Proceedings World Geothermal Congress 2015
Melbourne, Australia, 19-25 April 2015

Mt. Apo Acid Fluid Evolution: Exploring the Role of Rock Buffers in the Reservoir pH Changes with Time

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Keywords: Acidic Geothermal Fluids, Rock Buffer, Water-rock Interaction, Geochemical Modeling,

ABSTRACT

The Sandawa sector in the southeastern edge of the Mt. Apo Geothermal Project in the Philippines is characterized by geothermal fluids whose acidity has been increasing over time. This is pronounced in well KN2D wherein measured discharge pH at the wellhead dropped from 4-5 to 2.5 (at 20°C) after 12 years in production. The pH of the deep reservoir fluid feeding well KN2D has also declined from 6.1 to 4.7 based on SOLVEQ-XPT modelling of the discharge fluids to downhole conditions.

Geochemical evaluation of the discharge fluid shows that the surface acidity observed in Mt. Apo is due to HSO_4^- dissociation as the H_2SO_4-rich reservoir fluid ascends to the surface. The increase in acidity of the reservoir fluid, meanwhile, could be due to (1) the drawing in of more acidic fluids from deeper in the reservoir as a result of mass extraction, and (2) the loss of the buffering capacity of the exposed wall rock along fractures that have continuously conveyed the flowing acidic fluids since production began.

This study examines the likely role of rock buffers in the evolution of acidic fluids in Mt. Apo over 12 years of production. Rock titration of well KN2D fluid with host dacite rock is carried out using CHIM-XPT geochemical software and the modelled fluid chemistry is compared with the measured fluid chemistry of well KN2D in the last 12 years. Results show a close agreement of simulated rock-titrated fluid with actual historical data, indicating that water-rock reaction plays an important role in the evolution of acidic fluids in Mt. Apo.

1. INTRODUCTION

The Mt. Apo Geothermal Project (MAGP) is located at the northwestern flank of Mt. Apo. It is geographically divided into two production sectors, namely, Sandawa and Marbel. The Sandawa sector is characterized by reservoir fluid temperatures above 300°C and forms the upflow region of the geothermal resource. The hot fluid outflows laterally towards the Marbel sector where temperatures drop to 220-260°C.

Majority of the wells in MAGP discharge neutral fluids of pH above 5 but a few wells have shown acidic fluid discharges with pH ranging from 4.0 to as low as 2.5 (@20°C). One of these is well KN2D with downhole target towards Mt. Apo (Figure 1).

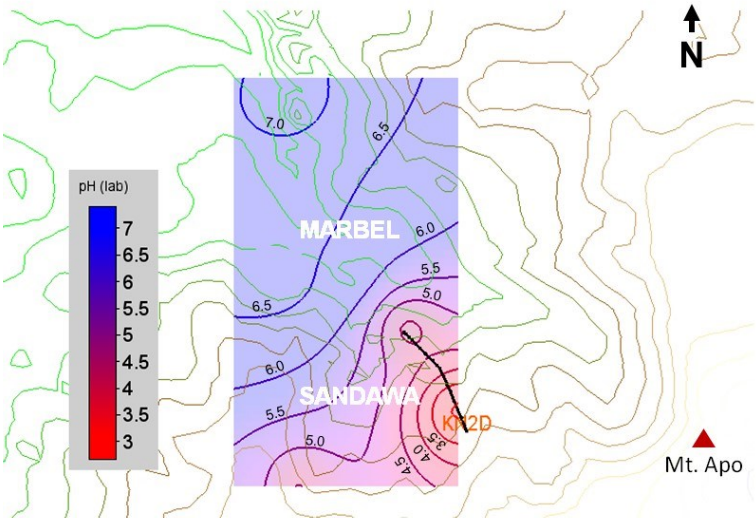


Figure 1: Field contour of discharge pH (measured at 20°C) of MAGP production wells. Acidic fluids (red) are located in the southeastern edge of the production field.

1.1 Geology and Petrology

The mineral alteration assemblage beneath KN2D indicates a linear relationship of temperature with depth based from the appearance of smectite to illite. The presence of secondary biotite and actinolite at the total depth penetrated by well KN2D suggests that the temperature is above 300°C. Temperatures predicted from mineral geothermometry were confirmed by initial downhole measurements wherein temperatures of 305-312°C were measured at the bottom of the well.

Well KN2D intersected a formation consisting of fresh to altered porphyritic andesitic-dacitic lavas, hyaloclastities and tuff breccias (Rosell, 1992). Beneath 1450 m depth, rocks are intensely or completely altered, as manifested by silicified, chloritized, or biotilized rock matrix. Among the notable minerals found in KN2D were quartz, epidote, dolomite, anhydrite, hematite, goethite, actinolite/tremolite, and biotite. Acidic assemblage consisting of relicts of diaspore, and pyrite were found at shallow depths of 800-1100 m, but a deeper acidic zone at 1900-2000 m with abundant pyrite was also identified.

1.2 Fluid Acidity

The acidity in Mt. Apo is primarily due to deep sulfuric acid (Salonga, 1996). This is evident in the high sulfate concentrations (600-3000 ppm) in wells with acidic discharges. HCl as contributing acid is ruled out as discharge Cl/Na+K ratio showed no excess in Cl ions (Fig. 2).

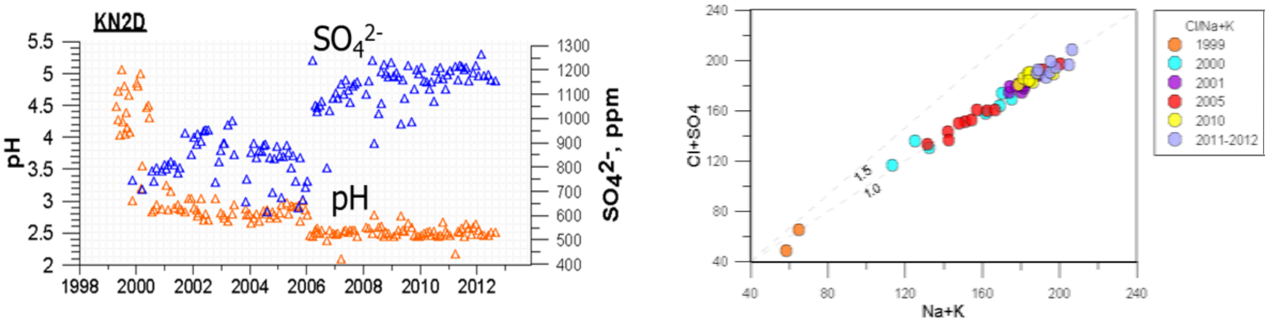


Figure 2: (Left) Well KN2D fluid pH (20°C) decreases with production, accompanied by a corresponding increase in SO_4. (Right) Molar ratio of major anions with major cations ($Cl+SO_4/Na+K$) is unity for KN2D, indicating no excess Cl.

Well KN2D has the lowest recorded fluid discharge pH among the producing wells in MAGP. During its initial discharge in 1999, its discharge fluids were only slightly acidic at pH of 4-5, but this dropped to 2.8 in 2000 and further to 2.5 since 2006. This drop in pH was mirrored by an increase in SO_4, suggesting direct correlation.

Geochemical simulation using SOLVEQ-XPT indicates that KN2D fluid is still near-neutral at the reservoir with pH of 4.7-6.1 (Figure 3). This is due to the weak dissociation of sulfuric acid at higher temperatures and pressures. As the fluid ascends to the surface, however, sulfuric acid readily dissociates into two hydrogen ions (H+) and one sulfate ion (SO_4^{2-}), effectively turning the fluid acidic.

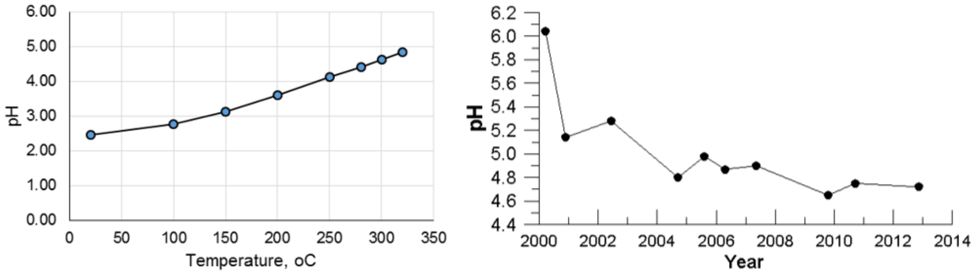


Figure 3: Geochemical modeling of KN2D using SOLVEQ-XPT. (Left) KN2D 2012 fluid pH (at 20°C) increases with temperature. (Right) Reservoir pH of KN2D based on quartz geothermometer decreases with time, from 6.1 in 2000 to 4.7 in 2012.

1.3 Rock Buffer Series

The pH drop in KN2D over time possibly suggests loss of the buffering capacity of reservoir rocks as deep acidic fluids are continually drawn in with production. Reed (1994) pointed out that rocks in contact with the acidic fluids neutralize these fluids through a series of buffers. The four (4) most significant of these are as follows:

The first in the series depends on alunite in a solution of concentrated sulfate:

$$8H^+{}_{(aq)} + \underset{\text{alunite}}{KAl_3(SO_4)_2(OH)_6} \leftrightarrow K^+{}_{(aq)} + 3Al^{3+}{}_{(aq)} + 2HSO_4{}^-{}_{(aq)} + 6H_2O_{(aq)} \; (1)$$

This buffer has a pH of 1.5 and prevails until K^+ is depleted by removal into alunite. The K^+ decline allows pH to increase to 2.4, where pyrophyllite precipitates, then buffers at 2.4 in concert with quartz and concentrated aqueous Al^{3+} according to the following equilibrium:

$$\underset{\text{pyrophyllite}}{Al_2Si_4O_{10}(OH)_2} + 6H^+{}_{(aq)} \leftrightarrow \underset{\text{quartz}}{4SiO_2} + 2Al^{3+}{}_{(aq)} + 4H_2O_{(aq)} \; (2)$$

The buffer capacity is consumed as Al^{3+} precipitates in pyrophyllite, allowing pH to increase until chlorite forms, establishing a buffer at pH 3.8 with pyrophyllite and quartz with concentrated aqueous Mg^{2+}:

$$10H^+_{(aq)} + \underset{\text{chlorite}}{Mg_5Al_2Si_3O_{10}(OH)_8} + \underset{\text{quartz}}{SiO_2} \leftrightarrow \underset{\text{pyrophyllite}}{Al_2Si_4O_{10}(OH)_2} + 5Mg^{2+}_{(aq)} + 8H_2O_{(aq)} \quad (3)$$

This buffer holds until aqueous Mg^{2+} is depleted allowing pH to rise until muscovite replaces pyrophyllite.

A propylitic assemblage that includes coexisting albite, microcline, quartz, and muscovite in the presence of a large sodium concentration buffers pH near 5.7 by the following equilibrium. This is the key propylitic assemblage buffer that established a propylitic pH in the neutral range under rock-dominated conditions.

$$\underset{\text{quartz}}{6SiO_2} + \underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_2} + 2Na^+_{(aq)} \leftrightarrow \underset{\text{microcline}}{KAlSi_3O_8} + \underset{\text{albite}}{2NaAlSi_3O_8} + 2H^+_{(aq)} \quad (4)$$

These buffer systems demonstrate that an increase in the pH of acidic geothermal fluids and consequent decline in major ionic species are expected under exposure with rocks. The series implies, however, that buffering only occurs to a certain level, and is a function of the area of exposure of unaltered rocks versus the fluid in contact, that is reflected in the w/r ratio. Continued and aggravated alteration of exposed rock surfaces theoretically decreases the buffering capacity of the rocks and would thus yield a resulting fluid of lower pH than otherwise possible for the same acidic source.

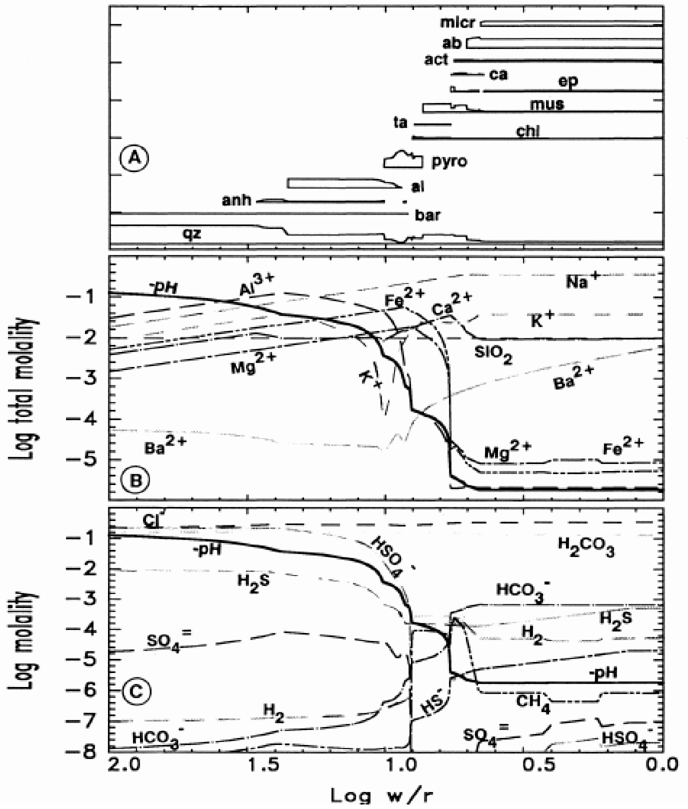


Figure 4: Sample calculation results for reaction of diluted acidic magmatic condensate with dacite. Plateaus in pH curve reflect mineral buffers (Reed, 1994)

2. GEOCHEMICAL MODELING

As suggested above, the decrease in the pH of KN2D fluid with time can be attributed to the loss of the buffering capacity of exposed rocks. This would imply that the recent fluid in KN2D is a "less buffered" version the 2000 fluid. To test this hypothesis, the recent KN2D fluid was reacted with a fresh (unaltered) dacite using the rock titration feature in CHIM-XPT. If the hypothesis is true, the resultant fluid would be similar to the KN2D fluid in 2000 at a certain water-rock ratio.

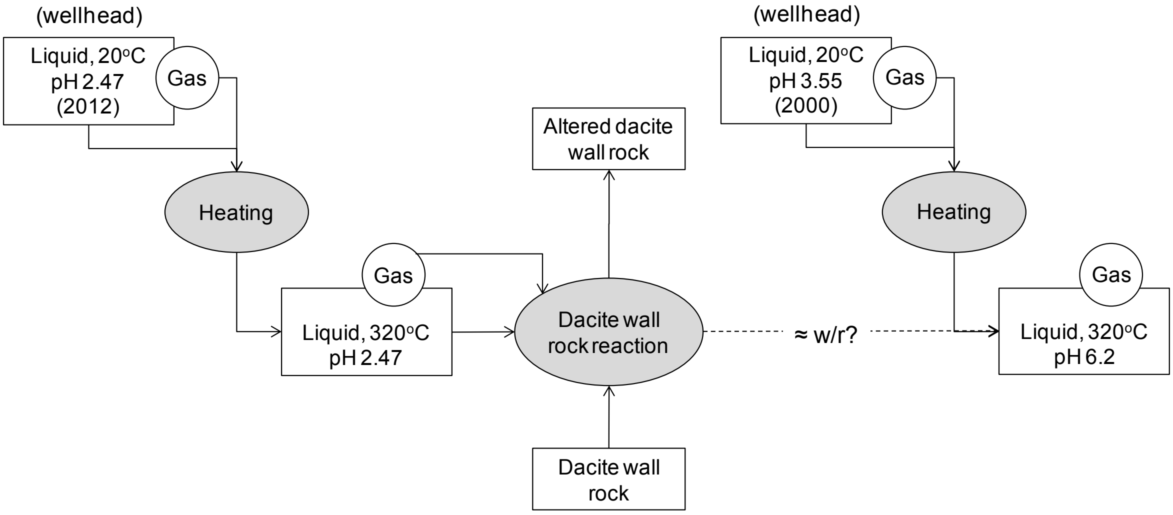


Figure 5: Schematic diagram showing the processes used in this model. Based on the working assumption that the Y2012 KN2D fluid is "less buffered", it is reacted with dacite wall rock to see if the resulting fluid would be comparable to the "more buffered" 2000 fluid at a certain w/r ratio.

The geochemical model is divided into two major processes, represented as shaded ellipses, in Figure 5: (a) heating and reconstruction of discharge fluid chemistry to downhole reservoir conditions, and (b) wall rock reaction of the reservoir fluid with fresh dacite rock. Because gas is an integral part of the buffer systems, especially in the reduction of sulfates to sulfides, it is imperative to react both liquid and gas components simultaneously with the rock.

2.1 Heating

KN2D multiphase equilibria at deep conditions were derived using SOLVEQ-XPT. The process involves completely re-dissolving the gas components back into the water in the assumption of a liquid-only reservoir fluid. In addition, FixAl method was introduced to compensate for the lack of Al analysis in the sampled water (Pang and Reed, 1997). The solution was then heated from 20°C to 350°C and the log Q/K graph plotted as shown in Fig. 6.

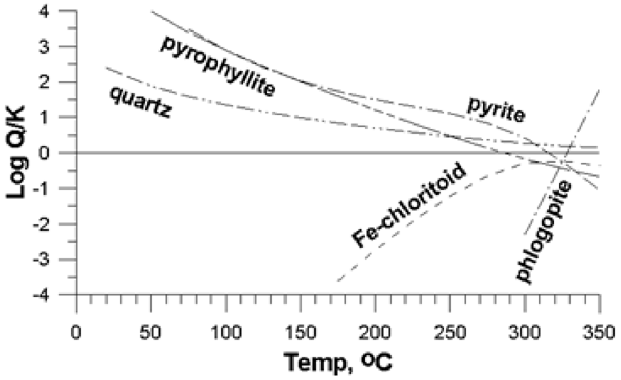


Figure 6: Mineral saturation plot with temperature of different minerals associated with well KN2D derived from geochemical simulation using SOLVEQ-XPT. The minerals converged at 320°C, signifying equilibrium at this temperature.

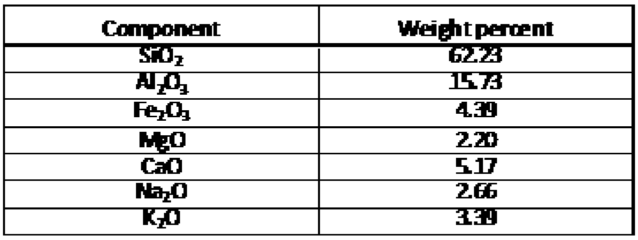
The actual observed minerals in KN2D core samples collected during drilling were the ones used in the log Q/K plot. However, some solid solution compositions, i.e. biotite, is not available in the soltherm database used for SOLVEQ-XPT, thus phlogopite is used instead. A similar argument is used for Fe-chloritoid which represents chlorite in the system.

2.2. Rock Titration

The derived equilibrated fluid at 320°C was used for the rock titration process. Rock titration is useful for elucidating the reactions involved in the formation of zoned alteration envelopes bordering the veins of rocks along a fluid flow path. The change in the composition of the bulk system is expressed as a function of the water/rock ratio, w/r, which is simply the ratio of the total amount of initial fluid to the total amount of rock titrated (Reed, 1994).

To model the reaction between KN2D fluid and its host rocks, the components of the rocks at the major permeable zone should be inputted. However, the rocks encountered at the production depth (1550-1650m) are already intensely altered, and cannot be used. While the remainder of the intersected formation consist of both andesite and dacite lavas, the closest "fresh" rock variety from the production zone is dacite. Thus, for this reaction, a whole rock analysis of a dacite rock sample from Mt. Apo was used (Table 1).

Table 1: Whole rock analysis of dacite rock sample from Mt. Apo (Corpuz, 1992).



Component	Weight percent
SiO_2	62.23
Al_2O_3	15.73
Fe_2O_3	4.39
MgO	2.20
CaO	5.17
Na_2O	2.66
K_2O	3.39

For the rock titration process, the minerals formed for every incremental addition of rock is retained to ensure that any change in the porosity is conserved. This is significant since a change in porosity would affect the buffering capacity of the rock. The resultant fluid is then compared with the equilibrated reservoir fluid in KN2D from 2000 to 2012 to examine the hypothesis.

3. RESULTS AND ANALYSIS

3.1. KN2D Fluid-Dacite Rock Reaction

Changes in the concentration of the aqueous species and the minerals formed during the rock titration process are plotted in Figure 7. The plot is read from left to right and aims to elucidate fluid chemistry changes with gradual loss of exposed fresh rock. At log w/r=1.0, dacite rock sample is moderately altered, corresponding to a propylitic alteration assemblage in contact with a neutral-pH fluid. At log w/r=4.0, fresh unaltered dacite rock is non-existent, and the fluid chemistry is simply the reservoir fluid chemistry of KN2D.

At low water-rock ratios, where rock dominates the reaction, the fluid is highly buffered at a neutral pH of 5.7-6.2. This buffering action extends even after two orders of magnitude of KN2D fluid has been added, forming a plateau in the fluid pH trend.

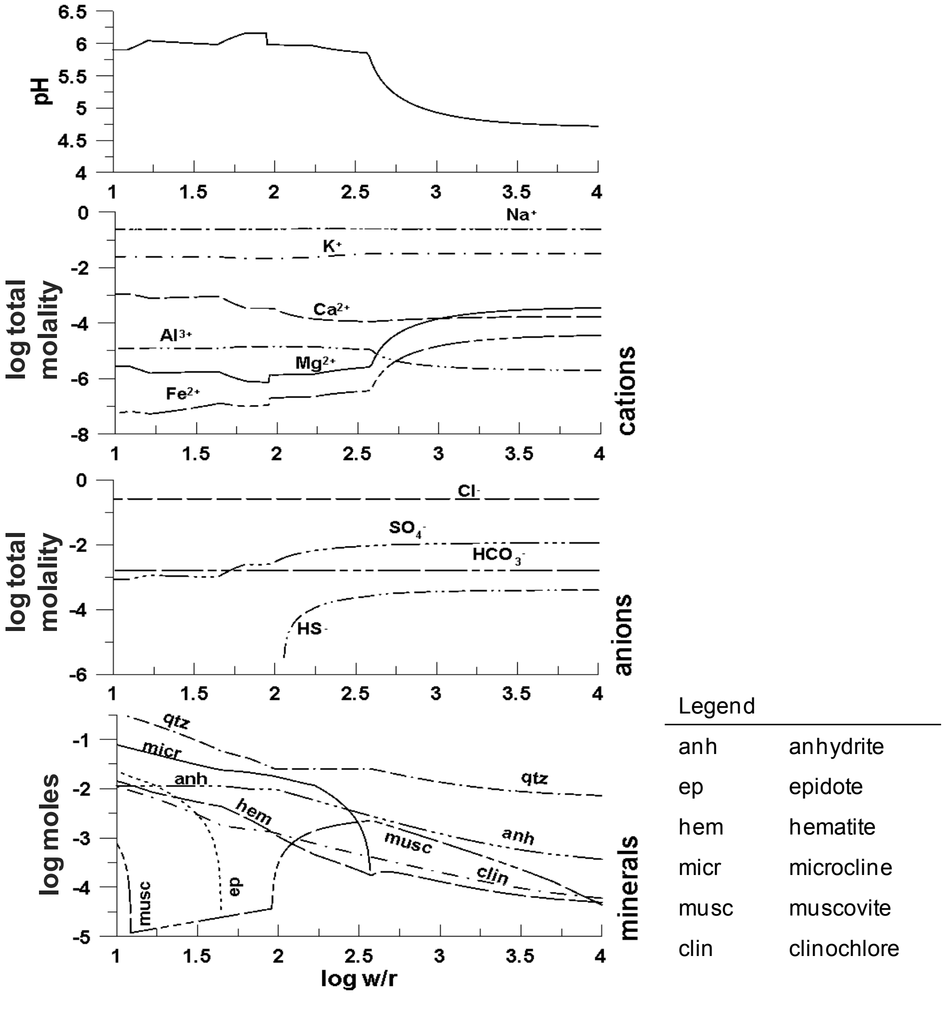


Figure 7: Rock titration of equilibrated KN2D fluid at 320°C with dacite rock using CHIM-XPT.

At this w/r ratio range, Ca^{2+} concentration decreases until log w/r = 2.5, but it stabilizes thereafter. Sulfate (SO4^{2+}), on the other hand, increases with increasing w/r while also stabilizing at log w/r ≅ 2.5. Na+ and K+ concentrations, which are naturally involved in water-rock interaction, remain stable and in relative excess to other aqueous species.

This strong buffer at pH 5.7-6.2 is due to the propylitic assemblage consisting of albite, microcline, quartz, and muscovite, which are the prevailing minerals at this pH level (Reed, 1994). The increase in H^+ as a result of higher w/r shifts the equilibrium assemblage to the left, favoring the formation of muscovite over microcline (eq. 4). At log w/r=2.5, microcline is finally consumed, but not without a corresponding increase in muscovite in the process (Fig. 7).

Beyond log w/r ≅ 2.5, this qtz-musc-micr buffer breaks down, and the pH starts to decrease exponentially, turning the fluid slightly acidic. This stage is marked by steep increases in the amounts of $Mg^{2+}$and Fe^{2+}, which indicates dissolution from the rock matrix, probably from chlorite and hematite. Al^{3+} concentration, on the other hand, shows a decreasing trend, which may suggest deposition into clay minerals.

Pyrite, which is found to be abundant at greater depths in the well, was absent in the results of the rock titration. Biotite, which is a high-temperature secondary mineral, was also absent, as well as phlogopite, which was initially used in its place during the SOLVEQ run.

3.2. Historical Matching

An overlay of pH, SO4, and Mg as representative species of the rock-titrated fluid with historical reservoir fluid data modeled from SOLVEQ-XPT is shown in Figure 8.

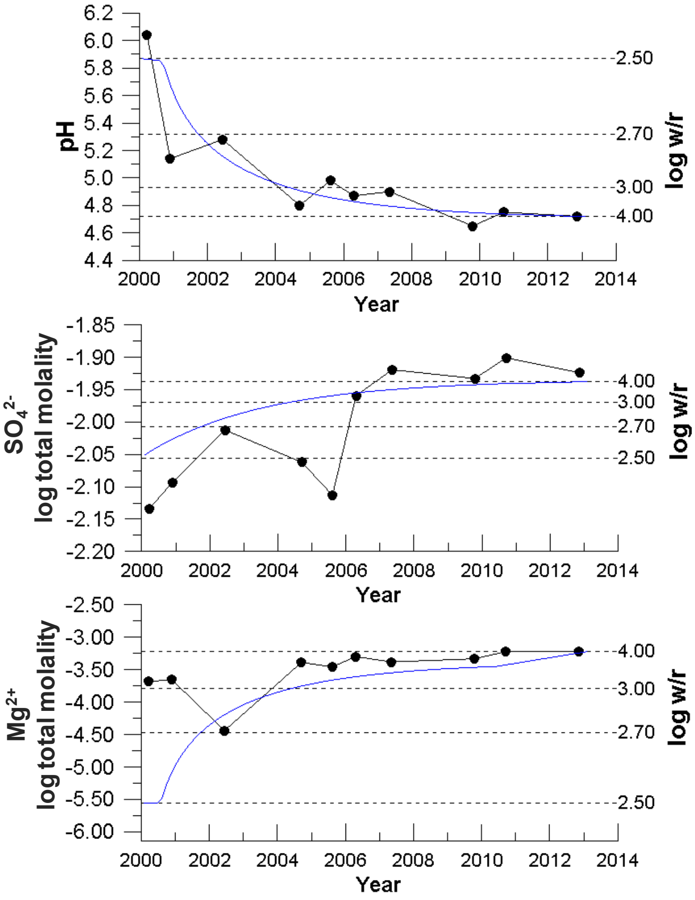


Figure 8: Plots of reservoir pH, SO4, and Mg concentrations with time show a general increase in w/r ratio from 2.5 to 4.0. Overlaying the rock titration curve over this w/r range (blue) showed closely similar trend with the historical data.

The decrease in the reservoir pH trend with time was modeled closely by the rock-titrated fluid, with log w/r ratio spanning from 2.5 to 4.0 from 2000 to 2012. This corresponds to 1.5 orders of magnitude of increase in the amount of fluid relative to the amount of unaltered rock.

Similarly, the reservoir trends of SO_4^{2-} and Mg^{2+} also matched with the fluid chemistry of the rock-titrated fluid for the same log w/r range of 2.5 to 4.0.

These plots support the hypothesis that the recent KN2D fluid is a by-product of the decrease in the amount of exposed fresh rock, which is expressed in the increase in w/r ratio with time. The near-neutral fluid in the initial discharges of KN2D in 2000, may then be a product only of the long undisturbed condition of the geothermal fluid prior to production which enabled the rock to completely buffer the already acidic fluid to near-neutral levels.

4. SUMMARY AND CONCLUSIONS

Geochemical software SOLVEQ-XPT and CHIM-XPT are useful tools in the study of reservoir fluid chemistry. It was determined that KN2D reservoir fluid pH has been declining with continued production, from 6.1 in 2000 to 4.7 in 2012. Results of rock titration of the most recent KN2D fluid with host dacite rock modeled this historical trend over an increasing w/r ratio from 2.5 to 4.0. This indicates that the observed decrease in reservoir fluid pH in Mt. Apo may be due to the decrease in the amount of exposed fresh rock, by alteration into secondary minerals, along the fluid flow path. These findings suggest that rock buffers, and water-rock interaction in general, play an important role in the evolution of acidic geothermal fluids in Mt. Apo.

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