SULPHUR ISOTOPE APPLICATIONS IN TWO PHILIPPINE GEOTHERMAL SYSTEMS

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Abstract

Sulphur isotope geothertnotnetry for SO_4^{2-}-H_2S fluid pairs, and oxygen isotope geothermometry for dissolved SO_4^{2-} and H_2O, gave teinperatures similar to those measured in wells (within 10°C) at the Mt. dpo geothermal field. The geothermometers also gave parent fluid temperature estimates identical to those calculated from cation and silica geotherntometers. In contrast, temperature estimates made using SO_4^{2-}-H_2S fluid and anhydrite-pyrite mineral pairs of Palinpinon wells are higher than actual bore temperatures. Sulphur isotope geothermometers used in this field may reflect isotopic equilibrium in the deeper portions of the geothermal system, unreached by drilled wells.

Dissolved SO_4^{2-} is believed to be a product of either (aj SO_2 disproportionation to H_2S and SO_4^{2-} at a temperature below 400°C, (b) H_2S oxidation at boiling depths, or (c) both. The first process accounts for the total dissolved SO_4^{2-}, but <15% of H_2S, present in well discharges. To account for the remaining H_2S, a direct magmatic input is invoked. The second process cannot be isotopically distinguished, but may be inferred because of the scatter of $\delta^{34}S$ values of sulphate. There is no evidence of major sulphate contribution from surface steam-heated SO_4^{2-} waters.

Anhydrite and pyrite have $\delta^{34}S$ values similar to fluid SO_4^{2-} and H_2S, respectively. These suggest that sulphur in anhydrite is derived from dissolved sulphate, while pyrite sulphur is supplied by H_2S.

1.0 INTRODUCTION

Sulphur isotope geochemistry has been widely applied in studies of fossil geothermal systems, especially ore-bearing hydrothermal deposits. Its application in active systems, on the other hand is not as popular. In the Philippines, the proposal to use sulphur isotope data came about because of the desire to determine the source of acid fluids in geothermal systems, especially since acid fluids in the Philippines are commonly SO_4^{2-}- dominated

This project is seen as a step towards understanding sulphur isotope geochemistry. Being more of an introductory work, most of the discussions will be general in scope. Its main aims, therefore. are two-fold: (a) to introduce the concept of sulphur isotopes. and (b) to present possible applications to geothermal studies, particularly the sources of sulphur in acid well discharges. Two Philippine geothermal fields are selected as case studies for the presentation of isotope applications. These are Palinpinon (in Southern Negros) and Mt. Apo (in South-central Mindanao). The former is a producing field which has been in operation for more than 10 years; the latter is a new field currently king developed for power generation. Acid fluids are present in some sectors of both areas: in Palinpinon. the acidity is thought to be caused by the inflow of surface acid-sulphate waters into wells, while acidity in Mt. Apo is believed to be of deep origin.

2.0 BACKGROUND

Sulphur is widely distributed in nature. It occurs in the oxidised form as sulphate in the oceans and in evaporite rocks. in its native state in the cap rock of salt domes and in rocks of certain volcanic origin, and as reduced species in sulphide minerals of igneous. sedimentary or metamorphic origin (Faure. 1986). In magmatic-geothermal environments. sulphur occurs in different oxidation states. such as sulphates. sulphur dioxide and hydrogen sulphide. There are 4 stable isotopes of terrestrial sulphur: ^{32}S (95 1%), ^{33}S

(0.7496)) ^{34}S (4.2%) and ^{36}S (0.0296)(Jensen. 1967). Most of the studies and applications of sulphur isotopes have dealt with ^{32}S and ^{34}S, the 2 most abundant isotopes of this element.

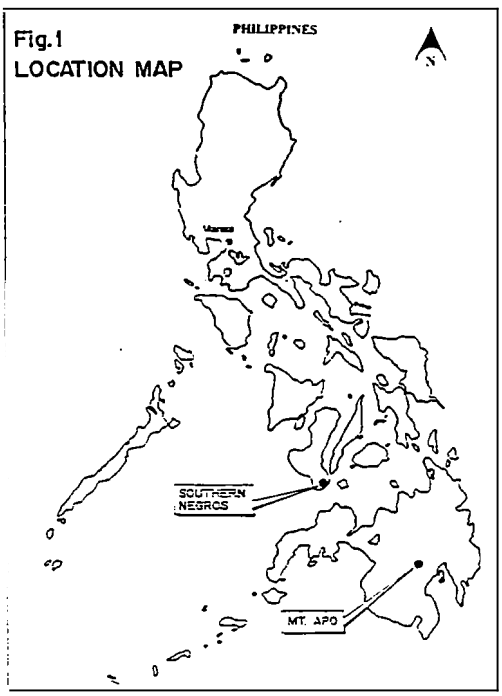
Like all other isotope determinations. the sulphur isotopic composition of a sample is expressed as $\delta^{34}S$, defined as its per mil $^{34}S/^{32}S$ ratio deviation relative to the accepted standard the troilite phase of the Canyon Diablo meteorite (CDT) (Ohmoto and Rye. 1979). To date, $\delta^{34}S$ variations of as much as 150‰ have been found as the heaviest sulphates have $\delta^{34}S$ >+90‰ and the lightest sulphides have $\delta^{34}S$ of around -65‰ (Hoefs. 1987).

Sulphur isotope fractionation at equilibrium conditions behave in such a way that the heavier isotope is enriched in species with stronger sulphur bonds. Thus. ^{34}S preferentially stays with the more oxidised sulphur species, and the general hierarchy of ^{34}S enrichment is as follows: $SO_4^{2-} > SO_3^{-} > SO_2 > S_x - H_2S - HS^{-} > S^{2-}$ (Ohmoto and Rye. 1979) and pyrite > sphalerite > chalcopyrite > galena in sulphide minerals (Faure, 1986). In sulphate-sulphide pairs at equilibrium. therefore, the sulphate can be expected to be enriched in ^{34}S compared to the contemporaneous sulphide.

Water, gas and mineral samples are analyzed for their sulphur isotope contents. Typically, water samples are analyzed for S in sulphates, gases for S in sulphides and sulphur, and minerals for S in both sulphates and sulphides. The mass spectrometer is used to determine isotopic ratios present in the sample. Extensive/detailed discussions on the theory of mass spectrometry are given elsewhere (e.g., Hulston and Shilton. 1958), and are not dealt with here.

3.0 APPLICATIONS

Two geothermal applications of sulphur isotopes are discussed in the section following. Discussion centres on two Philippine geothermal fields - Palinpinon (in Central Philippines) and Mt. Apo (in South-central Mindanao. Southern Philippines) (Fig. 1). Two fields are covered because of data constraints. For instance, oxygen isotope data for sulphate and water, used in the application of oxygen isotope geothermometry, are available for Mt. Apo field On the other hand there are numerous data on sulphate-sulphide fluid and mineral pairs for Palinpinon, which are most useful for the purely sulphur isotope geothermometers and sulphur species correlation.



All samples for sulphur isotope analysis were taken from either acid wells or acid thermal features. The main question which is hoped to be answered by the evaluation of S isotope data is the source of acid fluids in both these systems. At Palinpinon, the current postulate of acidity source is shallow or near-surface steam-heated acid-sulphate waters. These are believed to downflow through geologic structures, to mix with the deep Cl-fluid This mixture produces acidic discharges in some Palinpinon bores (Bayon, 1994). At Mt. Apo, the acidity is believed to be deep. probably due to direct magmatic fluid input into the system.

3.1 Geothermometry

Several sulphur pairs can be used for isotope geothermometry. Among them are SO_2- H_2S in volcanic gases, SO_4^{2-}- H_2S in thermal hot spring systems, sulphate-sulphide minerals (e.g., anhydrite-pyrite). pyrite-galena, sphalerite-galena and pyrite-

chalcopyrite. The last three have been used widely in hydrothermal mineral deposition studies. In geothermal systems. however, galena. sphalerite and chalcopyrite are rare. Pyrite is common and so is anhydnte. The sulphate-sulphidemineral system is. thus. more useful in geothermal studies. In addition to these pairs, oxygen isotope fractionation between dissolved sulphate and water in geothermal fluids can also be used as a geothermometer. In fact. past studies of the SO_4^{2-}-H_2O system show that this geothermometer is the most sensitive, as it re-equilibrates faster than the purely sulphur isotope geothermometers (Robinson, 1987).

To successfully apply the sulphur isotope geothermometers, certain assumptions have to be made. These are: (a) both phases are formed in equilibrium, (b) no isotopic exchange took place between the phases. or between one of the phases and a third sulphur species after the formation of the species (the equilibrium isotopic composition was frozen in), and (c) pure phases were separated for isotopic analysis (Ohmoto and Rye, 1979).

3.1.1 The SO_4^{2-}-H_2O System

Oxygen isotopes in dissolved SO_4^{2-} and water are involved in isotopic exchange while in solution. The reaction rate of this exchange is relatively fast, so that it records cooler O_2 isotopic equilibrium temperatures (< 300°C). This ability makes this geothermometer very useful in geothermal applications. as geothermal fluids are normally within this temperature regime. The accepted formula for the SO_4^{2-}-H_2O system is (Robinson, 1987):

$$T = [(2.88*10^6)/(\Delta^{18}O + 4.1)]^{1/2} - 273$$

where $\Delta^{18}O = \delta^{18}O_{SO4} - \delta^{18}O_{H2O}$ in ‰. and T is in °C (uncertainty range not discussed).

Tabulated below are the computed temperatures for a well and a surface thermal feature in Mt. Apo geothermal field made using this geothermometer. The isotopic composition of the water (H_2O) is taken from the baseline study in this field (Salonga. 1995) and are not the isotopic values for the same samples where the sulphate isotopes were measured. Although samples for water isotope analyses were also collected simultaneously with the S isotope samples. results are not available at this writing. Nevertheless. the water isotope values are not expected to differ much from those shown here.

le 1. Oxygen Isotopes in Water and Sulphate, Mt. Apo Geothermal Field

LOCATION	SOURCE/ YEAR	$\delta^{18}O$ (H_2O)	$\delta^{18}O$ (SO_4^{2-})	$\Delta^{18}O$	T (°C)
Mainit	1984	-9.84	+4.63	14.47	118
Hot Spring	1993	-7.59	+4.63	12.22	147
KN-3	webre	-2.87	+0.3	3.17	356
	reservoir	-4.44	+0.3	4.74	298
	condensate	-6.73	+0.3	7.0	236
	steam TD	-4.81	+0.3	5.11	286
	downhole	-4.43	+0.3	4.73	298
TM-2D	webre		-0.68		
TO-ID .	webre		-2.11		
parent fluid		4.13	+0.53**	4.66	300
(w/o spring)			-0.83	3.3	351

As seen from above, the calculated temperatures for the spring and well fluids range from about 150-300°C. For well KN-3, temperature estimates agree very well mith the measured temperature for the upper "steam zone" (condensate sample: 240°C), donnhole water (298°C) and water reduced to reservoir conditions (298°C; measured downhole temperature of the well is 300°C). Apparently. the weirbox sample collected was not in isotopic equilibrium, as th calculated temperature is too high (356°C). Likewise. the temperature estimated from steam in total discharge (286°C) does not closely correspond to the measured

aquifer temperature of 300°C. The effects of steam separation on $\delta^{18}O$ values for this and the weirbox sample may account for the temperature discrepancies. Taking the average of the $\delta^{18}O$ ratios in the well waters (KN-3, TO-1D and TM-2D) but excluding that for the spring, and using what is believed to be the parent fluid $\delta^{18}O$ for Mt. Apo (-4.13‰; Salonga, 1995), a temperature of 351°C is estimated. Again, this agrees with the interpreted temperature of parent fluid in this field (340-350°C; ibid).

Mainit hot spring is a steam-heated acid-sulphate spring located near the postulated upflow zone of the Mt. Apo hydrothermal system (Salonga, 1995). The temperature estimate given by this geothermometer is about 150°C, which can be taken as the temperature of steam/gas heating the surface meteoric water in this part of the field.

Based on the above results, it appears that the SO_4^{2-}-H_2O oxygen isotope geothermometer closely approximates measured downhole temperatures in Mt. Apo, and is thus applicable in this field.

3.1.2 The SO_4^{2-}-H_2S System

The most common sulphur species in geothermal fluids are dissolved sulphate and H_2S (either dissolved in liquid or present as a gas). To determine isotope equilibrium temperatures between these 2 sulphur species, the general formula used is (Robinson 1987):

$$T = [6.04*10^6 / (\Delta^{34}S_{A-B} - 2.6)]^{1/2} - 273,$$

where $\Delta^{34}S_{A-B} = \delta^{34}S_{sulphate} - \delta^{34}S_{H2S}$ and T = °C (uncertainty range not discussed).

The main problems associated with this geothermometer are the slow reaction rate and contamination. Because of the former, temperatures given by this geothermometer tend to be higher than measured bore temperatures, perhaps reflective of temperatures at greater depths. Furthermore, contamination effects such as bacterial reduction of sulphate at or near the surface have a tendency to disrupt preserved isotopic equilibrium between dissolved sulphate and hydrogen sulphide. Nevertheless, it has been proven to be useful in some instances.

Fluid $\delta^{34}S$ data from selected wells in Palinpinon and Mt. Apo are shown in Tables 2 and 3. Although most of these are for dissolved sulphate, a few for H_2S in gas are also available. In 3 wells at Palinpinon (NJ-6D, OK-9D, OK-10D) and 2 at Mt. Apo (TM-2D, TO-1D), $\Delta^{34}S$ for sulphate-sulphide pairs are given and the computed values for equilibrium temperatures are likewise shown.

Palinpinon Geothermal Field

For the fluid sulphur pairs, individual equilibrium temperatures are in the range of 300-400°C for $\Delta^{34}S$ of +15.9-+21.1‰. The dissolved sulphate in these pairs has $\delta^{34}S$ ranging from +14.6 to +20.6‰ (average at +17.17‰), while the H_2S has a $\delta^{34}S$ range of +0.4 to -3.2‰ (average at -0.89‰).

No well in the Palinpinon geothermal field, except perhaps for BL-ID, yields measured temperatures of ≥ 300°C. It appears that the SO_4^{2-}-H_2S system in Palinpinon is not in isotopic equilibrium at drilled depths, so that isotope temperatures do not correspond to those measured in wells (Fig. 2). As suggested earlier, the geothermometer is limited in its application because of slow reaction rate. Isotope equilibrium temperature estimates may reflect equilibrium of ^{34}S isotopes in dissolved sulphate and H_2S at deeper portions of the hydrothermal system.

Mt. Apo Geothermal Field

Temperatures estimated fiom this isotope geothermometer for wells TM-2D and TO-ID are 306°C and 276°C. respectively (Table 3). Well temperature estimates are in close agreement with measured temperatures of about 300°C and 265°C for TM-2D and TO-1D, respectively (M. Esberto, pers. comm.) (Fig. 2). These indicate isotope equilibrium between the sulphur species in the fluid at drilled depths.

Table 2. Fluid Sulphur Isotope Values, Palinpinon Geothermal Field

LOCATION	$\delta^{34}S$ (SO_4^{2-})	$\delta^{34}S$ (H_2S)	$\delta^{18}O$ (SO_4^{2-})	$\Delta^{34}S$	T (^0C)
PN-13D	8.8		2		
	21.5		1.13		
	174		11.67		
	18.9		1.74		
PN-18	8.1		9.62		
	17.8				
PN-20D	22.4		0.3		
	24.1		1.36		
PN-22D	21.6		0.25		
	21.5		0.86		
	18.2		4.72		
	21.6		0.11		
NJ-3D		-2.5			
NJ-5D	10.8		-2.0		
	14.3				
	17.8		1.67		
NJ-6D	14.6	-3.2		17.8	357
	18.0		-0.89		
BL-1D	20		0		
	23.0		1.83		
OK-9D	16.3	0.4	2.93	15.9	401
	20.9		8.91		
	17.1		9.51		
OK-10D	20.6	-0.24	6.42	21.02	300
		-0.5		21.10	298
	17.7		-0.24		
Kaipohan Sp.	-3.1		-1.82		
Mag-Aso pool	0.0		0.08		

*all values in ‰

TYPE	LOCATION	SOURCE	$\delta^{34}S$ (SO_4^{2-})	$\delta^{34}S$ (H_2S)	$\delta^{18}O$ (SO_4^{2-})	$\Delta^{34}S$	T(^0C)
FLUID	TM-2D	webre	17.4	-3.2	-0.68	20.6	306
	TO-1D	webre	18.2	-4.4	-2.14	22.6	276
	KN-3	weir	20.1		0.3		
	MAINIT	hot spring	13		4.63		
	APO SOLF.	gas vent		1.6			
	KUONG SOLF.	gas vent		-6.3			
	ADTAPAN	gas vent		-3.2			
	AGCO	gas vent		-2.2			
	MAND.	gas vent		-3.3			
MINERAL	APO SOLF.	pyrite		-5.4			
	KUONGSOLF.	pyrite		-3			
	TO-2D	pyrite		1.3			
	TO-ID	anhydrite	18.1				

3.1.3 Sulphate-sulphide mineral pairs

The most common and abundant (hydrothermal) sulphur mineral pair in geothermal systems is anhydrite-pyrite. Other sulphate minerals such as gypsum and alunite exist. but these are commonly non-cogenetic

with the pynte. Anhydrite is probably more coeval with the sulplude mineral than the other sulphates. Temperature estimates for the sulphate-sulphide pairs are possible using 2 equations (Ohmoto and Rye. 1979):

$$T = [2.76*10^3 / (\Delta^{34}S +/- 1)^{1/2}] - 273 \quad \text{for } T > 400^oC \ (+/-25^oC), \text{ and}$$

$$T = [2.16*10^3 / (\Delta^{34}S - 6 +/- 0.5)^{1/2}] - 273 \quad \text{for } T < 350^oC \ (+/-10^oC)$$

where $\Delta^{34}S = \delta^{34}S_{anhydrite} - \delta^{34}S_{pyrite}$ and T is in °C. Above about 300°C, the isotope temperature estimates generally agree with those obtained from other methods (i.e., fluid inclusions) so that isotopic equilibrium is likely achieved between sulphates and sulphides. Below 300°C, however, equilibrium is not always established (ibid).

Palinpinon Geothermal Field

Table 4 summarises $\delta^{34}S$ values for anhydrite and pyrite from a few wells in Palinpinon. Of these wells, BL-ID and NJ-6D have the most data for anhydnte-pyrite pairs. The calculated values for these pairs, as well as the temperature range based on the formulae given above, are also shown.

Table 4. Mineral Sulphur Isotope Values, Palinpinon Geothermal Field

SOURCE	DEPTH (m)	$\delta^{34}S$ ($CaSO_4$)	$\delta^{34}S$ (FeS_2)	$\delta^{18}O$ ($CaSO_4$)	$\Delta^{34}S$	T (°C) (±10°C)
BL-1D	1000	16.5	-2.2	4.11	18.7	322-345
	1050	22.7	-1.4	6.37	24.1	228-242
	1150	11.3		2.51		
	1600		-3.6			
	1710	13.6	-4.6	6.37	18.2	333-358
	2030		-31.5			
	2030		-27.3			
	2700		-0.1			
NJ-6D	1380	11.6	-1.0	4.35	12.60	475-537
	1380		0.4		12.0	492-559
	1750	19.9		2.9		
	2460	27.1	-1.3	1.11	28.4	178-189
PN-20D			-0.7			
PN-22D		20.8		1.0		
		22.4		0.8		
OK-10D		16.95		4.1		
		23.13		1.7		
		22.97		1.4		
OK-6D			-3.2			

*all values in ‰

Anhydrites in mineral pairs from these wells have a rather wide spread of $\delta^{34}S$ values, ranging from +11.6‰ to +27.1‰ (average = +18.3‰). The pyrite, on the other hand, has a narrow range between +0.4‰ and -4.6‰ (average = -1.7‰). Calculated temperatures vary from a low of about 180°C (NJ-6D, 2460m) to a high of 540°C (NJ-6D, 1380m). BL-ID temperatures range from 230°C to 360°C.

Again, most of the calculated equilibrium temperatures are above those measured in the 2 wells (<300°C for NJ-6D, 300°C at BL-1D bottomhole). If isotopic equilibrium of the sulphur species in the fluid source for anhydnte and pyrite is assumed these temperatures may represent the deeper portions of the convecting system.

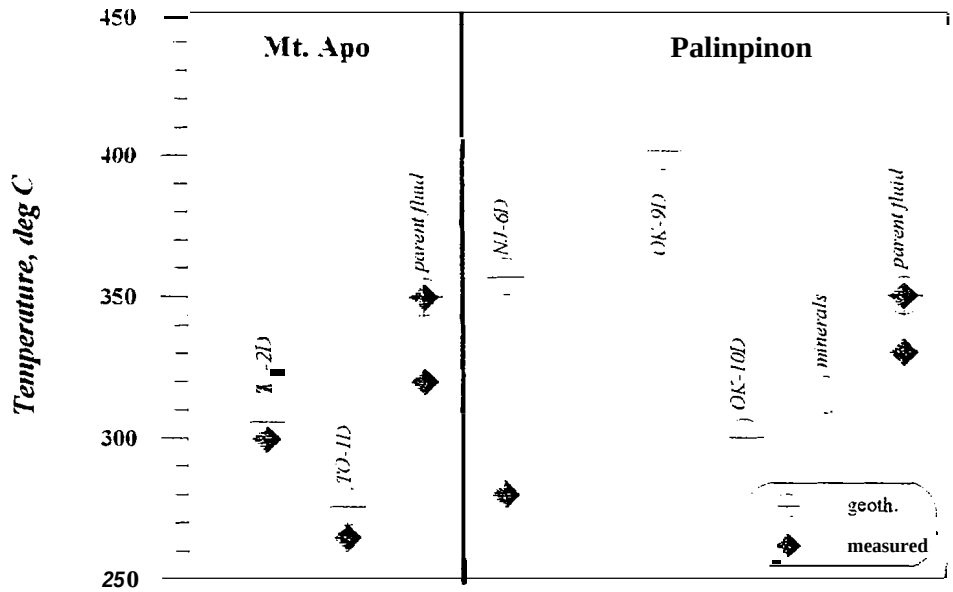


Figure 2. Comparison of S isotope geothermometry and actual well measured temperatures.

Mt. Apo Geothermal Field

There are no anhydrite-pyrite pairs sampled for S isotope analysis in this field, as shown in Table 3.

3.2 Possible Sources of Sulphur in Geothermal Fluids

Palinpinon Sulphur Species

Fluid samples from Palinpinon wells exhibit $\delta^{34}S$ in sulphate from +8.8‰ to +23‰, with an average of +18.04‰ (Table 2). H_2S samples. on the other hand have $\delta^{34}S$ behveen -3.2‰ to +0.4‰, averaging at -1.2‰. **A** graph of these values (Fig. 3) show the range of $\delta^{34}S$ for H_2S and SO_4^{2-}, and their averages. compared to averages for some other sulphur species. For anhydnte **and** pyrite in the same field. $\delta^{34}S$ in sulphate is more consistent compared to the dissolved species. rangng between +11.3‰ and +27.11‰ (average = +19.1‰) (Table 4); $\delta^{34}S$ in pyrite falls between -3.6‰ and +0.4‰ (average = -1.6‰), although 2 pyrite samples yielded very depleted $\delta^{34}S$ values of -27.3 and -31.5‰. Figure 3 also shows the range of values of $\delta^{34}S$ for minerals graphically. The range of values for fluid and mineral $\delta^{34}S$ in SO_4^{2-} and sulphide seem to be in close agreement.

The main source of geothermal fluid in Philippine systems **is** believed to be deeply circulating meteoric water. with **3** mixture of magmatic water coming from a degassing magma at some depth below the geothermal environment. Most if not all of the geothermal gases (including H_2S) are thought to have originated from a magmatic source. as are Cl **and** a few other ions. Hydrogen **and** oxygen isotopic studies have substantiated the above theories. The $\delta^{34}S$ of H_2S. although showing a scatter. lie close to the 0‰ value believed to represent magmatic-derived sulphur species. The **proximity** of $\delta^{34}S$ in H_2S to the magmatic value suggests that H_2S in directly or indirectly derived from the deep magma. $\delta^{34}S$ in H_2S of other Philippine geothermal systems (e.g.. Leyte. Bacon-Manito: unpublished **data)** has a consistent average of $\bar{}$ -1.5‰. This uniformity indicates that $\delta^{34}S_{H2S}$ from magmatic fluids of **island** arc melts. at least in the Philippines. is characteristically slightly depleted in ^{34}S compared to mantlederived melts. and that the H_2S in geothermal well discharges is directly derived from the magma. Slight deviations from the 0‰ $\delta^{34}S$ of mantle sulphur may be due to crustal contamination along the path of ascent of the andesitic magma. or later stage isotopic equilibration.

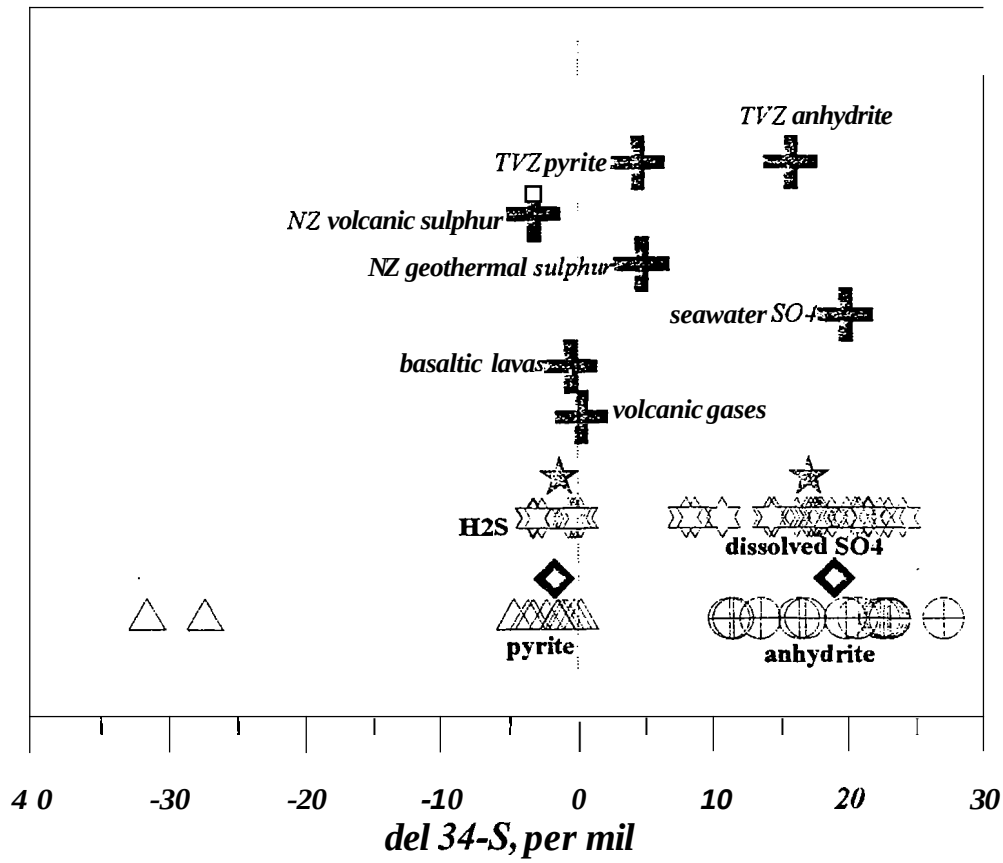


Figure 3. Range of S isotope ratios for Palinpinon; other data (+) from Steiner and Rafter (1966) and Torrsander (1988)

H_2S can also be indirectly derived from a magmatic source by way of disproportionation of SO_2 gas. At magmatic temperatures, SO_2 and H_2S are the most abundant sulphur species; fluids derived from mafic magmas tend to be H_2S rich, while fluids coming from silicic melts may be either H_2S or SO_2-rich (Ohmoto and Rye. 1979). Below about 400°C, SO_2 disproportionates to H_2S and SO_4^{2-} in the presence of H_2O, and follows the reaction (Ohmoto and Rye, 1979):

$$4H_2O_{(g)} + 4SO_{2(aq)} = H_2S_{(aq)} + 2H^+ + 3HSO_4^-$$

Thus, at 400°C, SO_4^{2-} becomes the dominant oxidised sulphur species

The amount of H_2S and dissolved sulphate in fluid discharges from wells BL-1D, NJ-6D, PN-20D and PN-22D (where chemical data are available) have radically increased with time. Whereas fluids in these wells were initially neutral-pH with low sulphate and H_2S contents during the first stage of discharge testing in 1991, 1984 and 1982 (for BL-ID, NJdD and PN-20D/PN-22D, respectively), the chemistry of each well has since shifted so that acidic fluids with high SO_4^{2-} and H_2S now dominate the discharge. A summary of the concentrations of sulphur species in the well discharges, referred to as initial (for near neutral fluids) and final (for acidic fluids), are shown below.

Table 5. Concentrations of Sulphur species in selected wells in Palinpinon

	BL-1D		NJ-6D		PN-22D	PN-20D
	initial	final	initial	final	final	final
H_2S (mm/100m TD)	15	48	8	28	18	18
ppm H_2S	283	906	151	529	340	340
ppm SO_4^{2-}	300	485	30	500	366	317
m H_2S	8.3E-3	2.7E-2	4.4E-3	1.6E-2	1.0E-2	1.0E-2
m SO_4^{2-}	3.1E-3	5.1E-3	3.1E-4	5.2E-3	3.8E-3	3.3E-3

The interpreted hydrology of Palinpinon is such that wells BL-1D and NJ-6D are closer to the upflow zone than PN-20D and PN-22D (J. Seastres. pers. comm.). A closer look at wells BL-ID and NJ-6D is attempted to see if the sulphate comes from SO_2 disproportionation neglecting shallow sulphate contribution (discussed later). For the amounts of sulphate in BL-1D and NJ-6D, equivalent amounts of H_2S (molal) produced from the reaction are $1.7*10^{-3}$ for both wells. This is 11-12% of the total hydrogen sulphide in the fluid and there is clearly a large excess of H_2S which cannot be accounted for by sulphur dioxide disproportionation. In any case, the amount of SO_2 needed to produce the total SO_4^{2-} and 12% of the H_2S in well fluids is about $6.9*10^{-3}$ moleskg, or 440 mg/kg (12.5 mmoles/100 moles steam). Given that equilibrium isotope fractionation between sulphate and H_2S results in the sulphate being enriched in ^{34}S by about 70% compared to the contemporaneous H S (Thode, 1963), the "parent" SO_2 should have a $\delta^{34}S$ of about +2.1‰ (this figure comes from fluid A3 S in NJ-6D, 17.8‰, since there is none for BL-ID). The estimated S isotopic signature of the parent SO_2 is reasonable for magmatic gas. as it lies within the range for fluids of magmatic origin (Ohmoto and Rye, 1979). The $\delta^{34}S$ of the associated H_2S (not the disproportionation product), considering the $\delta^{34}S$ of SO_2, should be in the vicinity of 0‰ (H_2S is slightly depleted in ^{34}S compared to cogenetic SO_2). $\delta^{34}S$ of dissolved sulphate and sulphide, and the theoretical $\delta^{34}S$ of the parent So,?, are evidences pointing to disproportionation as a possible major source of dissolved sulphate in geothermal fluids. But for H_2S, the contribution of the disproportionation reaction is minor compared to the total concentration in the well fluids. A direct magmatic input of H_2S is therefore invoked to account for the excess in hydrogen sulphide. since $\delta^{34}S$ in well H_2S at Palinpinon and the magmatic H_2S $\delta^{34}S$ signature are very similar.

The lower amounts of dissolved sulphate and H_2S in PN-20D and PN-22D is probably a consequence of sulphate and sulphide mineral deposition along the fluid path between the upflow, BL-1D/NJ-6D and the Puhagan sector, thus reducing the amount of S species in the fluid tapped by the PN wells.

The sulphur isotope data for fluids in Palinpinon contradict the theory that acidity is primarily caused by the downflow of surface acid-sulphate waters and mixing with neutral Cl fluid in wells (Bayon, 1994). If surface acid waters were indeed flowing into wells, the $\delta^{34}S$ of dissolved sulphate should be close to that of H_2S in fluid, since this sulphate comes from oxidation of H_2S at near-surface levels, and the sulphate adapts the isotopic signature of the oxidised sulphide because of slow equilibration at low temperatures. This observation was noted in the study of sulphur isotopes in sulphur minerals from geothermal wells in the Taupo Volcanic Zone (Steiner and Rafter, 1966). Supergene alunite ($\delta^{34}S$ = +5.6‰) was found to have $\delta^{34}S$ close to the hypogene pyrite from which it was interpreted to derive ($\delta^{34}S$ = +5.4‰). In contrast, hypogene anhydrite. thought to be cogenetic with the pyrite. had $\delta^{34}S$ of +16.1‰ (ibid). A similar situation exists in Palinpinon. Two samples from acid-sulphate cold springs (Kaipohan and Mag-Aso, Table 2), representing the near-surface steam-heated sulphate waters. have $\delta^{34}S$ values of -3 and 0‰. These are very close to the $\delta^{34}S$ of H_2S, and should have been reflected in the well fluid dissolved sulphate $\delta^{34}S$ if the two types of sulphates were related. Although there are well samples with low $\delta^{34}S$ in SO_4^{2-} (i.e., 8.8‰ in PN-13D, 8.1‰ in PN-18. & 10.8‰ in NJ-SD), which may be interpreted as a mixture of surface acid waters and the deep geothermal fluid most of the $\delta^{34}S$ in well SO_4^{2-} show that these are far more enriched. If there is surface acid-SO_4^{2-} contribution to well fluids. this is minor compared to the deep origin of dissolved sulphate discussed above.

Another possible source of dissolved sulphate is the oxidation of H_2S in boiling zones. as presented by McKibben and Eldridge (1990), according to the reaction:

$$H_2S_{(aq)} + 4H_2O = SO_4^{2-} + 2H^+ + 4H_{2(g)}$$

Since boiling zones in geothermal environments are almost always present. usually at temperatures <300°C. isotopic equilibrium between the residual H_2S and the produced SO_4^{2-} cannot always happen. To what extent boiling contributes to the amount of dissolved SO_4^{2-} present, and its isotopic effect on the total SO_4^{2-} in solution, cannot be answered The wide range of $\delta^{34}S$ in sulphates, nevertheless, may indicate that some sulphates do come from H_2S oxidation at boiling depths.

The presence of rather 'heavy'' sulphate in Palinpinon fluids are thought to be connected (i.e., only an initial postulate) to a seawater source by A.G. Reyes (pers. comm.). There is. after all, a thick sedimentary sequence underlying the young andesitic volcanic deposits in the field This, however, needs to be looked at in more detail. Well discharge chemistry in this field do not indicate any significant contribution of seawater (Cl content in the reservoir of 4000 mglkg). If there is seawater sulphate contribution, then it should be determined why the geothermal fluid appears to be preferentially taking in sulphate over Cl. In addition, the effect of sulphur-reducing bacteria on the S isotope compositions of H_2S and SO_4^{2-} in well fluids is believed to be absent, for the primary reason that the temperatures in wells are too high. These organisms are active where there is a combination of sulphate ion, organic matter, and temperatures <75°C (Ault and Kulp. 1959). The environments where the bacteria thrive, therefore, are in recent marine sediments, at the bottom of lagoons or seas, or the ocean surface. At subsurface geothermal temperatures. no sulphur-reducingbacteria are expected to be active; in surface acid-sulphate thermal features, these may be present and thus influence the $\delta^{34}S$ in sulphate and/or H_2S.

The $\delta^{34}S$ values of pyrites and anhydrites in Palinpinon approximate those for H_2S and SO_4^{2-} in fluids. respectively. This signifies that the pyrite derives its sulphur from H_2S, while dissolved sulphate supplies the sulphur for anhydrite. The anhydrite and pyrite may have precipitated from a fluid at a temperature of >300°C.

The largely S isotopedepleted pyrite samples from 2030m depth in BL-ID (-27.3 & -31.5‰) cannot be explained. These values are highly anomalous with respect to the other pyrites in the well and across the field, although much more depleted species occur elsewhere (e.g., USA, Jensen, 1967) (Hoefs, 1987). Large $\delta^{34}S$ variations of as much as 19‰ have been discovered in a single mineral over distances of only 25mm, as detected from SHRIMP microprobe analyses, in Salton Sea (McKibben and Eldridge. 1989) and Valles Caldera (McKibben and Eldridge, 1990) . These variations have been attributed to changes in fluid characteristics during boiling. when the minerals were precipitated. Evaluating the BL-ID discrepancy needs more in-depth studies, and no explanation is forwarded here.

Mt. Apo Sulphur Species

Neglecting the $\delta^{34}S$ value for Mainit hot spring, the $\delta^{34}S$ values of Mt. Apo fluid are similar to those in Palinpinon, so that similar sources for geothermal sulphur are most likely. At well TO-ID, where the postulated upflow zone is close, the dissolved sulphate and H_2S concentrations in well discharge are $2.4*10^{-3}$ and $1.2*10^{-2}$ moleskg, respectively (Salonga, 1995). Sulphur dioxide disproportionation translates to the above dissolved sulphate, and $8.0*10^{-4}$ moleskg of H_2S as products. Again. the total H_2S in the well fluid is 93% in excess of that produced from the disproportionation, so that most of the H_2S comes directly from magma. The amount of SO_2 needed to produce total SO_4^{2-} and <7% of H_2S is $3.2*10^{-3}$ moleskg (or 205 mg/kg, 6 mmoles/100 moles steam). The parent SO_2 is estimated to possess $\delta^{34}S$ of around +2.4‰.

Mineral sulphate and sulphide $\delta^{34}S$ are similar to those for dissolved sulphate and H_2S, respectively. As at Palinpinon, H_2S supplies sulphur to pyrite and dissolved sulphate is the source of sulphur for anhydnte in Mt. Apo.

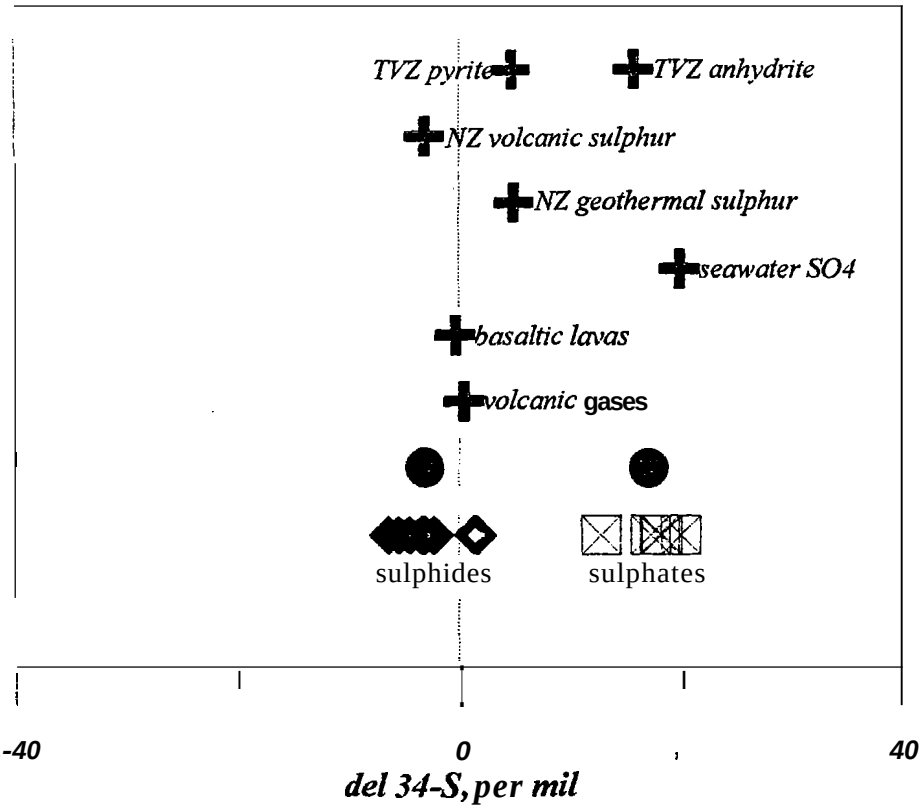


Figure 4. Range of S isotopes in Mt. Apo fluid; other data (+) from **Steiner and Rafter (1966) and Torrsander (1988)**

4.0 CONCLUSIONS

The major applications of sulphur isotopes to geothermal system investigations are geothermometry and the identification of the possible sources of sulphur present in fluids and hydrothermal minerals. As applied to 2 Philippine geothermal systems, the dependability of the sulphur isotope technique depends on the type of system to which it is applied.

At the Palinpinon geothermal field, sulphur isotope geothermometry results using dissolved sulphate and H_2S and anhydrite-pyrite mineral pairs, reflect isotope equilibration temperatures of deeper portions of the hydrothermal system below the geothermal environment. A consistent temperature estimate of ≥330°C is calculated, representing the isotopic equilibrium temperature of the different sulphur species. Below this temperature, S isotope species do not re-equilibrate, thus the non-agreement between S isotope geothermometry and well measured temperatures. In the Mt. Apo geothermal system, on the other hand, fluid sulphur isotope and oxygen isotope geothermometry give temperature estimates very close to those measured in wells, and parent fluid temperature estimation (340-350°C). The applicability of S isotope geothermometry to Mt. Apo waters may possibly be connected with the fact that sulphur species in solution control fluid behaviour and fluid-mineral equilibrium products in this area, as discussed by Salonga (1995).

Most of the H_2S in fluids at both Palinpinon and Mt. Apo are derived directly from a magma. The isotopic signature of H_2S ($\delta^{34}S$) is -3 to -1‰. Dissolved sulphate, with average $\delta^{34}S$ of +17 to +18‰, comes from 2 possible sources: SO_2 disproportionation and H_2S oxidation at boiling depths. For the first possible source. the parent SO_2 is estimated to have $\delta^{34}S = +2.0$‰; the other possible source of dissolved sulphate cannot be distinguished isotopically from the rest of the sulphate in solution. Anhydrite derives its sulphate

from dissolved SO_4^{2-}, while pyrite sulphur is being supplied by H_2S. Isotopic compositions of these minerals are close to their respective sources.

Sulphur isotope data contradicts the theory that shallow steam-heated waters are the major source of sulphate in acid wells in Palinpinon. This particular type of fluid has $\delta^{34}S$ in sulphate of -3 to 0‰

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