

## Applications of Sulfur Isotopes in Characterizing the Acid Fluids at the Tiwi Geothermal Field, Philippines

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**Keywords:** Tiwi, sulfur isotope, stable isotope, acid sulfate, isotope geothermometry, makeup well drilling

### ABSTRACT

Development of the Bariis (Bar) sector of the Tiwi Geothermal Field has been hindered by production of acid fluids in the earlier drilled wells. However, the successful isolation of acid fluids in two Bariis wells during 2005 and 2008 has opened up the Bar sector and, in general, the southwestern portion of the field for deep make-up well drilling. Initial estimates suggest that this portion of the Tiwi Field can provide significant additional steam.

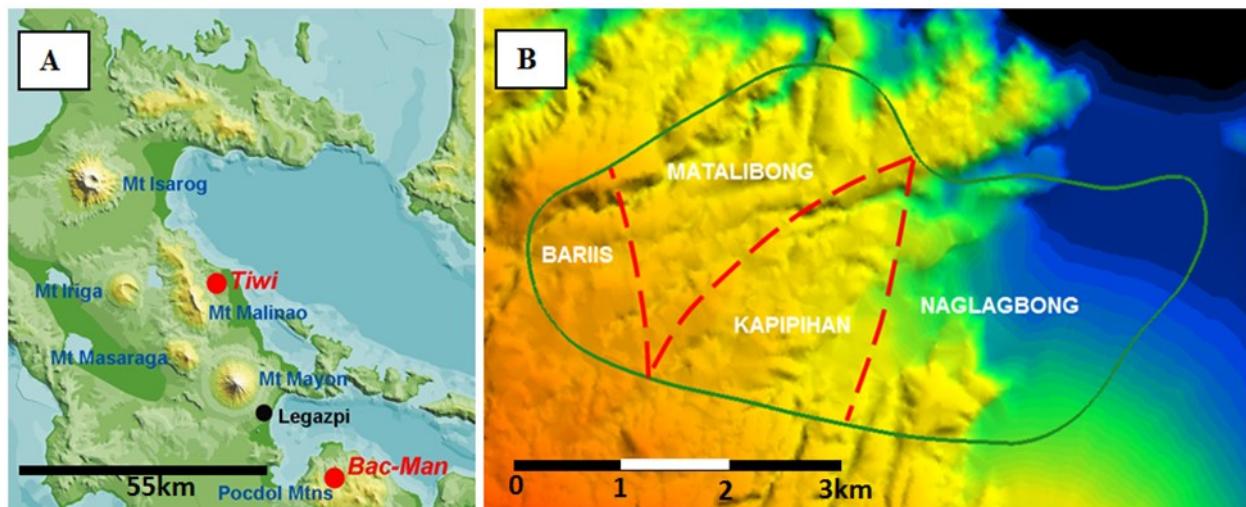
In preparation for the make-up well drilling in the Bar sector, a sulfur isotope study is being conducted to provide additional insight on the nature/origin of the Tiwi acid fluids. For this study, a total of 19 BaSO<sub>4</sub> ( $\delta^{34}\text{S}_{\text{SO}_4}$ ;  $\delta^{18}\text{O}_{\text{SO}_4}$ ) and 21 Ag<sub>2</sub>S ( $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ ) precipitates and 23  $\delta\text{D}_{\text{H}_2\text{O}}$ - $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  samples were collected from both neutral and known acid wells, including nine downhole liquid samples.

Results of the sulfur isotope study indicate a non-magmatic origin for the Tiwi acid fluids. The non-equilibrium in some fluids suggests shallow processes affecting the chemistry of the acid fluids. This implies that the risk of encountering deep acid in the target make-up well areas is low, except in the vicinity of the faults, which could act as a conduit for shallower acidic fluids to enter the deep reservoir.

The study also indicates potential use of  $\Delta$  ( $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ ) values in identifying higher temperature portions of geothermal. One of the difficulties encountered in the study, however, is the high pH values of samples from idle acid wells which hinders the full characterization of the acid fluids. It is thus recommended to attempt sampling acidic fluids in flowing wells going forward.

### 1. INTRODUCTION

The Tiwi Geothermal Field, with an area of about 12 square km, is a liquid-dominated and fracture-controlled geothermal field located on the lower flank of Mt. Malinao in Albay Province, Philippines (Figure 1A), ~350 km southeast of Manila. The field is divided into four geographic sectors: Naglagbong (Nag), Kapiuhan (Kap), Matalibong (Mat) and Bariis (Bar) (Figure 1B).



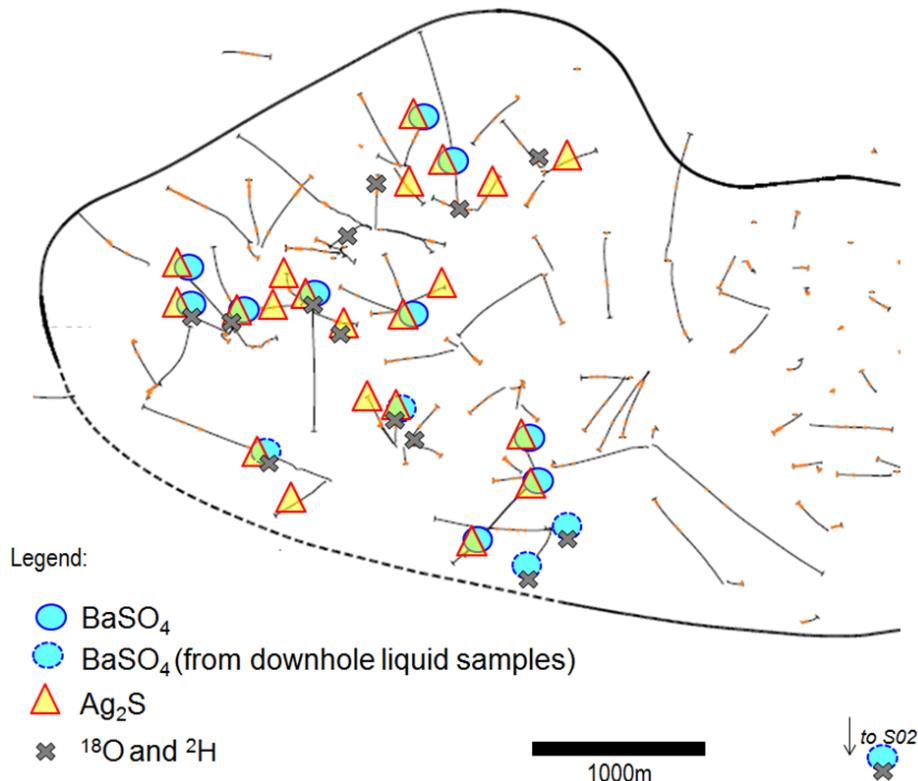
**Figure 1. A) Location map of the Tiwi Geothermal Field; B) Major Production Sectors of the Field.**

The Tiwi Field is currently producing ~140 MW (234 MW installed capacity) and being operated by the Philippine Geothermal Production Company, Inc. (PGPC). Details of the development history of Tiwi Field have been discussed in earlier papers, e.g. Alcaraz, *et al.*, 1989; Gambill and Beraquit, 1993; Sunio, *et al.*, 2005; Menzies, *et al.*, 2009.

The hydrologic model of the Tiwi reservoir includes two major upflow zones of neutral-chloride fluids located within Bariis (temperature up to 350°C) and South Kapiuhan (SoKap) (temperature up to 310°C) areas and a minor upflow in the southern Naglagbong area (Sunio *et al.*, 2005). The Bar and SoKap sectors will be the main target areas for the proposed future make-up

drilling in Tiwi. One of the key drilling risks in Bar and SoKap is the production of acid-sulfate fluids since most of the earlier wells drilled in these areas produced acid fluids. However, drilling in 2005 and 2008 showed that the acid fluids in Bar can be successfully isolated to produce from the deep hot and neutral liquid reservoir.

The primary goal of this study is to explore the use of sulfur isotopes in identifying the origin of the Tiwi acid fluids. A total of 19  $\text{BaSO}_4$  ( $\delta^{34}\text{S}_{\text{SO}_4}$ ;  $\delta^{18}\text{O}_{\text{SO}_4}$ ) and 21  $\text{Ag}_2\text{S}$  ( $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ ) precipitates and 23  $\delta\text{D}_{\text{H}_2\text{O}}-\delta^{18}\text{O}_{\text{H}_2\text{O}}$  samples were collected from both neutral and known acid (idle) wells, including nine downhole samples. Sampling for  $^{34}\text{S}$  in dissolved sulfate in liquid samples was done by adding  $\text{BaCl}_2$  solution to the liquid samples to form  $\text{BaSO}_4$  precipitates while sampling for  $^{34}\text{S}$  in  $\text{H}_2\text{S}$  was done using  $\text{AgNO}_3$  solution to absorb the  $\text{H}_2\text{S}$  gas to form  $\text{Ag}_2\text{S}$  precipitates. Figure 2 shows the sampling locations. It is important to note that most of the wells that have acid fluids are currently idle and the samples analyzed for isotopic composition were collected during non-flowing conditions (including downhole liquid samples).



**Figure 2. Tiwi Map Showing the Sampling Locations.**

## 2. OCCURRENCE OF ACID-SULFATE FLUIDS IN TIWI

Acid-sulfate fluids were encountered in numerous exploration and development wells in Tiwi. Sugiaman, *et al.* (2004) characterized the acid-sulfate fluids as being cooler and more dilute than the upflow fluids. The occurrence of acid fluids and the models generated to explain the origin of the acid fluids were compiled by Stimac (2000).

During the early development of the eastern portion of the Tiwi Field, it was noted that some of the wells that produced acid fluids were located near the Tiwi Fault (Rohrs, 1983) suggesting structural controls while Golla (1996) and Buban (2000) suggested that the spatial distribution of the wells could be related to the Takla Fault (Figure 3). It was also noted that these wells have advanced-argillic alteration intervals, although not all the wells with this type of alteration were corrosive and the zones of acid alteration were associated with intervals of recurring wellbore scale. The wells that are currently affected by acid fluids are concentrated primarily in the southern portion of the field (Figure 3), as the eastern Nag wells that originally produced acid fluids have ceased to flow.

Crisostomo, *et al.* (2014) also revisited the distribution of acid fluids in Tiwi and noted that most of the producing acid zones are located above -1100m elevation. This finding is consistent with Sugiaman, *et al.* (2004), where it was noted that the acid-sulfate fluid in the Tiwi reservoir is restricted to thin layers at depths between 500 and 750m bsl.

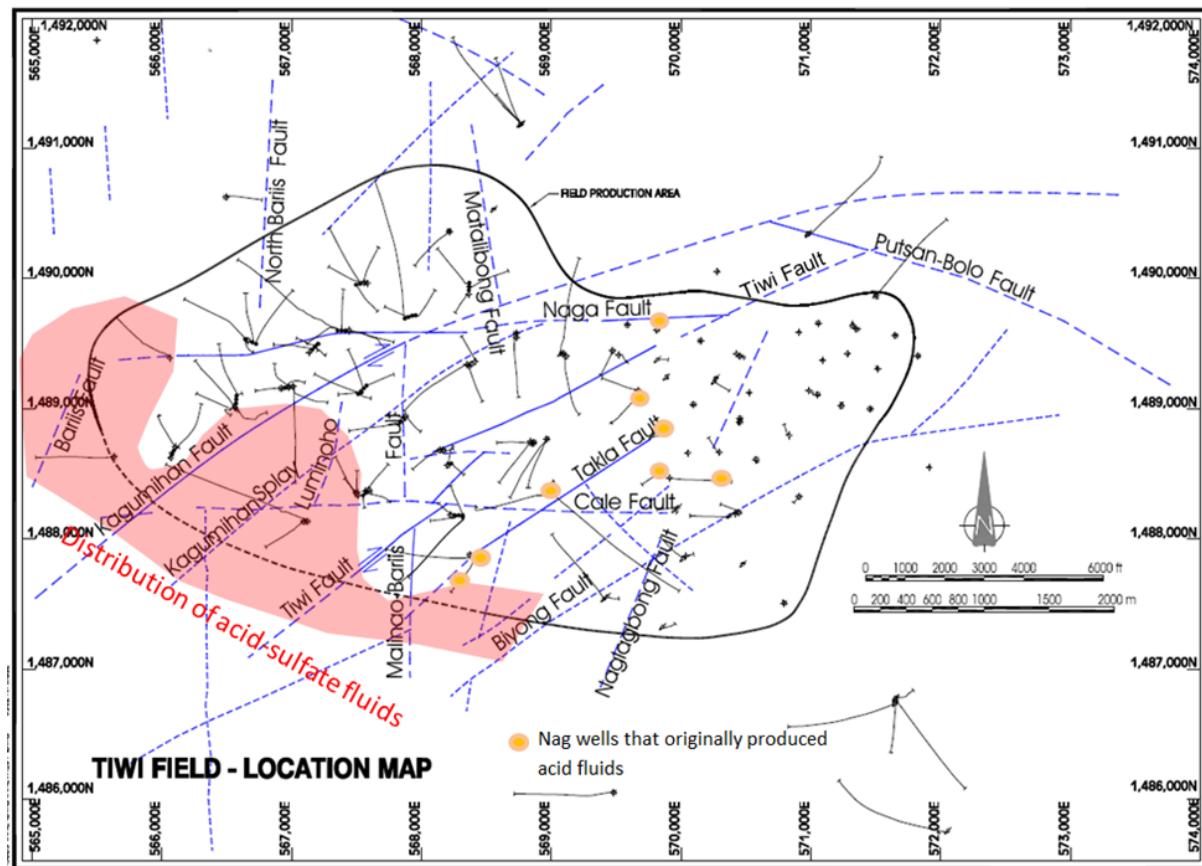


Figure 3. Current Distribution of Tiwi Acid-Sulfate Fluids.

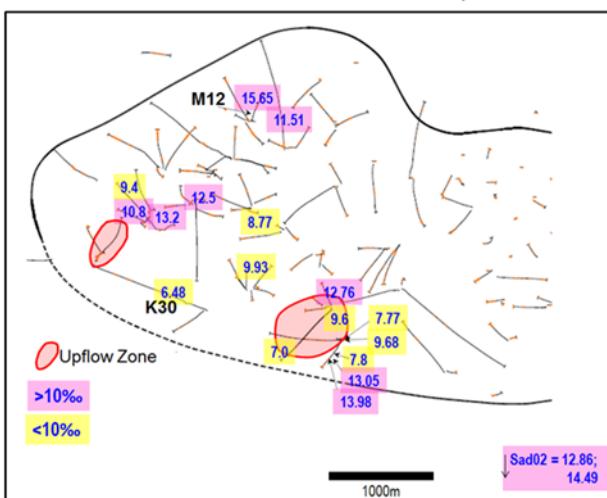
### 3. ISOTOPE SPATIAL DISTRIBUTION

Sulfur isotopes have been successfully used in other geothermal fields to determine the genesis of the acid fluids (e.g. Cortecci, *et al.*, 2005; Ferrer, *et al.*, 2005; Taguchi, *et al.*, 2003; Matsuda, *et al.*, 2005; Salonga, *et al.*, 2000). The spatial distribution of sulfur isotopes ( $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$ ) is normally compared with  $\text{SO}_4$  and  $\text{H}_2\text{S}$  concentrations to determine if the two data sets are consistent with each other.

#### 3.1 $\delta^{34}\text{S}_{\text{SO}_4}$ vs. $\text{SO}_4$ Distribution

The measured  $\delta^{34}\text{S}_{\text{SO}_4}$  ranges from 6.48 to 15.65‰ (Figure 4). The highest  $\delta^{34}\text{S}_{\text{SO}_4}$  was observed in an idle acid well in Mat (Mat-12) while the lowest value was measured in an idle acid well in SoKap (Kap-30). The  $\delta^{34}\text{S}_{\text{SO}_4}$  in the vicinity of the upflow zones vary widely with some wells in the upper end of the range (~12-14‰) and others having lower  $\delta^{34}\text{S}_{\text{SO}_4}$  values at 7.0 - 9.6‰ (Figure 4).

$\delta^{34}\text{S}_{\text{SO}_4}$  Distribution Map



$\text{SO}_4$  Distribution Map

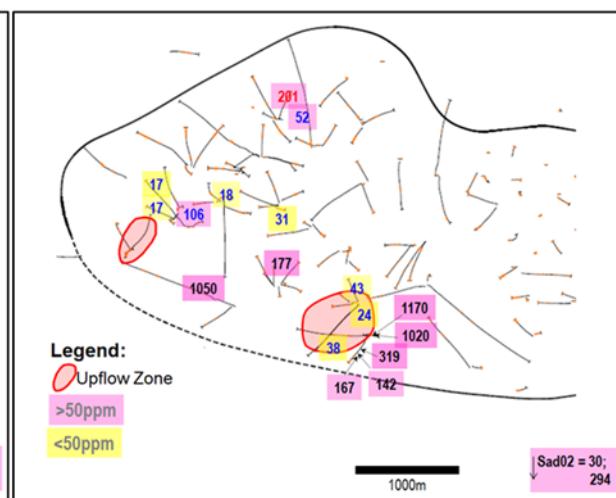


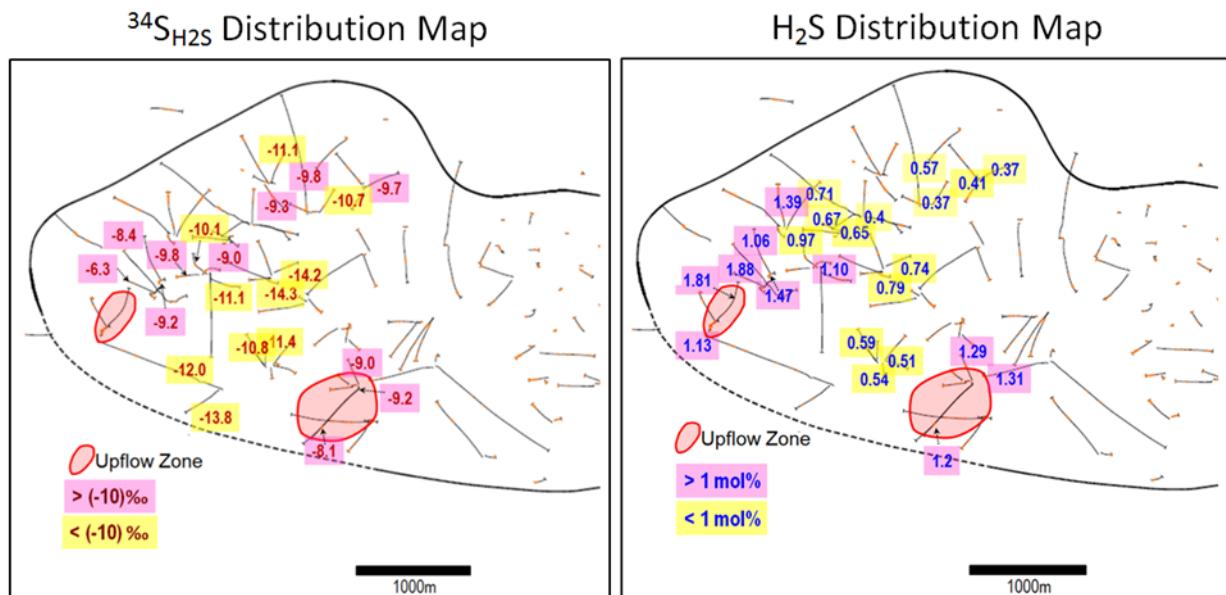
Figure 4. Spatial Distribution of  $\delta^{34}\text{S}_{\text{SO}_4}$  vs.  $\text{SO}_4$ .

The  $\text{SO}_4$  concentrations vary from ~20 to >1000 ppm (Figure 4). It should be noted that the very high  $\text{SO}_4$  (>1000ppm) values were obtained from the idle acid wells where  $\text{SO}_4$  may have been concentrated through cycling of the steam condensate.

### 3.2 $^{34}\text{S}_{\text{H}_2\text{S}}$ vs. $\text{H}_2\text{S}$ Distribution

The distribution of  $\text{H}_2\text{S}$  in steam at Tiwi seems to correlate with temperature. In Figure 5, areas with  $>1.0$  mol. %  $\text{H}_2\text{S}$  in the gas are related to the upflow regions while areas with  $<1.0$  mol. % are related to the outflow or cooler regions. The cooler regions are either areas affected by marginal recharge (e.g. tritiated waters or injectate) or areas with shallow entries.

The spatial distribution of the  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  is similar to the  $\text{H}_2\text{S}$  distribution. The three highest  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  values (-6.3, -8.4 and -8.1‰) were measured in wells near known upflow areas while the more depleted samples are seen in the cooler areas.

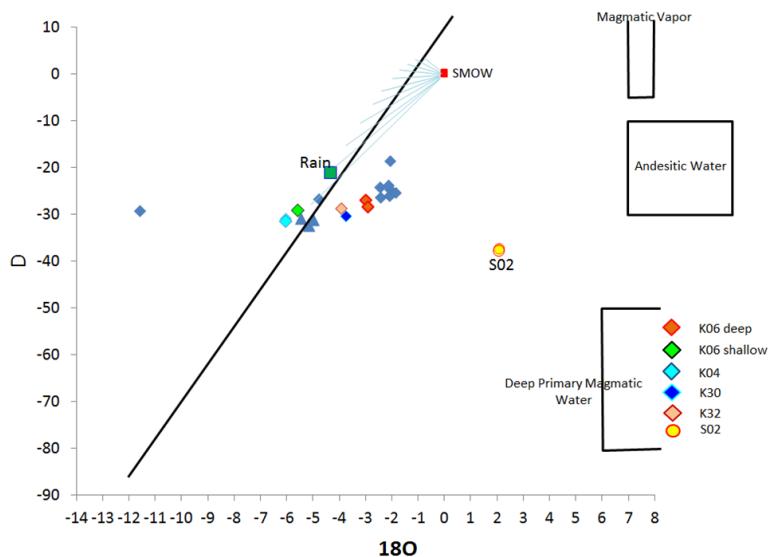


**Figure 5. Spatial Distribution of  $^{34}\text{S}_{\text{H}_2\text{S}}$  vs.  $\text{H}_2\text{S}$ .**

### 3.3 Stable Isotopes

Figure 6 illustrates the stable isotope composition of selected Tiwi wells. Significant  $\delta^{18}\text{O}$  enrichment is observed in the Sadurong sample (S02), an idle acid well located outside the Tiwi reservoir. It plots toward the region in the graph that represents magmatic water. The high chloride content ( $>3000$  ppm) of this well might be a signature of an acid sulfate-chloride fluid. At present, it is not clear whether this acid liquid is related to or has a similar origin to the acid liquids within the Tiwi reservoir boundary.

The other idle acid wells in the southern portion of the field (Kap-06 shallow and Kap-04) show lighter isotopes, i.e. plotting on the left-side of the meteoric water line. Considering that both wells have been idle for a long period of time, their stable isotope chemistry is consistent with a steam condensate that has been cycling in an idle well although the  $\sim 3500$  ppm chloride of the Kap-06 shallow fluid (Figure 7) indicates that it is not a steam condensate.



**Figure 6. Plot of  $^{18}\text{O}$  vs. Deuterium of Selected Tiwi Samples.**

### 3.4 Isotope Geothermometry

Sulfur isotope fractionation between dissolved  $\text{SO}_4$  and  $\text{H}_2\text{S}$  has found much use in assessing reservoir temperatures in geothermal systems Seal (2006). In Tiwi, two well samples are nearest to the  $\delta^{34}\text{S}_{\text{H}_2\text{S}} - \delta^{34}\text{S}_{\text{SO}_4}$  equilibrium line: Mat-12 and Bar-05 (Figure

7A). This suggests that their sulfur isotopic geothermometry could be valid. The cooler temperature ( $\sim 200^{\circ}\text{C}$ ) of Mat-12 is consistent with the known lower temperature recharge fluids (e.g. tritiated groundwater and/or injectate) while the hotter temperature ( $250^{\circ}\text{C}$ ) of Bar-05 is consistent with its location close to the upflow region (Figure 7B).

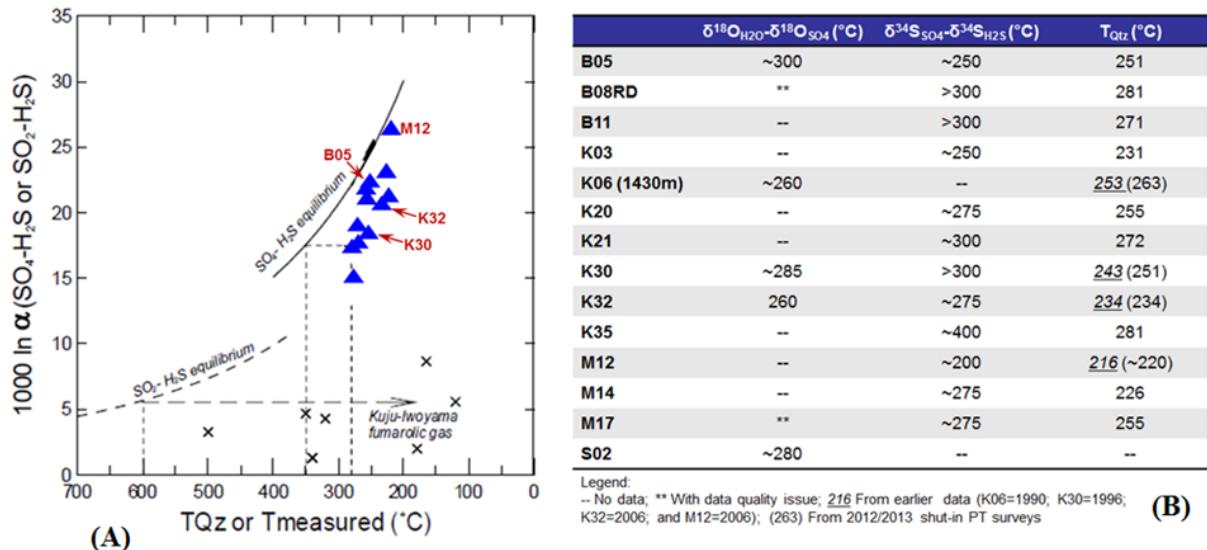


Figure 7. A) Sulfur Isotope Fractionation Factors Between  $\text{SO}_4$  (or  $\text{SO}_2$ ) and  $\text{H}_2\text{S}$  vs.  $T_{\text{Qz}}$  (or measured T) (modified from Matsuda, *et al.*, 2005). B) Summary Table of Geothermometry Temperatures.

#### 4. GENESIS OF ACID SULFATE FLUIDS IN TIWI

Historically, three different types of acid-sulfate fluids have been identified in Tiwi field: (1) low-pH liquid with dilute chloride (<100 ppm) and elevated sulfate (>400 ppm); (2) low-pH liquid with high chloride (3100 ppm) and variable sulfate and (3) low-pH liquid with very high chloride (>7000 ppm) and high sulfate (200 ppm). The first type of acid fluid was encountered in a down-flowing well in the Mat area. The well was suspended in 2009, hence no sample was obtained for the sulfur isotope study. The second and third types of acid fluids correspond to the southern acid and North Mat acid fluids, respectively.

The North Mat acid fluid, represented by Mat-12, is characterized by very high-chloride fluids (>7000 ppm). It plots similarly to Sad-02 in the  $\delta^{18}\text{O}_{\text{SO}_4}$  -  $\delta^{34}\text{S}_{\text{SO}_4}$  cross plot (Figure 8) and appears to be close to equilibrium with respect to  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  and  $\delta^{34}\text{S}_{\text{SO}_4}$  equilibrium (Figure 7A). Stable isotope chemistry of Mat-12 is, unfortunately, not available for this study. As shown in Figures 10 and 11, the shift to heavier  $\delta^{18}\text{O}_{\text{SO}_4}$  and  $\delta^{34}\text{S}_{\text{SO}_4}$  in Mat-12 is probably due to mixing with low-temperature, high  $\delta^{34}\text{S}_{\text{SO}_4}$ , res-Cl and res- $\text{SO}_4$  fluids. In the Hatchobaru Geothermal Field, sulfuric acid fluids in the northern portion of the field is attributed to  $\text{H}_2\text{S}$  oxidation from the reaction with air dissolved in wastewater re-injected close to the production area (Matsuda, *et al.*, 2005). However, in Mat-12, the high  $\text{SO}_4$  (~200 ppm) could not have originated from injectate (~40 ppm  $\text{SO}_4$ ). This implies that the majority of its  $\text{SO}_4$  come from other sources (e.g. localized dilute acid fluids in North Mat or acid fluids from the southern portion of the field).

The southern acid fluids, on the other hand, are represented by Kap-06, Kap-30, Kap-32 and Sad-02. The idle acid wells within the Tiwi reservoir (Kap-06, Kap-30 and Kap-32) show lower  $\delta^{34}\text{S}_{\text{SO}_4}$  values (Figure 8) and lighter stable isotopes (Figure 6) compared to the Sadurong acid fluid (Sad-02), which is found outside the Tiwi reservoir. The lighter stable isotopes of the wells within the Tiwi reservoir may indicate less water-rock interaction compared to Sadurong sample. This is corroborated with the lower  $\delta^{34}\text{S}_{\text{SO}_4}$  of the wells found within the reservoir suggesting that the  $\delta^{34}\text{S}$  of the  $\text{H}_2\text{S}$  has been retained, hence less equilibrated compared to Sad-02. Also, the wells found within the reservoir plot off the  $\text{SO}_4\text{-H}_2\text{S}$  equilibrium curve indicating partial or non-equilibrium. The Sad-02 samples show a distinct isotopic character with heavy  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  (~+2.1 per mil) (Figure 6) and  $\delta^{34}\text{S}_{\text{SO}_4}$  (12.86 and 14.49 per mil) (Figures 4 and 8).

The isotopic signatures of Sad-02 may suggest possible magmatic origin, however, it may not be the case for the samples collected within the Tiwi reservoir. Note that none of the stable isotopes from the Tiwi reservoir plot close to magmatic composition (Figure 6), unlike the Sadurong samples. In addition, none of the isotope values from wells within the Tiwi reservoir is either equal or near to zero suggesting that the fluid does not directly originate from a magmatic source (Cortecci, *et al.*, 2005 and Ferrer, *et al.*, 2005). All the samples obtained from the Tiwi reservoir also plot close to the  $\text{SO}_4\text{-H}_2\text{S}$  equilibrium curve on the  $\Delta(\text{SO}_4 \text{ or } \text{SO}_2 \text{ - H}_2\text{S})$  vs.  $T_{\text{Qz}}$  or measured temperature plot (Figure 7) and not on the  $\text{SO}_2 \text{ - H}_2\text{S}$  equilibrium curve. The observed non-equilibrium of some fluids, i.e., plotting away from the equilibrium curve (Figure 7), may indicate shallow processes or an immature origin. Another argument against magmatic origin for the samples within the Tiwi reservoir is that the maximum temperature of the sulfur-rich fluids in Tiwi ( $\sim 290^{\circ}\text{C}$  or  $\sim 1280\text{kJ/kg}$ ) (Figure 10) is well below the temperatures at which the hydrolysis of  $\text{SO}_2$  occurs, e.g.  $\sim 350\text{--}500^{\circ}\text{C}$  (Matsuda, *et al.*, 2005).

In terms of isotope values, the Tiwi sulfur isotopes would be categorized under the “transition group” using Ferrer, *et al.* (2005) classification of sulfur isotopes. The “transition group” has sulfate ratios between  $0\text{‰} > X > 15\text{‰}$  and is most likely produced by mixing of the deep,  $\delta^{34}\text{S}_{\text{SO}_4}$ -enriched fluid and the shallow  $\delta^{34}\text{S}_{\text{SO}_4}$ -depleted water (e.g. thermal features and steam condensates). Ferrer, *et al.* (2005) classification is based on the results of their study of four geothermal fields in the Philippines (Palinpinon, Mahanagdong, Mt. Apo and Bacon-Manito).

The downhole samples collected from Kap-06 may provide insights on the isotopic signature of mixed shallow dilute acid and neutral brine for Tiwi field. The three samples from Kap-06 represent two deep samples collected at 960m MD and 1430m MD, and a shallower sample at 350m MD. The relationship between Cl and SO<sub>4</sub> is consistent with the shallow sample having a higher component of acidic fluids (more dilute Cl and higher SO<sub>4</sub>) and the deep samples having a higher component of neutral reservoir brine (higher Cl and lower SO<sub>4</sub>) (Figure 9). The pH values are not consistent with this relationship and the plausible explanation for the inconsistency in the pH is that Kap-06 has been idle for over 20 years, hence its pH may have been neutralized after a long period of shut-in. On the δ<sup>34</sup>S<sub>SO4</sub> - δ<sup>18</sup>O<sub>SO4</sub> plot (Figure 9A), the shallow sample shows lighter δ<sup>34</sup>S and heavier δ<sup>18</sup>O compared to the deep samples. Stable isotope of the Kap-06 shallow sample is also lighter (plots on the left-side of the Meteoric Water line) compared to the deep samples (Figure 6). The lighter stable isotopes and δ<sup>34</sup>S<sub>SO4</sub> of the Kap-06 shallow sample are consistent with near surface processes. The Kap-06 shallow isotopic signatures can probably be used a representative of mixed shallow acid-sulfate fluid and neutral brine.

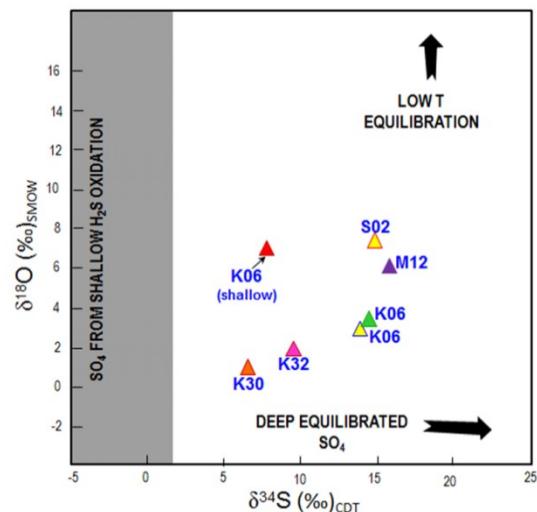


Figure 8. δ<sup>34</sup>S vs. δ<sup>18</sup>O Plot of Selected Tiwi Wells.

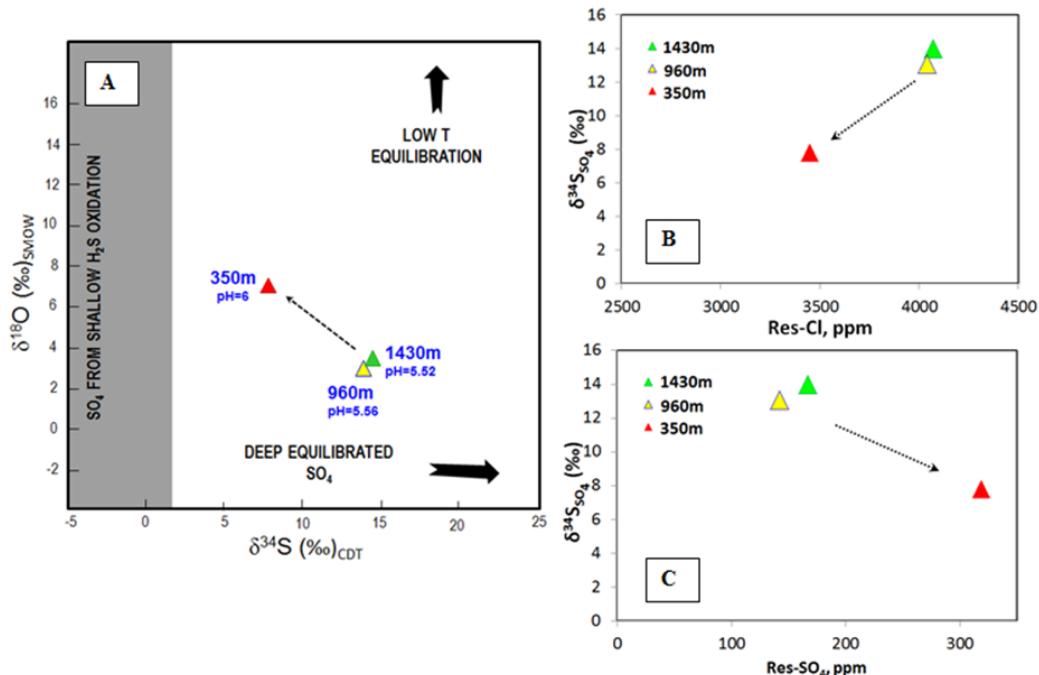


Figure 9. Kap-06 Shallow vs. Deep Samples. (The shallow Kap-06 sample A) shows a shift to lower δ<sup>34</sup>S and higher δ<sup>18</sup>O; B) more dilute res-Cl, and C) higher res-SO<sub>4</sub> compared to the deep samples.

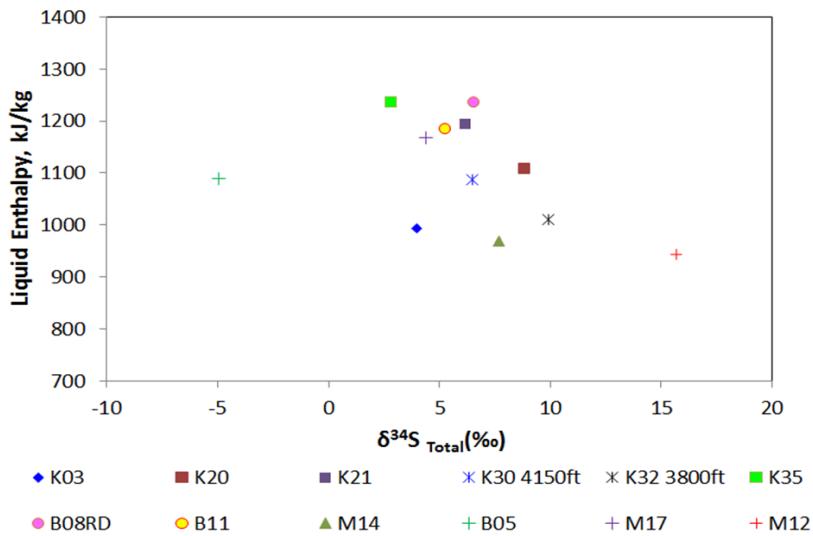


Figure 10. Cross Plot of  $^{34}\text{S}_{\text{Total}}$  vs. Liquid Enthalpy.

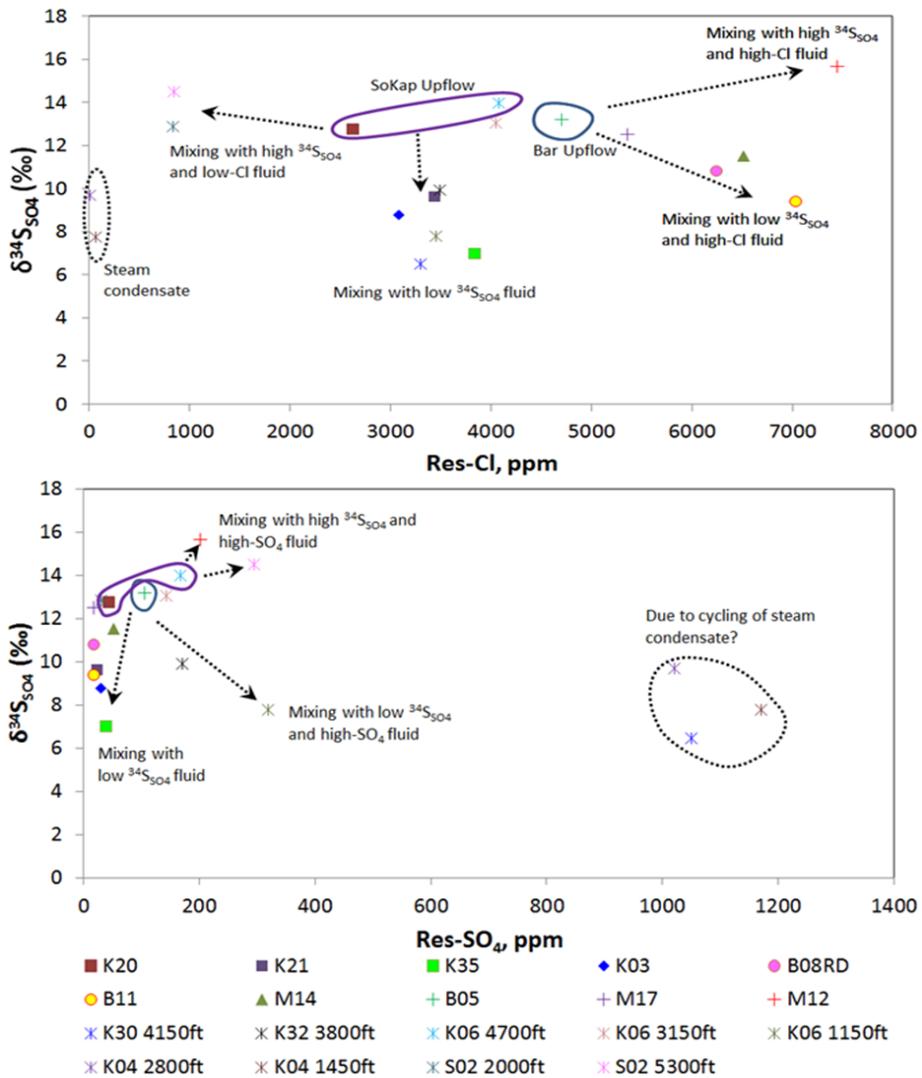


Figure 11. Cross Plots of  $^{34}\text{S}_{\text{SO}_4}$  vs. res-Cl and res- $\text{SO}_4$ .

## 5. IMPLICATIONS ON MAKE-UP WELL TARGETING IN SOUTHERN TIWI

The sulfur isotope study reveals that the Tiwi acid fluid has a non-magmatic origin, which indicates it is influenced by shallow processes, as detailed in section 4. This implies that the risk of encountering deep acid in the target make-up well areas is low, except in the vicinity of the faults, which could act as a conduit for shallower acidic fluids to enter the deep reservoir.

Moreover, the geothermometry temperatures from the sulfur and oxygen isotope pairs from  $\text{SO}_4$  of the neutral wells show significantly higher temperatures than  $T_{\text{Qtz}}$  (or measured temperatures) consistent with the existence of deep hotter fluids in the Bar and SoKap sectors. This validates the current Tiwi make-up well targets which are mainly the deep Bar and SoKap areas.

## 6. CONCLUSIONS AND RECOMMENDATIONS

Based on available Tiwi sulfur isotope data, it is believed that the Tiwi acid fluid has a non-magmatic origin. The non-equilibrium observed in some fluids may indicate shallow processes as the origin of the acid fluids. In terms of make up well drilling, this provides additional justification for drilling deep in Bar and SoKap. The geothermometry data also shows that a couple of wells reached near equilibrium with respect to  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{34}\text{S}_{\text{H}_2\text{S}}$  suggesting a future utility of  $\Delta(\delta^{34}\text{S}_{\text{SO}_4} \text{ and } \delta^{34}\text{S}_{\text{H}_2\text{S}})$  in identifying higher temperature portions of geothermal reservoirs.

However, one of the difficulties encountered in the study is the variable sulfate and sulfur isotope signatures of wells that previously produced acidic fluids complicated by processes associated with the wells being idle and no longer being productive. Confirmation of acid fluid chemistry was hindered by high pH values from these downhole samples. It is recommended to attempt sampling acidic fluids in flowing wells in the future. Sampling and analysis of sulfur isotopes from the whole-rock and alteration minerals is also suggested to decipher the evolution of sulfur isotopes in Tiwi.

## ACKNOWLEDGEMENTS

The authors would like to acknowledge the approval and encouragement provided by Philippine Geothermal Production Company and Chevron Geothermal Services Company to prepare and publish this paper.

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