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PRELIMINARY STABLE ISOTOPE INVESTIGATIONS OF ACID FLUIDS IN GEOTHERMAL SYSTEMS OF THE PHILIPPINES

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ABSTRACT

To determine the origin of the sulphate in the acid-sulphate fluids of the Bacon-Manito and Palinpinon Geothermal Projects, the sulphur isotopic compositions of H_2S gas, elemental sulphur, dissolved sulphate, anhydrite from well blockages and pyrite and anhydrite from well cores were measured. The H_2S gas has $\delta^{34}S$ values around 0‰ in the geothermal centres; this suggests an ultimate magmatic origin with no SO_2 gas present in the geothermal areas. Oxidation of this H_2S in the near surface environment produces acid-sulphate springs whose sulphate has similar $\delta^{34}S$ values to the H_2S. More positive values are produced by the sulphate starting to equilibrate isotopically with the H_2S under deeper, hotter conditions, a process which is accelerated by a low pH. Elemental sulphur is also formed by oxidation of H_2S gas with a kinetic isotope effect of at least 4‰ but it does not appear to be a contributor to the acid fluids.

Anhydrite from the cores and scraper samples from well blockages generally exhibit dissiniilar $\delta^{34}S$ and $\delta^{18}O$ values showing that the blockages were formed under different conditions to those in the geologic past. These new conditions have presumably been caused by the drilling which promoted mixing of shallow sulphate-rich waters with deep Ca-rich thermal waters.

INTRODUCTION

For some years the presence of acid fluids in the Bacon-Manito Geothermal Project (BMGP) and the Southern Negros (Palinpinon) Geothermal Project (SNGP) has been a cause of concern since such fluids can corrode casings, cause blockages from anhydrite precipitation in the bores and have a detrimental effect on steam quality. Theories for the origin of these fluids have included: i) introduction of volcanic SO_2 gas; ii) thermophylic low-pH tolerant bacteria; iii) remobilisation of buried sulphur deposits; and iv) condensation of steam/H_2S into groundwater.

The present study was aimed at using sulphur isotopes to trace the origin of the sulphate in these fluids. This involved analysing all sulphur containing phases from natural and well discharges, i.e., dissolved sulphate, H_2S gas, elemental sulphur, anhydrite and pyrite from cores and anhydrite from well blockages. These data were used together with other isotope analyses (primarily oxygen isotope analyses of sulphate) and available chemical data on samples collected from SNGP in 1985 and from BMGP in 1957 (for location, see Fig. 1).

Samples were analysed by the methods given in Robinson and Sheppard (1936) and the sulphur isotope analyses are reported as per mil deviation from CDT and the oxygen isotope analyses as per mil deviation from V-SMOW.

SOUTHERN NEGROS GEOTHERMAL PROJECT

SNGP (Palinpinon) is located on the south-eastern portion of the Negros Island (Fig. 1), which lies approximately 500 kilometers south of Manila. The production field is situated on the northern flanks of the Cuernos de Negros volcano, a relatively young volcanic edifice of Quaternary age.

Fig. 1: Location of the Bacon-Manito and Southern Negros (Palinpinon) Geothermal Projects (BMGP and SNGP).

The production field is divided into two sectors (Fig. 2): the hotter portion of the field, which was dedicated for the 112.5 MWe Palinpinon I Power Plant, is known as the Puhagan sector, while the second but relatively cooler area, situated west of Puhagan, is the Nasuji-Sogongon sector, which is proposed to be a development area for another 112.5 MWe power plant.

The youngest rock unit in the area is composed of dacitic and andesitic lavas and tuffs belonging to the Cuernos de Negros formation which is underlain by another volcanic unit known as the Southern Negros formation. This lithological unit is composed of moderately to intensely altered andesitic lavas and volcaniclastics. An oxidised zone is believed to be the transition between these two formations.

Beneath the Southern Negros formation, the lithology in the Puhagan and Nasuji-Sogongon sectors vary. The Puhagan sector is characterised by the presence of the Okoy formation which is composed of two members - a sedimentary unit which is a thick sequence of

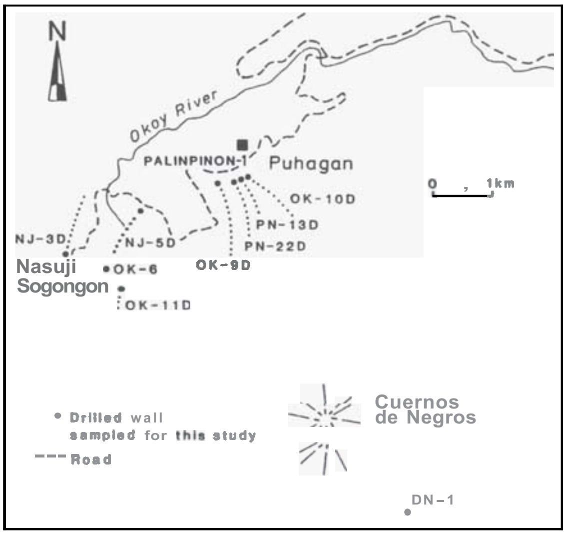

Fig. 2: Sampling sites in SNGP.

calcareous siltstone, sandstone, and sedimentary breccias and a volcanic member which is composed of andesitic lavas and breccias. In the Nasuji-Sogongon sectors, the Okoy formation disappears and is replaced by a hornblende-rich, quartz monzodiorite pluton.

Permeability in the area is thought to be mainly due to fracturing resulting from multiple vertical faults which criss-cross the area. However, significant permeability has similarly been attributed to the Southern Negros formation contacts, primary permeability of the volcanic units, and fracturing due to dike intrusions.

Sulphur and oxygen isotope analyses

All the sulphate samples analysed from this area are shown in Fig. 3 as a plot of $\delta^{34}S$ vs. $\delta^{18}O$ values. They comprise: dissolved sulphate in the well waters, anhydrite from cores and anhydrite from well-blockages (scraper and work-over anhydrite). In addition, H_2S gas was sampled from OK-9D, -10D and 6 and NJ-3D; $\delta^{34}S$ values are 1.3, -0.2, -3.2 and -2.5‰ respectively. A sample of elemental sulphur from the Dauin 1 well (DN-1) has a $\delta^{34}S$ value of -4‰, indicative of a kinetic fractionation during formation by oxidation of H_2S with $\delta^{34}S$ around 0‰.

The sulphate $\delta^{34}S$ values range from 3.5 to 22.9‰. Generally, the less positive values (around 0‰) represent sulphate formation by H_2S oxidation in the near-surface environment, whereas the more positive values represent a deeper sulphate which has reached some degree of isotopic equilibrium with sulphur in the H_2S. High temperature and low pH increase the rate of this isotopic exchange (see Robinson, 1978a). Many samples may represent the mixing of these two 'end-member' sulphates..

$\delta^{18}O$ values of the sulphates also vary considerably: -2 to 14.4‰. The deep thermal water has a $\delta^{18}O$ value of about -4 to -5‰ and the surface recharge water about -7‰. Oxygen in the dissolved sulphate will isotopically equilibrate with oxygen in these waters. The most positive values represent low temperature equilibrium (or exchange with an 0-13 rich water) probably at low pH (which increases the exchange rate) whereas the lower $\delta^{18}O$ values represent equilibrium at higher temperatures. This latter group of samples give calculated temperatures from H_2O-SO_4 oxygen isotope fractionation (Chiba et al., 1981) in agreement with fluid inclusion and measured downhole temperatures. However, the samples with higher $\delta^{18}O$ values represent temperatures much lower than present well temperatures and they may have continued to equilibrate down to lower temperatures especially if the pH is low (Chiba and Sakai, 1985).

Scraper samples also fell into two groups: one with high $\delta^{34}S$ and low $\delta^{18}O$ values, the other with low $\delta^{34}S$ and high $\delta^{18}O$ values. The former represent sulphate which has equilibrated at depth whereas the latter (two samples from OK-100 represent sulphate formed from shallow H_2S oxidation). Here, a low pH must have promoted exchange down to temperatures less than 100 C. Such high $\delta^{18}O$ values have only normally been observed in acid springs and crater-lake environments (Robinson, 1987). To precipitate anhydrite, the cooler water must have moved downwards (being heavier) and mixed with the deeper Ca-rich thermal waters without an opportunity to isotopically re-equilibrate to the new conditions because of an increase in pH during mixing.

Dissolved sulphate and core samples from OK-10D lie between the two main groups presumably on a mixing line. Other core samples (OK-10D and PN-18) have more positive $\delta^{18}O$ values than most present-day samples and may

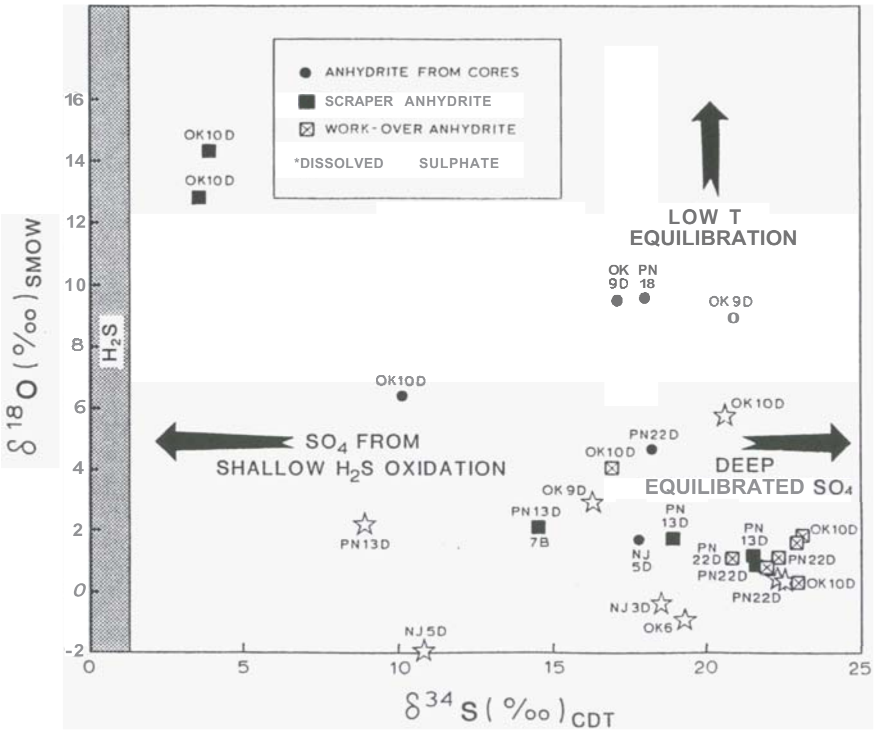

Fig. 3: Isotopic composition of all sulphate samples from SNGP.

represent equilibrium at low temperature, e.g., precipitation of anhydrite during the 'warming up' period of the geothermal system. Generally, the scraper and work-over samples represent different conditions to those which led to precipitation of anhydrite in the rocks. In some cases such as PN-22D and some OK-10D samples, the present dissolved sulphate is isotopically similar to the blockage anhydrite whereas other fluids have sulphate which is isotopically different to the blockage and has changed within a short period of time.

BACON-MANITO GEOTHERMAL PROJECT

The Bacon-Manito Geothermal Project lies astride the boundary of the Sorsogon and Albay provinces in the Bicol Peninsula, Southern Luzon (see Fig. 1). Geo-scientific studies conducted in the prospect have outlined a geothermal resource in the Palayang Bayan-Cawayan area (Fig. 4).

Surface geological mapping showed three lithological units: the San Lorenzo sediments, the Pocdol Volcanics, and the Rangas Intrusive to be present. Subsequent deep drilling showed that the SLS and RI are correlative to the Gayong Sedimentary Formation and the Cawayan Intrusive Complex respectively. They have been intersected by several wells in the Palayang Bayan and Cawayan areas.

Geological structures in the area serve as conduits for the movement of the hot geothermal fluids. Good permeability in the wells especially in the eastern sector of the field has primarily been due to the tensional character of these structures. Wells in Bacon-Manito indicate multiple (three to four), permeable zones that occur between -600 m to -1600 m below sea level. These permeable zones are predominatly associated with known structures such as faults and sometimes with the contact between the Cawayan Intrusive Complex and the overlying Pocdol Volcanics.

The vertical and horizontal distribution of hydrothermal alteration minerals show that hot fluids are upwelling in the eastern sector of Palayang Bayan. Homogenisation temperatures of fluid inclusions in vein minerals point to at least two hydrothermal events: the present reservoir temperatures and a relict higher temperature system.

Geophysical and geochemical surveys show a water-dominated geothermal system outflowing from this central portion towards the northeast to Osiao, west to Inang Maharang and further on to the Manito lowlands (see Fig. 4). Consistent with the typical hydrology of a geothermal system associated with andesitic volcanism, the thermal waters mapped in the area consist of acid-sulphate springs and solfataras at high elevations grading to neutral bicarbonate and sulphate-bicarbonate springs at intermediate elevations and to neutral chloride springs in the lowlands.

Most of the wells in Bacon-Manito discharge near-neutral to neutral. sodium chloride waters containing 0.9 to 1.04 wt% NaCl before flash. At shallower levels, secondary waters of the neutral, dilute sodium chloride, neutral bicarbonate, and acid-sulphate rich fluids are also produced by some wells. CO_2 and H_2S comprise about 90 to 38 vol% of the non-condensible gases in the steam phase.

High gas and reservoir chloride concentrations, and quartz temperature estimates in the eastern and northeastern sector of Palayang Bayan indicate the upflow to be near this region. Downhole temperature measurements show a distribution which confirms an upwelling zone in the general area of Mt Pangas. The highest measured temperature is $326^{\circ}C$ in PAL-10D which is drilled towards the Pangas crater.

Gas-rich two-phase feed zones in some wells indicate that gas accumulation had occurred and are probably responsible for the secondary water types found in the shallower portions of the reservoir. This is particularly observed in the eastern sector of the Palayang Bayan plateau. This gas-rich zone, however, does not define a single contiguous horizon but is confined to specific geologic structures in the eastern Palayang Bayan area.

The preliminary hydrogeological flow model for the Bacon-Manito geothermal field indicates an upwelling of hot fluids in the eastern sector of the Palayang Bayan area with fractures in the periphery of Mt Pangas serving as vertical conduits. This fluid then preferentially migrates laterally to the Manito lowlands. The fluid also outflows to the east to Osiao and Sorsogon. The major outflow is characterised by temperature reversals at shallow levels and downflow at deeper levels. Self-sealing in fractures due to mineral deposition at shallow depths caused the trapping of gas and steam and created an apparent shallow zone of poor permeability. This extends until the Cawayan fault, an identified feeder of acid fluids.

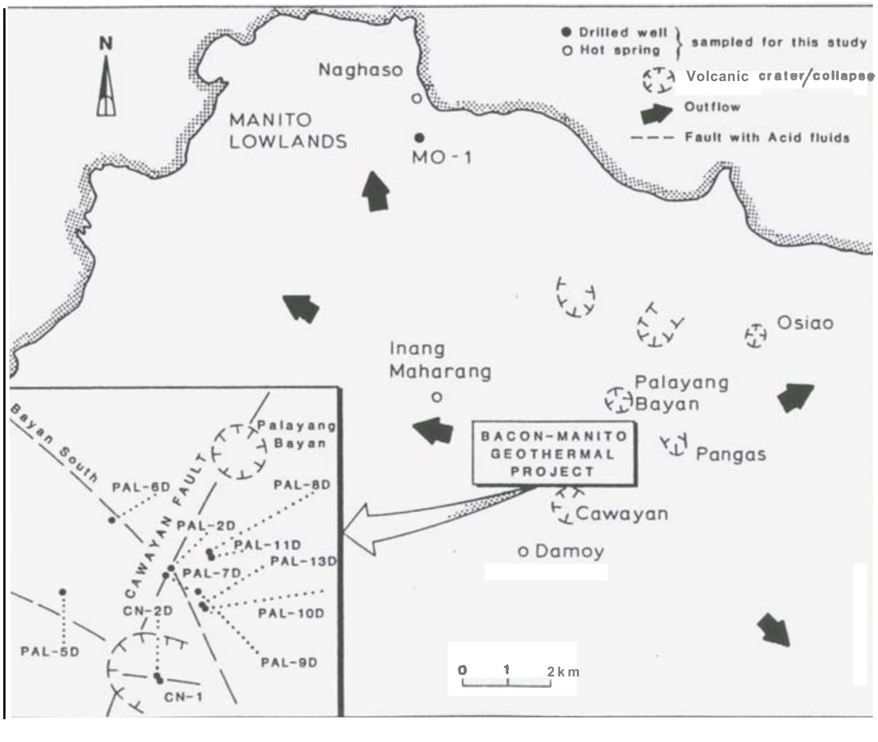

Fig. 4: Sampling sites in the BMGP.

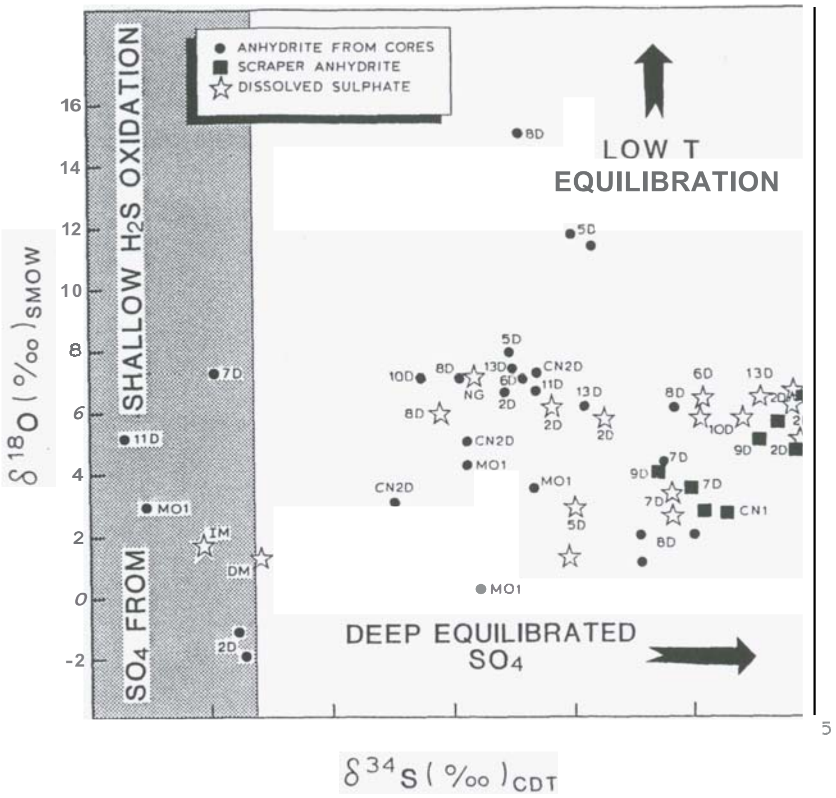

Fig. 5: Isotopic composition of all sulphate samples from BMGP. Non-prefixed well numbers are PAL- .

Sulphur and oxygen isotope analyses

Elemental sulphur was collected from the cold acid-sulphate springs of Damoy and from some of the wells down to 400 m below the surface in MO-1 and PAL-50 and 1200 m in CN-2D. The $\delta^{34}S$ values are in the range -2.5 to -11‰. A kinetic isotope effect of at least 4‰ occurs when H_2S gas is oxidised to elemental sulphur (Robinson, 1987) so the sulphur is formed from H_2S with $\delta^{34}S$ values close to magmatic (0‰) or slightly negative. Seven H_2S gas samples were collected from surface and well discharges and their $\delta^{34}S$ values lie from 1.6 to -4.9‰ with a cluster around 0‰. The most positive values are from PAL-10D and Damoy (possibly due to a loss of S-32 into the elemental sulphur) and the most negative value is from MO-1. In a study of elemental sulphur in geothermal areas of Japan, $\delta^{34}S$ values werg found to vary from 7 to -9‰ with an average at -4‰ (Ueda et al., 1979). As in the Philippines the sulphur appears to have formed by oxidation of magmatic H_2S.

The negative $\delta^{34}S$ value of H_2S gas from NO-1 (-4.9‰) coupled with a very low H_2S/SO_4 ratio for the discharge suggests that magmatic H_2S has been fractionated away from the Pangas source by sulphate formation. Since S-3' preferentially enters the sulphate, the H_2S gradually becomes depleted and the $\delta^{34}S$ values decrease away from the source.

All the sulphate analyses for BMGP: dissolved sulphate, scraper samples and anhydrite from the cores are shown in Fig. 5: a $\delta^{34}S$ vs. $\delta^{18}O$ plot. In general, the samples form a band across the plot from low to high $\delta^{34}S$ values. Near-surface oxidation of H_2S gives rise to the low-$\delta^{34}S$ sulphates such as MO-1 and the natural discharges: Inang Maharang and Damoy. In the extreme case the sulphate acquires the same $\delta^{34}S$ values of the H_2S: a phenomenon typical of many acid springs, e.g., Ketetahi Springs, Mt Ruapehu, New Zealand (Robinson, 1987).

However, sulphate formed at depth or moved into deeper, hotter environments exchanges sulphur isotopes with the H_2S depending on the temperature. For example, at 300°C the fractionation between H_2S and SO_4 is about 20‰. If only a small amount of sulphate is present then its $\delta^{34}S$ values will be 20‰ compared to the H_2S with 0‰. As the SO_4/H_2S ratio increases both the sulphate and H_2S will acquire lower $\delta^{34}S$ values for conditions of equilibrium. Figure 6 is a plot of sulphate concentration vs $\delta^{34}S$ of the sulphate. Samples with high sulphate concentrations such as Inang Maharang have lower $\delta^{34}S$ values, close to the H_2S from which they were formed, whereas samples with lower sulphate concentrations have the higher $\delta^{34}S$ values which represent some degree of equilibrium with the H_2S.

Kiyosu and Kurahashi (1933) show that, for the Kusatsu geothermal areas in Japan, the $\delta^{34}S$ values of sulphate tend to be lower with decreasing Cl/SO_4 ratio. This is also noted for the BMGP (see Fig. 7) where samples from Inang Maharang and Damoy have both low $\delta^{34}S$ and low Cl/SO_4 values. This is further evidence for sulphuric acid formed by surfitial oxidation of H_2S. There is no evidence for the involvement of SO_2 gas in this process. If SO_2 were present it would be found in the hot source of the geothermal area where, because SO_2 would be enriched in S-34, the H_2S would have negative values for 0‰ sulphur source. This is not the case, and the only negative $\delta^{34}S$ values for H_2S occur in the peripheral areas.

The oxygen isotopic composition of the sulphate samples averages around 6‰ SMOW. Considering first the dissolved sulphates: PAL-2D, -6D, -8D, -100 and -130, they give a temperature of 215°C assuming equilibrium with a deep water of $\delta^{18}O$ = -2‰, based on HSO_4- H_2O fractionation (Robinson, 1978b). This is lower than the measured downhole temperatures and must demonstrate a 'quench in' temperature as the water moves to the surface; more rapid exchange is promoted by acid conditions. Only one sample from the acid well PAL-2D has a lower $\delta^{18}O$ value of 4.9‰ which gives a HSO_4-H_2O temperature of 240°C, the same as that for the acid feed zone of this well. Sulphate which equilibrates at depth with a deep water of $\delta^{18}O$ = -2‰ at, say, 300°C will have a $\delta^{18}O$ value of about +3‰. These 'deep values' are unfortunately in the same range as the surface samples.

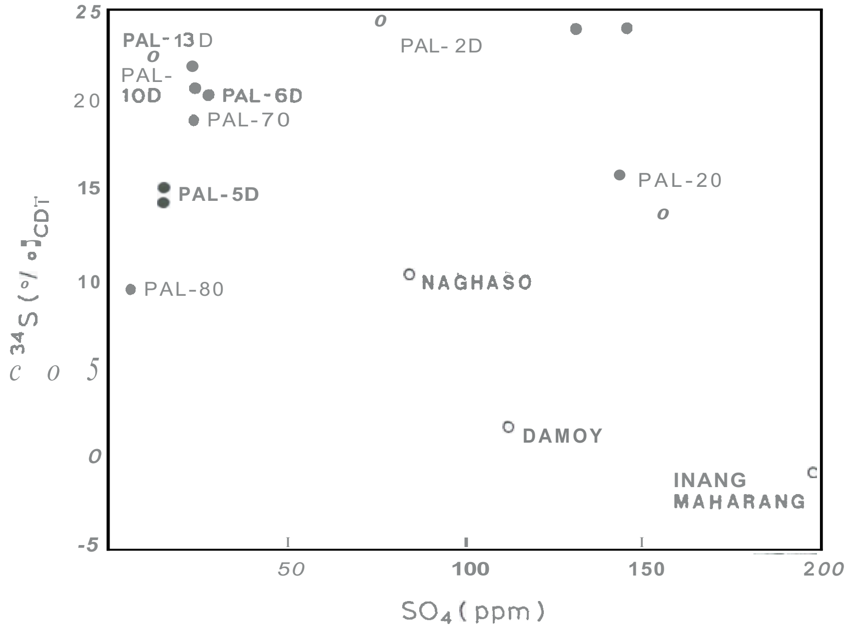

Fig. 6: Sulphate concentration vs $\delta^{34}S$ for BMGP dissolved sulphate samples.

Consider sulphate formed by near surface oxidation of H_2S, the isotopic composition of both atmospheric and water oxygen are passed on to the sulphate with relative contributions of about one-third and two-thirds respectively. If the $\delta^{18}O$ value of the surface water is taken as -5°/oo for this area, 23.5°/oo for atmospheric oxygen (with a kinetic fractionation factor of -8.7°/oo for the incorporation of atmospheric oxygen in the sulphate), then the resulting sulphate will have a $\delta^{18}O$ value of about +1.5°/oo (Matsuo et al., 1985), i.e., similar to samples like MO-1, Inang Maharang and Damoy.

Pyrite and anhydrite were separated from core samples and their $\delta^{34}S$ values are shown in Fig. 8. The $\delta^{34}S$ values of the pyrite represent those of the H_2S in the geological past since there is little fractionation between H_2S and pyrite at higher temperatures. Excluding sample PAL-3D which will be discussed later, values vary from 0 to about -12°/oo. Two groups of pyrite can be seen in Fig. 3, both trending back to the source $\delta^{34}S$ value of 0°/oo with a discontinuity at -600 m RSL. It is not yet clear what geological or geochemical feature this discontinuity represents. Obviously some H_2S with more negative values than seen today must have been present in the past in areas where increased sulphate formation occurred.

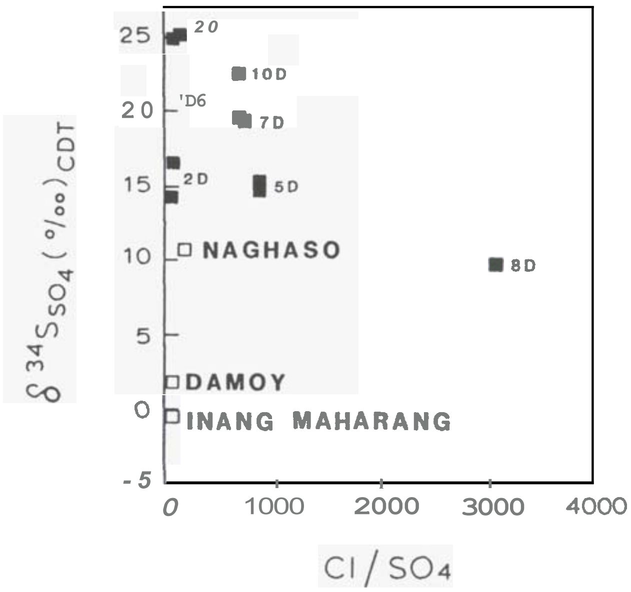

Fig. 7: Dissolved SO_4 in BMGP thermal waters. Well numbers should all be prefixed PAL- .

The anhydrite samples also show a break at -608 m RSL (see Fig. 8) with $\delta^{34}S$ values spreading from 0°/oo (complete H_2S oxidation) to 20°/oo where some degree of isotopic equilibrium had been established with the H_2S. The more positive $\delta^{34}S$ values (25°/oo) seen in sulphates today did not occur in the past presumably the sulphate did not come as close to equilibrium because of unfavourable pH or temperature regimes.

A pyrite from the deepest part of PAL-80 has a $\delta^{34}S$ value of -20°/oo. This section of the core intersects sedimentary material and the pyrite is of biogenic not geothermal origin. The anhydrites from this part of the core may also be affected by this local source of isotopically light sulphur, i.e., leaching of the sedimentary pyrite by the geothermal fluids and subsequent oxidation. It is unlikely that the sediments actually supplied sulphate to the fluids since the concentration of sulphate in PAL-80 waters is very low.

It has been mentioned previously that some wells in the Bacon-Manito geothermal project develop anhydrite blockages. At present, it is not clear whether these blockages were formed while the well was flowing or when the well was shut. Well measurements conducted while a well is shut showed a temperature profile which represents a condition where a cool fluid is entering the well at a shallow permeable zone and exits through a deeper zone. In some cases, downhole water samples were able to show that this fluid has a chloride concentration that is lower than what is found at deeper levels and is richer in either sulphate and/or bicarbonate. In a lot of cases though, this fluid has a high sulphate concentration. Downhole sampling conducted while a well was flowing also showed that this zone contributes to the total discharge.

Scraper surveys have been used to sample these anhydrite blockages. Isotope analyses of these anhydrite samples showed $\delta^{18}O$ values ranging from 2.6 to 6.4°/oo SMOW, and $\delta^{34}S$ values of 18.4 to 24.6°/oo CDT. The $\delta^{18}O$ values for the blockage samples are within the oxygen-18 range of the anhydrite samples from the drillcores and cuttings. The S-34 values of the blockage samples, however, are heavier than those obtained from the cores and cuttings. This establishes that the anhydrite blockages were formed under different conditions to those which led to the precipitation of anhydrite in the rocks.

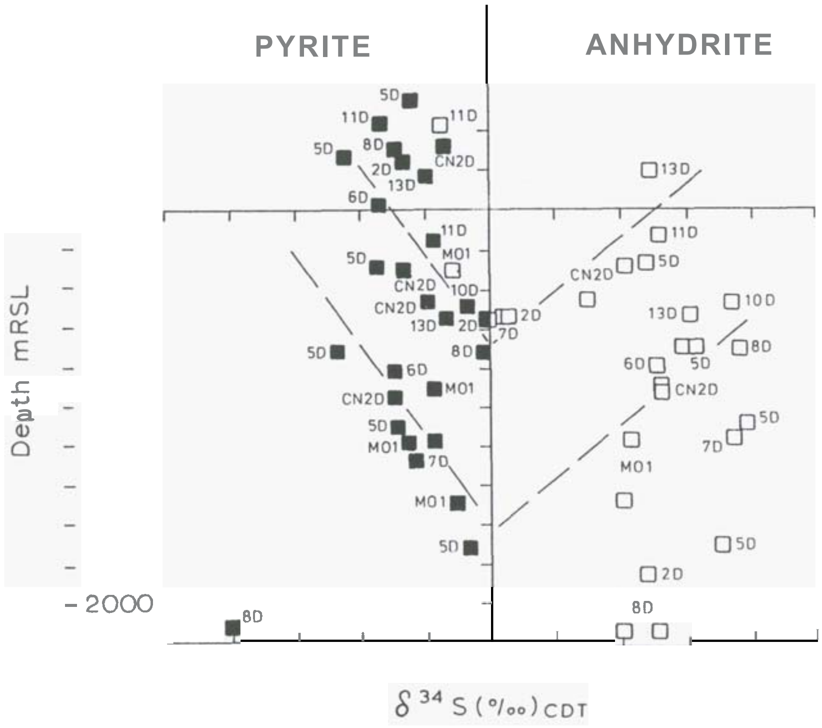

Fig. 8: Sulphur isotope analyses of pyrite and anhydrite from BMGP cores.

Only in well PAL-7D do we see a fluid sulphate, a core anhydrite and a scraper anhydrite with similar isotopic compositions. In wells such as PAL-2D the fluid sulphate and the blockages are similar but the cores are different and reflect different conditions in the past. The scraper samples lie in the area of Fig. 5 described as 'deep equilibrated sulphate'. Equilibrium may have been accelerated by the acid conditions and although the bulk of the sulphate may have originated from near surface oxidation of H_2S, its isotopic composition had shifted towards very positive values due to equilibrium with H_2S under higher temperatures.

CONCLUSIONS

In both the SNGP and BMGP we have found that:

i) The isotopic composition of elemental sulphur shows it to be a product of H_2S oxidation in the shallower portions of the fields. It plays no role in the formation of the acid fluids.

ii) $\delta^{34}S$ values of H_2S gas from the hottest areas of the fields lie within the magmatic range around 0‰. More negative values correspond to sulphate formation in peripheral areas.

iii) There is no evidence for the presence of SO_2 gas nor for its involvement in the formation of acid fluids.

iv) Sulphate in the acid fluids is formed from H_2S oxidation. It either has $\delta^{34}S$ values similar to the H_2S where it is formed near the surface or if it moves to deeper, hotter conditions it acquires much more positive $\delta^{34}S$ values due to isotopic exchange with the H_2S.

v) The sulphur isotopic compositions of the anhydrite in the cores is distinct from those in the well blockages. Anhydrite presently being deposited in the wells is formed under different conditions created by drilling, whereby the shallow sulphate-rich waters descend and come into contact with the neutral Ca-Cl waters at depth.

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