INVESTIGATION OF DISSOLVED SULPHATE IN VARIOUS GEOTHERMAL FIELDS OF SUMATRA USING OXYGEN AND SULPHUR ISOTOPES

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Received 31 March 2006; Accepted 11 April 2006

ABSTRACT

There are at least 30 high temperature systems; eleven active volcanoes, five degassing volcanoes and one caldera volcano controlled by Sumatra Fault Zone over a length of 1700 km. To understand this geothermal field system, some information about geochemistry including isotope composition in its fluid is needed. Sulphur-34 and oxygen-18 isotopes in dissolved sulphate pair have been used to determine the origin of acidic fluid of sulphate and to evaluate the process involved. The fluids from eight hot springs, two fumaroles, four deep wells and crater have been collected in along Sumatra geothermal fields. Sulphur-34 ($\delta^{34}S_{(SO4)}$, $^0/_{00}$ CDT) and oxygen-18 ($\delta^{18}O_{(SO4)}$, $^0/_{00}$ SMOW) in sulphate is analyzed according to Robinson-Kusakabe and Rafter method, respectively. The $\delta^{34}S_{(SO4)}$ values from Sibayak wells are more enriched of 16.8 $^0/_{00}$ to 18.2 $^0/_0$ that may indicate the dissolution of anhydrite minerals or isotope partitioning in hydration of SO_2. The $\delta^{34}S_{(SO4)}$ values from two fumaroles (Pusuk Bukit – North Sumatra and Rantau Dadap – South Sumatra) are at depleted value of –0.15$^0/_{00}$ and 1.8$^0/_{00}$, those are close to $\delta^{34}S$ from magmatic sulphur. In general, the $\delta^{34}S_{(SO4)}$ of springs spread in a wide range of 5.25$^0/_{00}$ to14.2$^0/_{00}$ and show a mixing process between atmospheric sulphate and sulphate from deep wells. The $\delta^{18}O_{(SO4)}$ from wells exhibits depleted value around –3.6$^0/_{00}$ suggesting that 87.5% of sulphate oxygen is derived from groundwater oxygen and 12.5% is derived from atmospheric molecular oxygen in sulphide oxidation reaction. In the other hand, hot springs (except Semurup), crater and fumaroles have enriched value of $\delta^{18}O_{(SO4)}$. These enriched values suggest that a higher percentage of atmospherically derived oxygen compared to those from the depth.

Keywords: *isotope, geothermal, Sumatra*.

INTRODUCTION

The whole of western Sumatra geological formation is a part of an active volcanic arc that has a length over 1700 km. There are at least 30 high temperature systems (reservoir temperatures > 200 ^oC) along the active Sumatra Arc that transfer heat from crustal intrusion to the surface. These systems together with eleven active volcanoes, five degassing volcanoes and one caldera volcano (Lake Toba), are controlled by Sumatra Fault Zone. At least half of the active and degassing volcanoes are associated with volcanoes geothermal reservoirs containing magmatic gases and acid fluids [1].

To understand this geothermal field system, some information about geochemistry composition of fluid is needed, including isotope geochemistry. The chemical and isotopic compositions of geothermal fluid components provide information about sub surface reservoir temperature, their origin of fluid and recharge area as well as flow patterns. In addition, cooling processes of the fluid during ascent to the surface due to heat conduction, admixtures with cold water or steam loses can be studied by means of chemical and isotopic compositions as well as their variations [2-4].

Isotope techniques are a valuable tool in geothermal prospecting as well as in studying the evaluation of geothermal fields as a consequence of exploitation. Since 1970, some natural isotopes such as ^{18}O, ^{13}C, and ^{2}H, ^{34}S have been applied in geothermal fields to evaluate their reservoir temperature in addition of chemical data. These isotopes are contained in some of the major fluid components, for examples: water or steam, carbon dioxide, sulphur dioxide, methane, dissolved sulphate and sulphide [2,3]. Indonesia has applied an ^{18}O and ^{34}S isotope in dissolved sulphate since 1992 namely after installing of sulphide and sulphate preparation line and Delta-S mass spectrometer in hydrology laboratory of PATIR-BATAN.

Over three decades, sulphur isotope abundances have been used to unravel the geochemistry of natural sulphates. In recent years oxygen isotope composition of sulphate have been applied in hydrological as well as geothermal research. New Zealand has applied both isotopes in many geothermal system and volcanoes since early 1960's for geothermometry, but recently these isotopic data have been used for residence time and for determining the origin of sulphur [3].

In this investigation, ^{18}O and ^{34}S in dissolved sulphates are used to determine the origin of sulphates

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and to evaluate the process influencing the abundance of both isotopes. Fluid samples are collected from crater, wells, fumaroles and hot springs in Sumatra geothermal fields.

EXPERIMENTAL SECTION

Material

The materials used in this experiment were $HgCl_2$, liquid nitrogen, acetone p.a, CO_2 gas high pure 99.9% , graphite, distilled water , $BaCl_2$ 10%, dry ice, Cl^- anion exchange resin (Dowex 50-100 mesh), HCl 6 M, NaCl 1 M, Cu_2O, $AgNO_3$ 0.1N M

Equipments

The equipments used in this experiment were Sira 9 ISOGAS mass spectrometer and isoprep ^{18}O line, Delta S Finnigan mass spectrometer, sulphate preparation line, sulphide preparation line, analytical balance, pH meter, digital thermometer, agate mortar, hot plate, platinum foil, dewar, condenser and separator, 20-mL glass vials and 10-L plastic bottles, glass column: internal diameter 28 mm and height 200 mm.

Procedures

Sampling methods

Fluid samples were collected in 20 mL glass vial, for O-18 in water analysis. These samples must be sealed tightly to prevent evaporation process. For ^{18}O and ^{34}S in dissolved sulphate, the fluid samples were collected in 10-Lt plastic bottles or depend on their sulphate content, then 1 mg $HgCl_2$ was added for sulphate preservation from bacterial activities. For collecting fluid samples from production wells, condenser and separator were installed at their wellheads and used to separate the liquid fluid from vapor.

Analysis of O-18 isotope in water [5]

Isotope of ^{18}O in water was analyzed according to Epstein-Mayeda method. Analysis was based on carbon dioxide released from ^{18}O isotopic exchange reaction between water samples and CO_2 reference. About 2 mL water samples in vessel reaction, which has been evacuated, were flown by CO_2 gas reference and shaked for overnight at constant temperature (usually 25 °C) in order to equilibrate both compounds. The following isotopic exchange reaction will occur:

$$H_2\,^{18}O_{liquid} + C\,^{16}O_{2\ gas} \rightleftharpoons H_2\,^{16}O_{liquid} + C\,^{18}O_{2\ gas} \quad (1)$$

The reaction above was occurred in isoprep-18 consisting of 24 vessel reactions in water bath and connected directly to mass spectrometer. The result was isotopic ratio of ^{18}O to ^{16}O.

Preparation of CO_2 gas for ^{18}O isotope analysis in dissolved sulphates [6].

^{18}O in dissolved sulphates from geothermal fluids was analyzed according to Rafter method. For pretreatment purpose, sulphate concentration should be determined previously. If sulphate concentration in fluids is higher than 50 ppm, the samples can be directly precipitated as $BaSO_4$ by adding $BaCl_2$ whereas the low sulphate samples should be passed through the ionic resin column. Ionic resin column was conditioned by eluting 150 mL of HCl at a rate of 4-5 mL/min and then 300 mL of distilled water at the same rate. About 10 L of filtered sample was passed through the column at flow rate of 150-200 mL/min, allowing the sulphate compound to be absorbed completely. 300 ml of NaCl was eluted through column at a flow rate of 1 mL/min in order to dissolve the absorbed sulphate then this concentrated sulphate was put in beaker glass. This sample was reduced its pH to 4 by dropping 10 % HCl and heated (90 – 100 °C) to remove CO_2 gas. An amount of $BaCl_2$ was added to form the white precipitation of $BaSO_4$.

About 50 mg precipitation of $BaSO_4$ was grinded with graphite. This sample was transferred to platinum boat and placed to reactor in sulphate preparation line. Reduction process was taken place at temperature of 1200°C under vacuum condition, its reaction as follow:

$$BaSO_4 + 3C \rightleftharpoons BaS + CO_2 + 2CO \quad (2)$$

The released water vapor was trapped using acetone-dry ice mixture (about -78 °C) whereas CO and CO_2 gas were passed and trapped in a discharge tube which was placed in liquid nitrogen dewar (-196 °C). Conversion of CO to CO_2 gas was taken place under high voltage current (1.2 KV), which passed through two platinum electrodes in the discharge tube. The evolved CO_2 gas was transferred to a sample bottle and ready to be injected to mass spectrometer.

Preparation of SO_2 gas for ^{34}S isotope analysis [7]

Analysis of ^{34}S in dissolved sulphates was conducted in sulphide preparation line according to Robinson-Kusakabe oxidizing method. Samples of dissolved sulphate should be in the form of Ag_2S. Sulphate reduction as explained above would remain in the form of BaS that can be precipitated as Ag_2S by adding $AgNO_3$. The important process in sulphide preparation line consist of some steps that are evacuating line, burning samples at 800-1100 °C, and collecting SO_2 gas. About 20-30 mg of Ag_2S that have been grinded with 60-80 mg Cu_2O were placed in platinum foil and then inserted in reactor. This line can be loaded with six samples in one running through queue system. After evacuating line completely, warming samples at about 100 °C was started in which to release water vapor and other contaminating gases 1998.

Table 1. Locations, various manifestations, temperature and pH data of Sumatra geothermal fields

No.	Code	Locations	Manifestations	Temp. (^oC)	PH
1	TSA	Tambang Sawah-Bengkulu	Spring	96,2	7
2	WP	Waipanas-Lampung	Spring	93	7
3	SLW	Seulawah-Aceh	Spring	84	7
4	RDD-7	Rantau Dadap-Baturaja-Sumsel	Fumarole	98	<1
5	RDD-8	Rantau Dadap-Baturaja-Sumsel	Spring	85	7
6	Crater	Sibayak-Sumut	Crater		
7	SBY-3	Sibayak-Sumut	Well		
8	SBY-4	Sibayak-Sumut	Well		
9	SBY-5	Sibayak-Sumut	Well		
10	SBY-6	Sibayak-Sumut	Well		
11	SMR	Semurup-Kerinci-Jambi	Spring	95	6,7
12	PBT-1	Pusuk Bukit-Samosir-Sumut	Fumarole	65	2
13	PBT-2	Pusuk Bukit-Samosir-Sumut	Spring	76	2
14	RNT-3	Samosir-Sumut	Spring	82	3
15	SBL-1	Samosir-Sumut	Spring	45	<1

that could be trapped in chiller-1 kept at temperature of -80 ^oC. Sample was burned at the temperature of 800-1100 ^oC in 8 minutes to release SO_2 gas completely, 99% to 100% as theoretical yield of SO_2. This gas was trapped at temperature of -135 ^oC in chiller-2 after purifying at -80 ^oC in chiller-1 whereas CO_2 gas will be pumped out. By heating chiller-2 at -80 ^oC, SO_2 gas was re-evaporated and transferred to bottle sample dipped at liquid nitrogen temperature. SO_2 gas was injected to Delta S mass spectrometer to measure isotopic ratio of S-34 to S-32. Sulphide oxidation follows this reaction:

$$Ag_2S + 3\,Cu_2O \rightleftharpoons 6\,Cu + SO_2 + Ag_2O \qquad (3)$$

Measurements of isotopic ratio value [2,4,6]

Isotopic ratio value was expressed with (delta) notation in per mill ($^0/_{00}$) and defined as follows:

$$\delta\ (^0/_{00}) = \frac{R_{sample} - R_{reference}}{R_{reference}} x1000 \qquad (4)$$

Where the "R" is, in the case of water, the $^{18}O/^{16}O$. As reference for oxygen and deuterium in water are SMOW international standard (Standard Mean Ocean Water). Whereas $^{18}O/^{16}O$ isotope ratio of sulphates or carbonates should be compared to PDB-barium carbonates international standard (Pee Dee Balemnitella). To simplify data interpretation, mostly, this value was related to $^{18}O/^{16}O$ in water samples that has SMOW standard. Conversion of PDB to SMOW standard followed to this equation:

$$\delta^{18}O_{Sample}\,(^0/_{00})_{SMOW} = \delta^{18}O_{Sample}\,(^0/_{00})_{PDB} + 1.04143 \qquad (5)$$

The same as oxygen isotope ratio, the "R" of sulphur is $^{34}S/^{32}S$ and expressed as $\delta\ ^{34}S$ related to CDT (Canon Diablo Treolite –FeS) international standard.

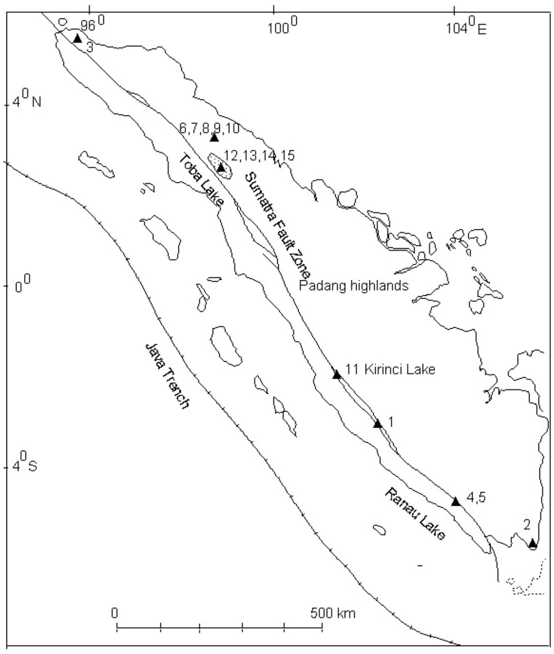

Fig 1. Sampling location hot springs, wells, fumaroles and crater along Sumatra geothermal fields.

RESULT AND DISCUSSION

Sampling locations of some hot springs, fumaroles, wells and crater along Sumatra geothermal fields are shown at Fig 1 whereas the kind of manifestations of each sites, locations and in-situ measurements such as pH and temperature are presented at Table 1.

Temperature of those fluids, in general, is in the range of 45 ^oC to 98 ^oC whereas pH average measurements of springs fall at neutral pH but few of them and fumaroles show acidic fluids in low pH even

Table 2. Isotope data of ^{18}O of water, ^{34}S and ^{8}O of dissolved sulphates in various geothermal fluids of Sumatra

No.	Code	δ ^{18}O (H_2O) ($^{0}/_{00\ SMOW}$)	δ ^{18}O (SO_4) ($^{0}/_{00\ SMOW}$)	δ ^{34}S (SO_4) ($^{0}/_{00\ CDT}$)
1	TSA	-7.20	1.42	14.20
2	WP	-6.50	2.13	13.90
3	SLW	-6.20	16.70	14.00
4	RDD-7	-2.30	6.60	-0.15
5	RDD-8	-8.60	3.96	12.50
6	crater	-10.00	2.64	3.47
7	SBY-3	-9.40	-3.07	18.20
8	SBY-4	-8.90	-3.77	16.80
9	SBY-5	-9.20	-3.67	17.13
10	SBY-6	-9.16	-3.87	17.87
11	SMR	-4.70	-4.90	18.90
12	PBT-1	-8.40	7.56	1.80
13	PBT-2	-7.10	4.43	7.20
14	RNT-3	-9.10	8.67	8.63
15	SBL-1	-9.00	2.10	5.25

less than 1. Hochstein has classified some geothermal high temperature system in Sumatra, which some sampling locations were also collected in this experiment. The high temperature in Sumatra basin is probably caused by cooling of deep intrusions or some input in basement granites or deep lateral flows of heated fluid or some combinations of these mechanisms [1].

As mentioned above that the objective of this experiment is to evaluate the state of sulphur and oxygen isotopes of dissolved sulphates from various manifestations in Sumatra geothermal fields and hopefully will answer the question of the origin of acidic fluids through the correlation both isotopes. Oxygen isotope in water is also enclosed in these results in order to know the percentage of water in oxidation reaction of sulphides. Isotope data of ^{18}O in water, ^{34}S and ^{18}O of dissolved sulphates in various geothermal fluids of Sumatra are presented at Table 2.

Presented in Fig 2 are the results of sulphur (δ ^{34}S, $^{0}/_{00}$ CDT) and oxygen (δ ^{18}O, $^{0}/_{00}$ SMOW) isotope analysis in the pair of dissolved sulphates of geothermal fluids. Based on the δ $^{34}S_{(SO4)}$ value from all manifestation samples analyzed, they can be grouped in three, namely: (a) δ $^{34}S_{(SO4)}$ > 16 $^{0}/_{00}$CDT, (b) near $0^{0}/_{00}$CDT and (c) $0^{0}/_{00}$ < δ $^{34}S_{(SO4)}$ $^{0}/_{00}$CDT < 16 $^{0}/_{00}$.

Fluids from deep wells such as SBY 3,4,5,6 (SBY 3 well is approximately 600 m depth) have a narrow range of δ $^{34}S_{(SO4)}$ value from 16.8 $^{0}/_{00}$ to 18.2 $^{0}/_{00}$, SMR spring has also the similar δ $^{34}S_{(SO4)}$ to SBY wells (group a) but they do not exceed to 21 $^{0}/_{00}$. These enriched value, relative to other fluids, the range of δ $^{34}S_{(SO4)}$ in deep fluid of SBY and SMR spring are rather close to $+21^{0}/_{00}$ value of gypsum ($CaSO_4$ $2H_2O$) and its anhydrite ($CaSO_4$) of marine evaporites in sedimentary strata but significantly far from the 0±3 $^{0}/_{00}$ value of magmatic dissolved sulphur [8,9]. Mineral of gypsum and anhydrite as major evaporate sulphates have δ $^{34}S_{(SO4)}$ value 10 $^{0}/_{00}$ to 27 $^{0}/_{00}$ [4], hydrothermal anhydrite of Mt. Pinatubo has an average composition of δ $^{34}S_{(SO4)}$ value +20 $^{0}/_{00}$ [8]. Unfortunately, $^{34}S_{(SO4)}$ of anhydrite samples from SBY were not analyzed in this experiment, but from three literatures above, sulphate fluids from deep wells of SBY and SMR spring might be influenced by the sulphur dissolution of anhydrite minerals.

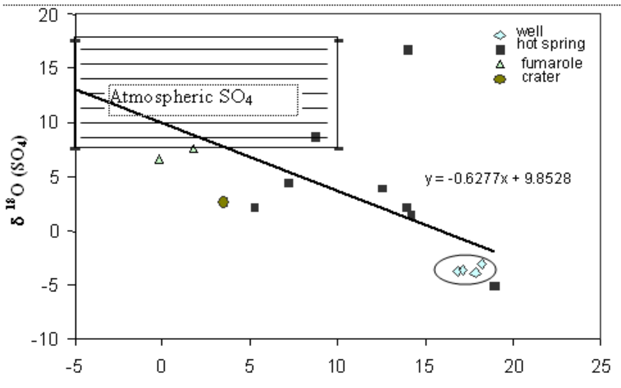

Fig 2. The relationship between δ $^{34}S_{(SO4)}$ and δ $^{18}O_{(SO4)}$ of hot springs, fumaroles, crater and Sibayak wells in Sumatra

Hydrothermal anhydrite is obviously derived from SO_4^{2-} in solution according to the following reaction:

$$Ca^{2+} + SO_4^{2--} \rightleftharpoons CaSO_{4\,(s)} \qquad (6)$$

This mineral merely adopts the isotopic signatures of the source SO_4^{2-} and δ ^{34}S of dissolved sulphate will be similar to δ ^{34}S of anhydrite. The enriched $^{34}S_{(SO4)}$ (16.8 $^{0}/_{00}$ to $18.9^{0}/_{00}$) also suggest that isotope partitioning of original magmatic sulphur has occurred possibly as a consequence of the hydration of primary SO_2 below the critical temperature of water (at about 370 °C) according to this reaction:

$$4\,H_2O + 4\,SO_2 \rightleftharpoons H_2S + 3H^+ + 3HSO_4^- \qquad (7)$$

Much (up to 70%) of the heavy isotopes go to SO_4^{2}, leaving an isotopically depleted in H_2S. At temperatures of around 350 – 370 °C, the SO_4^{2-} formed would have $^{34}S_{(SO4)}$ of $17^{0}/_{00}$ to $18^{0}/_{00}$ [8].

The δ $^{34}S_{(SO4)}$ value from two different sites of fumaroles (RDD-7 and PBT-1) is a quite narrow value between –0.15 $^{0}/_{00}$ and $1.80^{0}/_{00}$. The δ ^{34}S of meteorites and magmatic sulphur is closed to the standard Canon Diablo Troilite (FeS) 0 $^{0}/_{00}$ [8,9], the value of δ ^{34}S in sulphide of volcanic and hydrothermal source is approximately 0 $^{0}/_{00}$ [8], gas samples collected from fumaroles shows that the samples associated with volcanic geothermal system are also partly of magmatic origin [10].

The δ $^{34}S_{(SO4)}$ from two fumarolic samples collected have a similarity with standard δ ^{34}S for magmatic sulphur. At the high temperatures of magmatic source, the main sulphur containing gases are SO_2 and H_2S. Seemly, the sulphur isotopic composition of dissolved sulphate formed around fumarolic areas can greatly affected by sulphur isotopic composition of hydrogen sulphide from magma. Analysis of δ ^{34}S for sulphide fluids, δ $^{34}S_{(H2S)}$, and pyrite mineral might be able to ensure these relationships (not yet analyzed in this experiment), because pyrite is also composed in granites rocks as mainly constituent of the basement of southern Sumatra [1].

The dissolved sulphate from hot springs shows a wider range of δ $^{34}S_{(SO4)}$ from $5.25^{0}/_{00}$ to $14.20^{0}/_{00}$ whereas δ $^{34}S_{(SO4)}$ of crater is between the cluster of springs and fumaroles. In fact, those δ $^{34}S_{(SO4)}$ collected at the surfaces (more exposed to atmosphere) might not have the same isotopic composition as at depth (from wells). Mixing with sulphate bearing shallow groundwater also affects the isotopic composition of dissolved sulphate, which will no longer reflect that of the deep geothermal sulphate.

However, the sulphate dissolved in these shallow groundwater often also show changed δ $^{34}S_{(SO4)}$ values as a consequence of their origin, from oxidation of volcanic sulphur, reducing bacteria actively in marine sediment and soil or because they were affected by hydrogen sulphide in fumaroles areas. The composition of δ $^{34}S_{(SO4)}$ in atmospheric sulphates is greatly affected by δ $^{34}S_{(SO4)}$ from gases released in fumaroles and some anthropogenic activities (example, sour-gas plant). The δ $^{34}S_{(SO4)}$ of atmospheric sulphate vary at the range of -$5^{0}/_{00}$ to $10^{0}/_{00}$ [9].

Plot δ $^{34}S_{(SO4)}$ vs δ $^{18}O_{(SO4)}$ is linier and its slope can be used to identify at least four mechanisms, one of them is mixing of two waters with SO_4^{2-} of different isotopic composition [11]. At Fig 2 clearly presents that the δ $^{34}S_{(SO4)}$ of most hot springs spread in mixing line, δ $^{18}O_{(SO4)}$ = -0.6277 δ $^{34}S_{(SO4)}$ + 9.8528, between two sulphate sources namely the enriched δ $^{34}S_{(SO4)}$ from deep wells and more depleted δ $^{34}S_{(SO4)}$ from atmospheric sulphates.

Fig 3 presents δ $^{18}O_{(SO4)}$ versus δ $^{18}O_{(H2O)}$ values of geothermal fluids collected according to percent water in the sulphide oxidation reaction, as modified from Krouse and van Everdingen (12). The δ $^{18}O_{(SO4)}$ composition of sulphates depends on the contributions of both atmospheric in molecular oxygen (δ $^{18}O_{O2}$ = 23 $^{0}/_{00}$) and oxygen in the water molecules present during sulphide oxidation [9,12]. δ $^{18}O_{(H2O)}$ in groundwater depends on the δ $^{18}O_{(H2O)}$ in atmospheric during infiltrating into the recharge area [4,9,12].

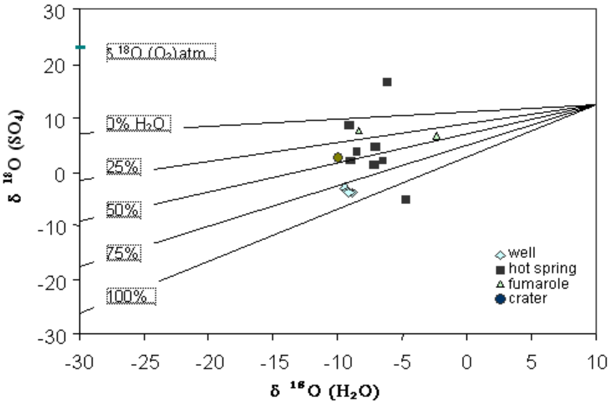

Fig 3. The relationship between $^{18}O_{(SO4)}$ and δ $^{18}O_{(H2O)}$ values of hot springs, wells fumaroles and crater in Sumatra according to percent water in oxidation reaction.

The δ $^{18}O_{(SO4)}$ of four Sibayak wells and SMR hot spring show more depleted value around –3.6 $^{0}/_{00}$ and –4.9 $^{0}/_{00}$, respectively. Seemly, the sulphate oxygen of SBY wells is derived from oxygen from water molecules with percentage around 87.5 %, according to Taylor's reaction-1 below, and 12.5% is derived from molecular oxygen in atmosphere (reaction-3). Its consequence, the δ $^{18}O_{(SO4)}$ of SBY wells will be more similar to the δ $^{18}O_{(H2O)}$ in groundwater having negative values. Sulphate oxygen of SMR spring is solely derived from oxygen in groundwater (100%).

Besides in contact with δ $^{18}O_{(H2O)}$, the lowering δ $^{18}O_{(SO4)}$ depends on reduction of some sulphate followed by oxidation of the product sulphide (HS^-), subsurface oxidation of sulphur organic and heavy metal sulphides (Fe, Cu, Zn, Pb, U). Taylor suggests that reaction oxidation of FeS_2 (commonly contents in granite rock) controlled by the following reaction [13]:

$$FeS_2 + 4Fe^{3+} + 8H_2O \longrightarrow 5Fe^{2+} + 2SO_4^{2-} + 6H^+$$

$$Fe^{2+} + 1/4O_2 \longrightarrow Fe^{3+} + ½\,H_2O \qquad (8)$$

$$FeS_2 + 7/2O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$

In contrast to the δ $^{18}O_{(SO4)}$ from wells, the δ $^{18}O_{(SO4)}$ of most hot springs except SMR, fumaroles and crater collected in this experiment have enriched values. At figure 3, the δ $^{18}O_{(SO4)}$ of springs spread in the wider range of percentage of water from 0% to 62.5%, δ $^{18}O_{(SO4)}$ of fumaroles fall at 20% and 50% whereas those of crater is 50% participating in sulphide oxidation reaction. Mostly, δ $^{18}O_{(SO4)}$ of springs exhibited at the mixture around 50% percentage of water. It means that δ $^{18}O_{(H2O)}$ and δ $^{18}O_{(O2)}$ have the same portion to derivate its oxygen isotope in δ $^{18}O_{(SO4)}$ value of hot spring. These lower percentages of water suggest that molecular oxygen from atmosphere more affected to δ $^{18}O_{(SO4)}$ value in these fluids and reaction-3 above may be important process in sulphide oxidation. Even, the SLW springs has most enriched $\delta\ ^{18}O_{(SO4)}$ by 16.7 $^{0}/_{00}$ (opposite to SMR spring), that is more closed to the value of $\delta\ ^{18}O$ from atmospheric oxygen.

CONCLUSION

The relatively enriched values of $\delta\ ^{34}S_{\ (SO4)}$ of Sibayak wells (16.8 $^{0}/_{00}$ to 18.2 $^{0}/_{0}$) may indicate the dissolution of anhydrite minerals or isotope partitioning in hydration of SO_2. The more depleted values of $\delta\ ^{34}S_{\ (SO4)}$ of two fumaroles (-0.15$^{0}/_{00}$ and 1.8$^{0}/_{0}$) may originate from magmatic sulphur. In general, the $\delta\ ^{34}S_{\ (SO4)}$ of springs spread in a wide range of 5.25$^{0}/_{00}$ to14.2$^{0}/_{00}$ that show a mixing process between atmospheric sulphate and sulphate from deep wells. The $\delta\ ^{18}O_{\ (SO4)}$ from deep wells exhibits depleted value of -3.6$^{0}/_{00}$ suggesting that 87.5% of sulphate oxygen is derived from groundwater oxygen and 12.5% is derived from atmospheric molecular oxygen in sulphide oxidation reaction. In the other hand, hot springs (except Semurup), crater and fumaroles have enriched value of $\delta\ ^{18}O_{\ (SO4)}$. These enriched values suggest that the percentage of atmospherically derived oxygen is higher than those from the depth.

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