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THE IMPLICATION OF ^{34}S AND ^{18}O ISOTOPE SYSTEMATICS ON THE SULFUR CYCLE IN MAHANAGDONG HYDROTHERMAL SYSTEM (PHILIPPINESS)

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ABSTRACT

The study of ^{18}O and ^{34}S stable isotopes in fluid and minerals of the Mahanagdong hydrothermal system aims to identify the origin of the acidic SO_4-rich waters in the deep reservoir. The results of the study suggest that the Mahanagdong neutral-pH and acidic fluids are hydrothermal in origin, as these ratios depart from the primary magmatic fluid composition of $\delta^{34}S$ in dissolved S and solid sulfur, and $\delta^{18}O$ in water $+10^{o}/_{oo}$.

The $\delta^{34}S_{SO4-H2S}$ geothermometer appears to be applicable only in acidic wells, possibly because of enhanced isotope fractionation in low pH and high total dissolved sulfur environment. The $\delta^{18}O_{SO4-H2O}$ geothermometer failed to give meaningful results, suggesting that ^{18}O in Mahanagdong is not primarily dependent on the fractionation between water and SO_4. Similarly, the $\delta^{34}S_{AH-PY}$ mineral isotope geothermometers, when applied to suspected acidic feed zones, predicted higher than measured temperatures, possibly because anhydrite and pyrite formed from different, and not a single, reaction.

Unaltered volcanic rocks in the Mahanagdong geothermal system has total sulfur of 560 mg/kg_r, the expected composition of granodiorites. Addition of about 4,000-8,000 mg/kg_r sulfur took place in the neutral-pH reservoir possibly through the continuous circulation of mineralising fluids. In the acidic reservoir, about 10,000-43,000 mg/kg_r total sulfur has been added.

1.0 INTRODUCTION

Stable isotope geochemistry studies of hydrothermal systems have been applied to help answer many specific problems, for example, the question on the origin of deep-seated sulfur-rich, acidic waters. Some of the postulates forwarded on their origin include direct SO_2 input from magmatic sources, mixing of shallow formed acid condensates, and dissolution of sulfide minerals. Since these processes occur in different thermodynamic conditions, the study of ^{34}S stable isotope systematics and other relevant isotopes (i.e., ^{18}O in sulfate) has the potential to elucidate the origin of the acidic fluids in geothermal reservoirs.

In line with the above general concept, this paper has the objective of evaluating the state of sulfur and oxygen isotope equilibrium in fluids of the Mahanagdong hydrothermal system (Fig. 1), and hopefully answer the question on the origin of the acidic fluids through the correlation of ^{34}S and ^{18}O in SO_4 stable isotopes. This paper is part of the coordinated research project of the International Atomic Energy Agency (IAEA RC No. 9718/RO) on the application of stable isotopes in the studies of acidic fluids in geothermal systems.

2.0 THE MAHANAGDONG HYDROTHERMAL SYSTEM

The Mahanagdong hydrothermal system is underlain by a suite of rocks composed of a metamorphic basement, a conglomerate complex, an impermeable claystone unit, and young andesitic lavas and pyroclastics. The spatial and vertical distributions of these rock units control the size of the hydrothermal reservoir. In the west, fluid flow appears to terminate on the claystone and metamorphic units where lithologic permeability is poor. Likewise, the ascent of the fluids to the surface stops upon encountering the more than 1-km thick impermeable sequence of lavas and pyroclastics. Structures related to the Philippine Fault provide channels for fluid movement in the reservoir. In the southern sector, the presence of interconnected northeast and northwest trending fractures enhance fluid mixing and influence the direction of the fluid outflow towards the southeast. In the northern part, the absence of the same structural fabric confines fluid movement, and consequently suppresses fluid-rock interaction.

The center of the Mahanagdong hydrothermal system hosts the parent fluid with temperature of above 290°C with Cl_{res} of around 4,000 to 4,200 mg/kg, high CO_2 content (> 400 mmole/100 mole H_2O_g) and enriched water isotope ($> -1.0^{o}/_{oo}$ $\delta^{18}O$) (Fig. 1) In the northeastern sector, the fluid is acidic with high SO_4 in the liquid and high H_2S in vapour. Cl_{res} ranges from 3,000 to 4,000 mg/kg and CO_2 ranges from 200 to 400 mmoles/100 moles H_2O here. This fluid has a temperature range of 260-280°C and slightly depleted $\delta^{18}O$ (-3.0 to $-2.0^{o}/_{oo}$).

Towards the south, the fluid has alkaline to neutral-pH level. It has a temperature range of 260 to 280°C and Cl_{res} of 2,500 to 3,000 mg/kg. CO_2 level in this area are below 200 mmoles/100 moles H_2O while the CO_2/H_2S ratios are as high as 100 indicating low H_2S content in vapour. The fluid has slightly depleted $\delta^{18}O$ ranging from -3.0 to -2.0 $^{o}/_{oo}$, with a uniform Cl/B ratio of 21-24 indicating satisfactory permeability that enhances substantial equilibration of the reservoir fluid.

The western wells have temperatures of less than 240°C, the coolest in the production sector. The wells also discharge the most dilute fluids with less than 2,500 mg/kg Cl_{res} and less than $-3.0‰$ $\delta^{18}O$, with low CO_2 and H_2S contents. All of these indicate the presence of cooler waters in the western part of the field. Table 1 presents the summary of the geochemical trends in Mahanagdong.

3.0 SULFUR INVENTORY IN ROCKS

The unaltered rock in Mahanagdong, represented by a sample of andesite from Paril Dome, has low sulfur content of

0.056%, or about 560 mg/ kg of rock (mg/kg$_r$) (Table 2). Relative to fresh granodiorite and granitoid bodies which have a range of total sulfur content of 200-2,000 mg/kg$_r$, mostly in the form of sulfides, and magmatic melts saturated with sulfates (i.e., El Chichon volcanics) with total sulfur is in the order of 8,000 mg/kg$_r$ (Ohmoto, 1986), the unaltered rocks in Mahanagdong fall within the range of fresh granodiorite rock.

Cores affected by typical neutral-pH alteration (MG-3D and MG-16D) have higher sulfur content, possibly in the form of rare pyrite, relative to the fresh rock sample by one order of magnitude (0.454-0.848%). These values suggest that about 4,000-8,000 mg/kg$_r$ total sulfur have been added to the host rocks (Table 2). The probable source of these sulfur is a mineralizing fluid with a temperature of <350^{o}C (Ohmoto, 1986). On the other hand, total sulfur, in the form of abundant pyrite and anhydrite, from cores in acid wells (MG-9D and MG-15D) are higher by two orders of magnitude (1.179-4.304%) relative to the unaltered rock. The voluminous sulfur added, which is in the order of 10,000 to 43,000 mg/kg$_{r,}$ could have come from either a direct magmatic source having 5.0% total sulfur or accumulation of total sulfur in the waters which have not fully attained equilibrium with the rocks.

If the sulfur concentration in the fresh rocks is assumed to be uniform throughout the Mahanagdong reservoir, the amount of sulfur present in the alteration minerals brought by the mineralising thermal fluids can be calculated (Column 5 of Table 2, in mg/kg of total rock). These are compared with the average contents of all sulfur-bearing species in the fluids, in this case SO_4 and H_2S in terms of mg/kg solution (Column 4). The resulting fluid to rock sulfur ratio of both the acid and neutral-pH reservoirs have a range of 7.07-9.54% (average of 8.2%).

4.0 STABLE ISOTOPE SYSTEMATICS

Presented in Figure 2 are the results of sulfur (δ^{34}S CDT, ‰) and oxygen (δ^{18}O, SMOW) isotope analyses of fluid and mineral samples. The isotope ratios of dissolved sulfate samples ($\delta^{34}S_{SO4}$) can be grouped into two, namely: (**a**) those with >15‰ (well samples); and (**b**) those near 0‰ (Mamban and Paril springs. Curiously, isotope ratios for neutral wells in group (**a**) do not exceed 20‰. In contrast, samples from acid wells have more enriched ratios of +22.5‰. Depleted ratios, close to or within H_2S range, can be seen from the surface spring samples (group **b**). Relative to other fluids, the range of δ^{34}S in Mahanagdong deep fluids is close to the +20‰ value of seawater but significantly far from the 0±3‰ value of magmatic dissolved sulfur (Ohmoto, 1986).

The values for fluid sulfide (δ^{34}S H_2S) fall within a narrow range of between –1.4 and +1.2‰. The general homogeneity of the δ^{34}S in H_2S in Mahanagdong is consistent with the composition of fluid sulfide of a volcanic and hydrothermal source, which is approximately 0‰, as mentioned by Ohmoto (1986) and Bayon (1996). Hence, samples with no available $\delta^{34}S_{H2S}$ analysis can be assigned a default value of –0.03‰, the average $\delta^{34}S_{H2S}$ in Mahanagdong.

Pyrite samples show a little wider range of δ^{34}S from –1.37 in MG-13D to +2.09‰ in MG-20D. In general, though, the δ^{34}S ratios of pyrite are similar to the near 0‰ ratios of H_2S. Moreover, pyrite in Mahanagdong have close isotopic affinity with the pyrites found in porphyry copper environments, having δ^{34}S of close to 0‰ (Ohmoto and Rye, 1979). Anhydrite samples analysed for δ^{34}S, unfortunately, were not as many as desired. Nonetheless, ratios from MG-9D and MG-21D are akin to ratios in group (**a**) of the dissolved SO_4 samples. For comparison, primary anhydrite samples recovered from Mt. Pinatubo yielded δ^{34}S ratios of 5-11‰, or an average of +7‰ (McKibben, *et al.*, 1997). The Mahanagdong samples are rather close to the hydrothermal anhydrite in well PIN-2D of Mt. Pinatubo, which has an average composition of +20‰ (McKibbin *et al.*, 1997), and to other hydrothermal anhydrites (Bayon, 1996).

The δ^{18}O composition in water has a narrow range of –5 to 0‰; samples with highly depleted stable isotopes are the acid-SO_4 springs while the most enriched sample is the water from MG-14D which also has the highest T(Quartz) value. The range of $\delta^{18}O_{H2O}$ composition is far from the +10‰ level of primary magmatic waters (Giggenbach, 1992).

Oxygen isotope ratios in sulfate for wells are within a range of +2 to +6‰. MG-18D with $\delta^{18}O_{SO4}$ of 11.69‰ is considered an outlier, as the other isotopic an chemical characteristics of the well are similar to other neutral-pH wells. Spring samples exhibited the most depleted $\delta^{18}O_{SO4}$ ratios of –1.39‰ (Paril) and –0.77‰ (Mamban).

Fluid pH is supposed to play a major role in the rate of sulfur isotope exchange between species, there appears to be no obvious correlation between deep fluid pH and total sulfur with the ratios of δ^{34}S in H_2S and δ^{18}O in SO_4. However in Figure 3, where the isotopic fractionation is plotted against the concentration of H_2S and SO_4 in the fluids, the samples with the highest level of these sulfur species also exhibit the greatest degree of isotopic fractionation.

5.0 ISOTOPE GEOTHERMOMETERS

Figures 4 and 5 graphically show computed δ^{18}O and δ^{34}S isotope geothermometer temperatures vs. theoretical temperatures based on isotope fractionation (equations are given in Robinson, 1978 and Ohmoto and Rye, 1979).

All estimated temperatures in neutral wells fall within the range of around 300-400^{o}C. These values are much 50-100^{O}C higher than those given by the solute and gas geothermometers Taking the T(Quartz) as synonymous with actual downhole temperature in wells (n*ote: T(Quartz) is close to the measured downhole temperature*), it can be concluded that the fluid sulfur isotope geothermometer does not reflect present day well temperatures in Mahanagdong, as fluid sulfur isotopes are not in equilibrium in the geothermal system. If the isotope temperatures ***do*** represent temperatures of sulfur isotopic equilibrium between SO_4 and H_2S, then the environment for equilibration to take place should be at much hotter, deeper levels than drilled depths. The consistent range of isotope temperatures (300-400^{o}C) tends to suggest that these are indeed reflective of deeper equilibration.

On the other hand, the δ^{34}S isotope geothermometers predicted about 280^{o}C for acid wells. This is within 10-15^{o}C of the temperatures estimated from quartz geothermometry.

The mineral equivalent of the fluid sulfur isotope geothermometer for geothermal systems is the Ah-Py pair. Unfortunately for this study, not enough anhydrite were analyzed due to its scarcity in occurrence; only Ah from acid wells were picked. The resultant temperatures calculated are 302-354°C. Like its fluid counterpart, therefore, the sulfur isotope mineral geothermometer provides temperatures representive of a deeper, hotter equilibration environment for sulfur isotopes. The reason could be the assumption of this geothermometer that isotopic exchange between pyrite and anhydrite takes place during their formation. In hydrothermal systems, anhydrite precipitates directly from dissolved SO_4 and pyrite from H_2S. There is no direct fractionation between the sulfur-bearing minerals, thus, the temperature recorded is most probably the temperature of precipitation.

6.0 ORIGIN OF FLUIDS

Magmatic input to the geothermal fluid of Mahanagdong is evidenced by the $\delta^{34}S$ of H_2S close to 0‰, the signature of magmatic sulfur of about 0 ± 3‰ as against the isotopically lighter H_2S of sedimentary origin (-20‰; Ohmoto and Rye, 1979). The variation in ratios among the Mahanagdong H_2S samples (-1.4 to +1.2‰) is most probably due to exchange reactions with SO_4 or SO_2 at sub-magmatic temperatures. Because of the uniform $\delta^{34}S$ in H_2S, pyrite formed from the reaction of H_2S with Fe has similar isotopic composition of near 0‰.

The enriched $\delta^{34}S$ ratios in dissolved SO_4 (16-22‰), which is within the range for hydrothermal sulfate, suggest that isotope partitioning of the original magmatic sulfur has occurred as a consequence of the hydration of primary SO_2. Based on Ohmoto and Rye (1979), much (up to 70%) of the heavy isotope goes to SO_4, leaving an isotopically depleted H_2S pair. At temperature of around 350-370°C, the SO_4 formed would have $\delta^{34}S$ ratios of +17 to +18‰ (assuming $\delta^{34}S_{H2S}$ is at 0‰), and at around 280°C, the $\delta^{34}S$ ratio is around +23‰.

The hydrothermal origin of the fluids is reinforced by the ^{18}O in H_2O with a range of –5.0‰ in springs and 0‰ in the hottest wells. Assuming that the meteoric recharge to the Mahanagdong reservoir has $\delta^{18}O$ of –6.6‰ (Salonga and Siega, 1996) and magmatic waters have $\delta^{18}O$ of +10‰ (Giggenbach, 1992), the Mahanagdong deep waters (with about 35% volcanic and 65% meteoric components) should have an ideal $\delta^{18}O_{H2O}$ of –0.8‰. In other words, from the point of view of sulfur and oxygen isotopes, the whole system is presently within the hydrothermal environment.

The surface acid-SO_4 waters have depleted $\delta^{34}S$ of near 0‰. This isotopic characteristic merely reflects another origin of SO_4 - the oxidation of H_2S in the vadose zone. Since H_2S coming from depths has $\delta^{34}S$ ratios of near 0‰, the acid-SO_4 solution produced at the surface features of Paril and Mamban have isotopic compositions similar to H_2S.

7.0 SULFUR CYCLE

Upon crossing the critical temperature of water at about 370°C, SO_2 in Mahanagdong becomes hydrated as a result of interaction with groundwater (Fig. 6). In Mahanagdong, the $\delta^{34}S_{SO4-H2S}$ geothermometer suggests that the reaction takes place between 300-400°C, and the resultant fluid has $\delta^{34}S$ in SO_4 of +16-19‰ and about 0‰ in H_2S. At a temperature between 250-300°C, the primary waters are admixed with more volume of meteoric waters with an assumed $\delta^{18}O_{H2O}$ content of –6.6‰. Mixing with 65% meteoric water produced the waters in the hottest part of the reservoir with $\delta^{18}O$ of around 0‰. In the outflow zone, the meteoric water fraction is about 75%, generating hydrothermal fluids with $\delta^{18}O$ between –3.0 to –1.0‰.

From the center of the hydrothermal system, the hydrothermal fluid follows two paths of evolution. The fluids flowing towards the south are channeled by interconnected fractures and assured of continuous circulation and full mixing; thus, having a more homogeneous characteristics. Since the fluid is exposed to more volume of rock, it attains full equilibrium with the rocks by scrubbing-off excess sulfur, possibly in the form of sulfides, from the reaction of H_2S with Fe, and anhydrite, from the reaction of SO_4 with Ca. The present total sulfur in the water ranges from 60 to 450 mg/kg, while the rocks altered with neutral-pH secondary minerals have present total sulfur of 4,000 to 8,000 mg/kg. With high pH and low total sulfur in the fluids, $\delta^{34}S$ in SO_4 is slow in re-equilibrating at the prevailing temperature.

On the other hand, the movement of the fluid in the north is confined by poorly interconnected fractures, thus limiting interaction with rocks. Consequently, dissolved sulfur remains in excessive amounts. At reservoir conditions, dissolved sulfur possibly exists as HSO_4 and H_2S. But at lower temperature, HSO_4 dissociates to SO_4, making the well discharges highly acidic. Because of the lower pH and high total sulfur in the fluids, $\delta^{34}S$ in SO_4 has the chance to re-equilibrate to +22.5‰, close to the ideal ratio at reservoir temperature of 270°C. The present total sulfur in the rocks suspected to host acidic fluid ranges from 10,000-43,000 mg/kg_r.

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Table 1: *Brief descriptions of the different types of fluids in Mahanagdong geothermal field based on the chemical trends across the field.*

Fluid Type	Geographic Location	Brief Description	Wells included in this study*
neutral-pH, high gas	Northeast	Temperature of 290-300°C, Cl_{res} of 4,000 – 4,200 ppm; CO_{2td} of above 400 mM/100M; $\delta^{18}O$ of greater than –1.0°/oo	MG-3D, 14D, 24D
neutral-pH low gas	South and Southeast	Temperature of 260-280°C, Cl_{res} of 2,500 – 3,000 ppm; CO_{2td} of below 400 mM/100M; CO_2/H_2S of 40-100 $\delta^{18}O$ of –3.0 to -2.0°/oo	MG-1, 18D, 23D, 27D, 29D and 31D
acidic fluids	Northwest	Temperature of 260-280°C, Cl_{res} of 3,000 – 4,000 ppm; SO_{4res} of above 100 ppm CO_{2td} of 200-400 mM/100M; CO_2/H_2S of 20-40 $\delta^{18}O$ of –3.0 to -2.0°/oo	MG-9D, 15D
cooler fluids	West	Temperature of less 240°C, Cl_{res} of less 2,500 ppm; $\delta^{18}O$ of less than –3.0°/oo	None

Table 2: *Inventory of sulfur in fluids and alteration minerals in Mahanagdong samples.*

Well	$SO_{4liquid}$[1]	H_2S_{vapor}[1]	$\Sigma(SO_4 + H_2S)$[1]	S_{min}[2]	S_{fluid}/S_{min} (%)
MG-3D	13	433	446	5,070	8.79
MG-9D	350	450	800	11,230	7.12
MG-15D	120	240	360	42,480	8.47
MG-16D[3]	21	35	56	7,920	7.07
MG-16D[4]	18	20	38	3,980	9.54

[1] in mg/kg water; [2] in mg/kg rock

[3] Upper feed zone; [4] Lower feed zone

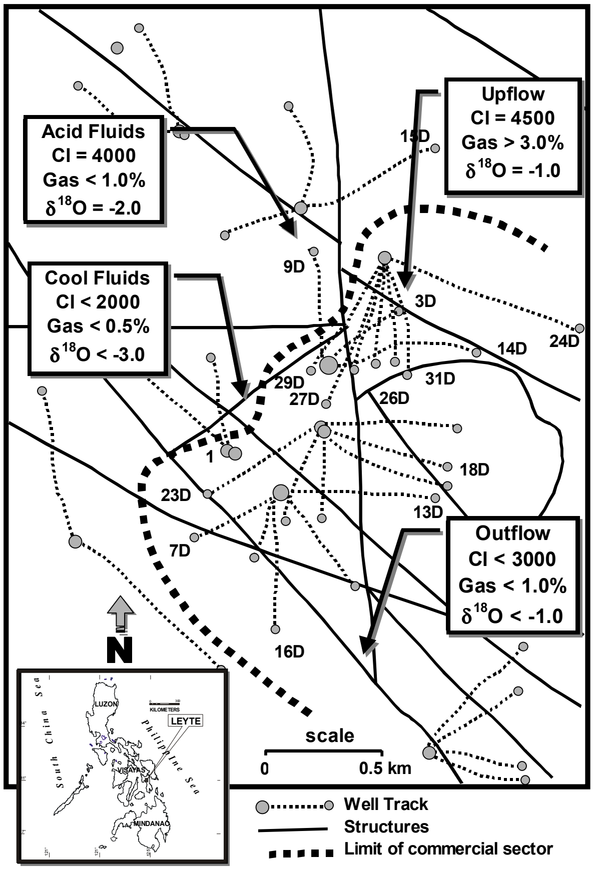

Figure 1: General map of Mahanagdong geothermal field showing the major structures, direction of well tracks and relative location in the central Philippines. The names of the wells included in this study are also shown.

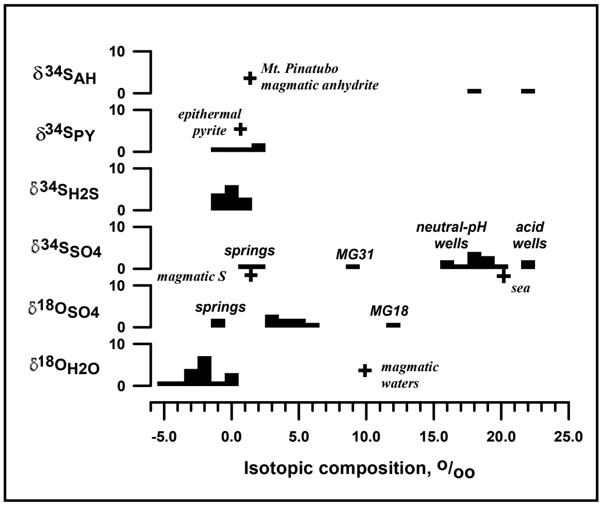

Figure 2: Isotope systematic of the water, gas and mineral samples in Mahanagdong

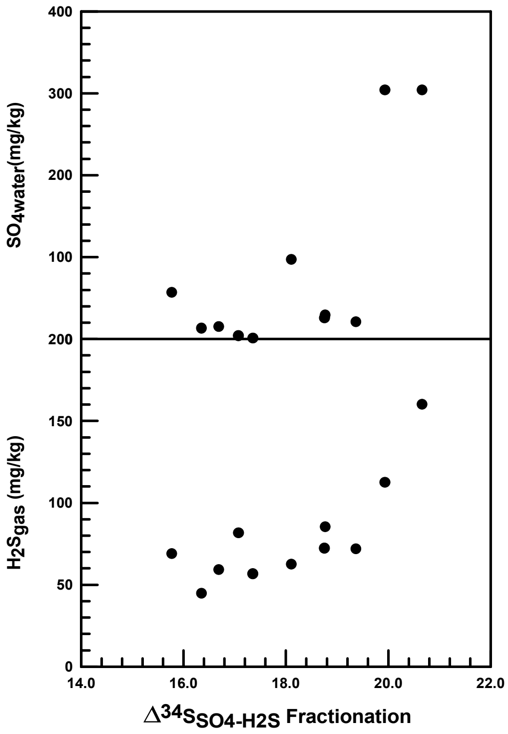

Figure 3: Cross plot of isotopic fractionation (Δ) with the composition of SO_4 and H_2S.

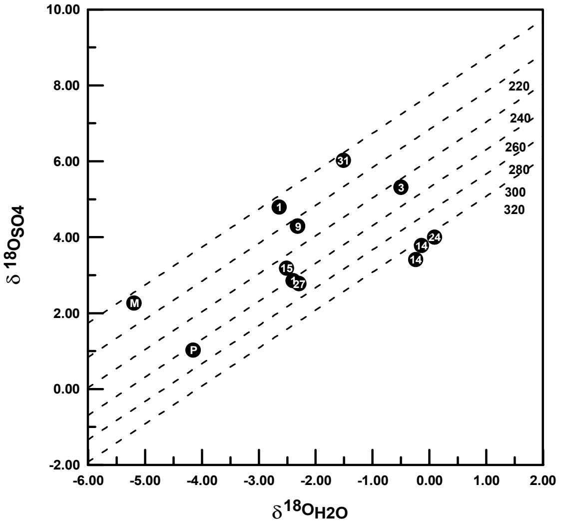

Figure 4: Isotopic geothermometer based on $\Delta^{18}O$ of SO_4 and H_2O.

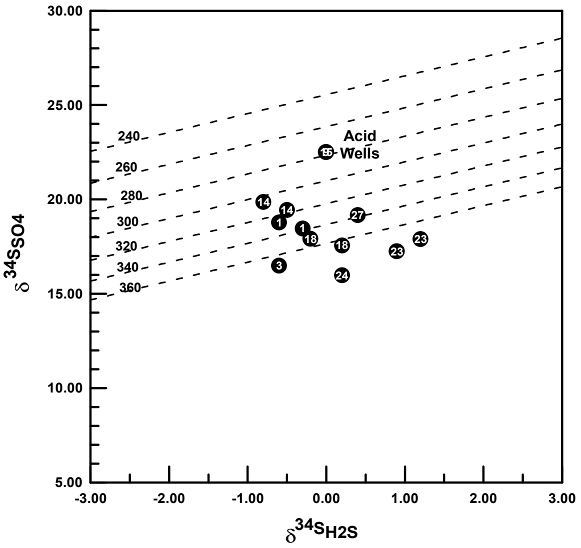

Figure 5: *Isotopic geothermometry based on $\Delta^{34}S$ of SO_4 and H_2S.*

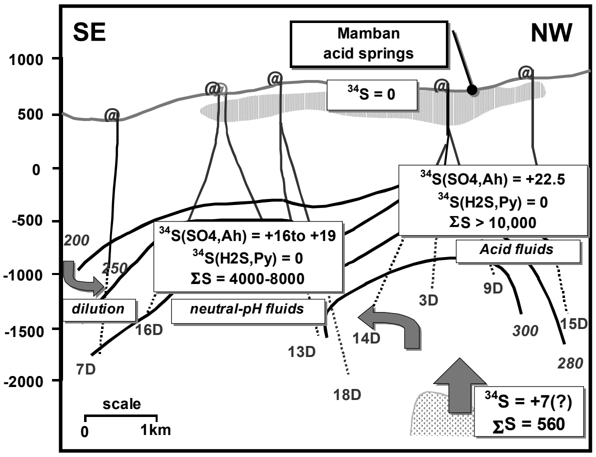

Figure 6: *Simplified diagram showing the mobilisation of sulfur in Mahanagdong hydrothermal system. Sulfur in rock are in mg/kg_r, while stable isotopes are in per mille CDT.*