Acid minerals in the drillholes include alunite, diaspore, pyrophyllite, dickite, anhydrite, and pyrite. These occur at depths as shallow as 165 m to as deep as -514 m, where temperatures range from 164° to 302°C. The limited distribution of acid minerals, despite the widespread occurrence of acid fluids in the boreholes, implies restricted permeability within the hydrothermal system.

3. GEOCHEMICAL MODELLING

Using the speciation program SOLVEQ (Reed and Spycher, 1984) and the database SOLTHERM (Spycher and Reed, 1993) accurate values for the activities of aqueous ions in a given water at high temperature were calculated from 300°C to 50°C. These are then used to calculate an ion activity product (Q) for each mineral. A measure of proximity of the equilibrium between the aqueous solution with the mineral is given by the ratio of the Q vs. K ($\log(Q/K)$) or the

mineral saturation index. By plotting $\log(Q/K)$ vs. T for natural waters, one would be able to determine (a) if there was equilibrium between the solution and the host rock mineral assemblage (2) probable equilibrium mineral assemblage and (3) equilibrium temperature (Reed and Spycher, 1984). The numerical value of $\log(Q/K)$ greater than zero are for supersaturated minerals and less than zero for undersaturated minerals. The convergence of $\log(Q/K)$ curves for the equilibrium assemblage to zero at the temperature of equilibration establishes the basis for determination of the mineral assemblage as well as the temperature equilibration of the natural geothermal waters from water analysis alone (Reed and Spycher, 1984).

Water and gas analysis from Delfin et al. (1996) were used for the calculations (Table 1). There was no Al analysis included hence, the waters were arbitrarily equilibrated with albite to obtain concentrations of Al for the waters.

4. RESULTS AND DISCUSSIONS

Figure 3 shows a $\log(Q/K)$ plot for Pinatubo waters as follows: a) PIN 1 sited at the southeastern flank of Mt. Pinatubo, b) PIN 2D, a directional well located northwestern flank of Mt. Pinatubo and was drilled to test the presence of high temperature adjacent to a resistivity anomaly, and c) PIN 3D drilled also at the northwestern flank with the intention of finding neutral fluids ascending through the Marunot outflow channel (Figure 2). Of the three wells studied, only PIN 1 showed defined clustering of $\log(Q/K)$ at zero values. Many of the minerals observed in the Pinatubo cores and cuttings (Villarosa et al., 1989, Pagado and Villarosa, 1989; Pagado and Ramos, 1990) including anhydrite, chlorite, epidote, hematite, pyrite, illite (represented as muscovite in the calculation) and tremolite appear to be formed at depths.

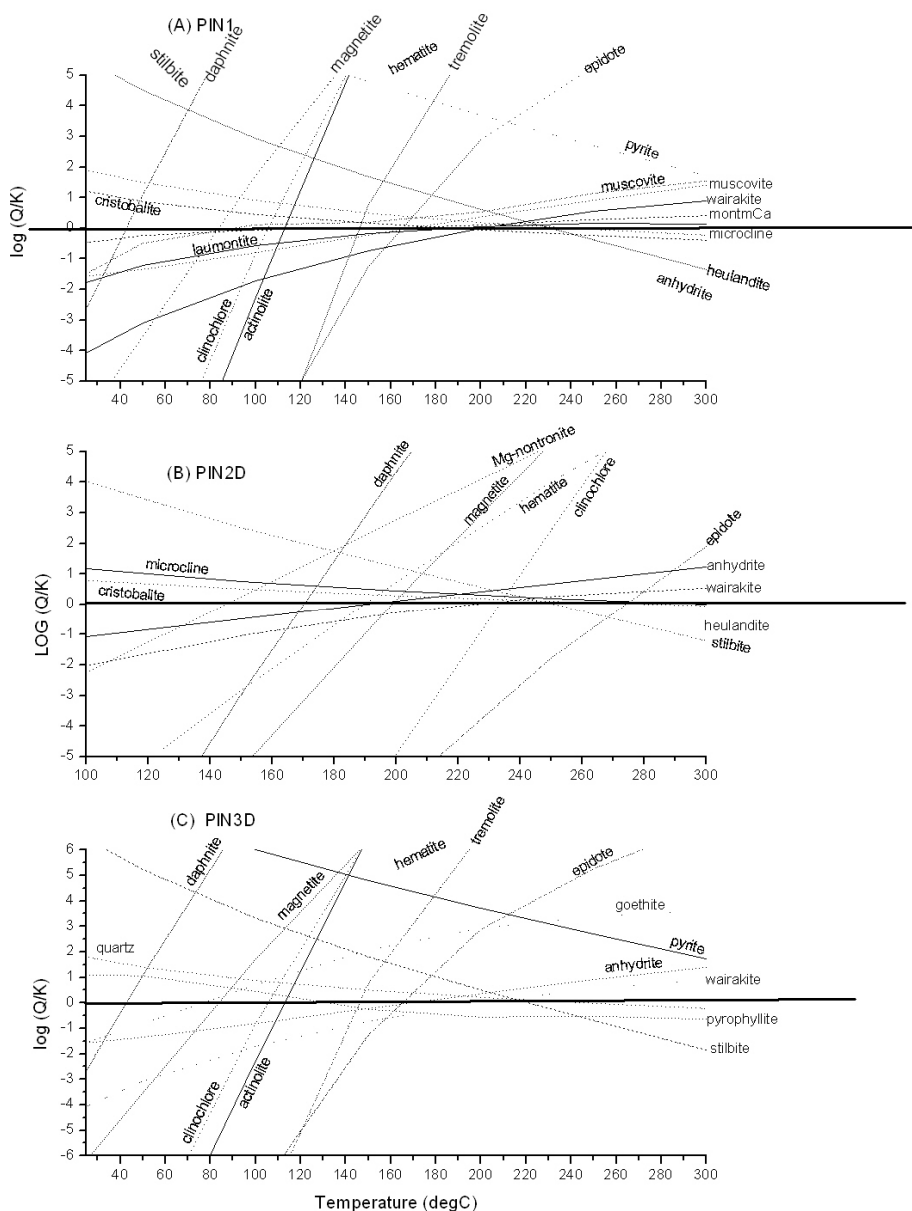


Figure 3 Log (Q/K) vs. temperature for water from Pinatubo wells (A) PIN 1, (B) PIN 2D and (C) PIN3D.

For the PIN 1 water the Na-K-Ca temperature (Fournier and Truesdell, 1973) for this water is 232°C while the measured temperature is 260°C. The Q/K plot (Figure 3a) indicates an equilibration temperature of about 200-230°C. Pyrite is saturated for the whole range of temperature. It appears that the equilibrium assemblage for PIN 1 may include K-spar, zeolite minerals like stilbite, heulandite, laumontite and possibly montmorillonite (Figure 3a). It apparently excludes epidote, muscovite, and Fe-bearing minerals like chlorites and the oxides. These minerals cross the zero log (Q/K) at lower temperature (160°C).

The maximum measured temperature for PIN 2D waters is 320°C while the calculated Na-K-Ca=267°C. The calculated pH at 300 is 4.96 while the degassed water has a very low pH of 2.32. Curves for some alteration minerals (epidote, cristobalite and K-spar) cluster around temperature of 280°C

(Figure 3b). Curves for most zeolite cross zero at 230° with clinocllore while hematite and anhydrite cross the zero Q/K at 190°C.

The Na-K-Ca temperature for PIN 3D is 275 °C and the maximum temperature is 320°C. The pH at 300°C is 5.41 compared to the pH of the degassed water at 25°C of 4.19. There is no clustering of curves for alteration minerals at the zero Q/K for this well (Figure 3C). The curves for epidote, and pyrophyllite cross the zero at 165 and 135 °C, respectively while clinocllore, together with actinolite at 100°C and daphnite and goethite at 40°C and 70°, respectively.

The possibility that the observed hydrothermal mineral assemblage was not formed by the present-day geothermal system was proposed by previous workers (Delfin et

al.,1996; Villarosa et al., 1989, Pagado and Villarosa, 1989; Pagado and Ramos, 1990) based on the overprinting of hydrothermal alteration and geochemical data. Modeling of mineral-fluid equilibria also supports this hypothesis. The first appearance of epidote in well cuttings and cores has been used as a geothermometer to gauge the temperature of the water (Reyes, 1990). It has been reported to indicate temperatures 200°C or more. The occurrence of epidote at temperatures 40° lower than the theoretical temperature of 200°C or more indicates it is not at equilibrium with the PIN 1D water. However, in the case of PIN 2D and PIN 3D, epidote seemed to be stable as its Q/K curve crosses the zero value near this temperature.

The supersaturation of the three wells with acidic minerals like pyrite and pyrophyllite (for temperatures lower than 130°C) also observed in the cores and cuttings, indicate that these minerals are at stable at the pH measured for the fluids and thus, may have been formed by the present-day system.

The spread of temperatures for the alteration minerals indicates that equilibrium between the minerals and the geothermal waters for PIN 2D and 3D was not attained, could be resulting from the postulated mixing of magmatic volatiles with the geothermal waters (Ruaya and others 1992). Delfin et al., (1996) also suggested the short-time between drilling and sampling of the discharge waters for PIN 2D and PIN 3D has to be considered in evaluating equilibrium in these wells.

CONCLUSIONS

Log (Q/K) plots for the Pinatubo geothermal waters revealed that the hydrothermal minerals observed in cores and cuttings have been partly formed by the present-day geothermal system and partly by earlier systems.

ACKNOWLEDGEMENTS

The authors would like to thank the National Institute of Geological Sciences, University of the Philippines, the Geothermal Division-Energy Development Corporation, Philippine National Oil Corporation for assess to data and samples. We are highly indebted to the Office of the Vice-Chancellor for Research and Development, University of the Philippines-Diliman for funding the research study.

REFERENCES

Delfin, F.G., Jr., 1984, Geology and geothermal potential of Mt. Pinatubo: Philippine National Oil Company, unpublished report, 36 p.

Delfin, F. G., Villarosa, H.G., Layugan, D.B., Clemente, V.C., Candelaria, M.R. and Ruaya, J.R. (1996). Geothermal Exploration of the pre-1991 Mt. Pinatubo Hydrothermal System, in Newhall,C.G and Punongbayan, R.S. (1996), Fire and Mud: Eruptions and Lahars of Mount Pinatubo, Philippines, University Of Washington Press, Seattle,

Fournier, R.O. and Truesdell, A.H. (1973). An empirical Na-K-Ca geothermometer for natural water: Geochim. Cosmochim. Acta., 37, 1255 - 1275.

Pagado, E.S. and Villarosa, H.G.A. (1989), Geology and Petrology of Well PIN-2D, Philippine National Oil Company, unpublished report.

Pagado, E.S. and Ramos, S.G. (1990), Geology and Petrology of Well PIN-3D, Philippine National Oil Company, unpublished report.

PNOC-EDC, 1990, Mt. Pinatubo resource assessment report: Philippine National Oil Company-Energy Development Corporation (PNOC-EDC) internal report, 46 p.

Reed, M.H. and Spycher, N. F. (1984). Calculation of pH and mineral equilibria in hydrothermal waters with application to geothermometry and studies of boiling and dilution: Geochim. Cosmochim. Acta, 48, 1479-1492.

_____ (1993). SOLTHERM: Data Base of Equilibrium Constants for Aqueous-Mineral-Gas equilibria.

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

Ruaya, J.R., Ramos, M.N. and Gonfiantini, R. (1992). Assessment of Magmatic Components of the Fluids at Mt. Pinatubo Volcanic Geothermal System, Philippines from Chemical and Isotopic Data. Rept. Geol. Surv. Japan No. 279, pp. 142-152.

Villarosa, H.G.A., Pagado, E.S. and Lapuz, R.G. (1989), Geology and Petrology of Well PIN-1D, Philippine National Oil Company, unpublished report.

Table 1. Selected chemical analyses of discharge and downhole waters from Pinatubo wells. Concentrations in milligrams per kilogram. (Modified from Delfin et al., 1996)

Well no.	PH (at 25°C)	Na	K	Ca	Mg	Fe	Cl	SO ₄	SiO ₂
PIN-1	5.04	5,417	531	92.2	206	114	8,778	1,532	418
PIN-2D	2.32	2,717	492	39.2	233	407	4,768	2,627	1,129
PIN-3D	4.19	17,400	3,540	2,207	133	525	37,760	500	1,660