Exploring mildly acidic to neutral hot fluids through carbonate clumped isotope (Δ47) thermometer in the Liuhuangtzuping Area

Yi-Chia Lu[1], Sheng-Rong Song[2], Pei-Ling Wang[3], Ting-Jui Song[4], Po-Hsiu Lin[4], Chyi Wang[2], and Li-Hung Lin[2]

[1]Graduate Institute of Applied Geology, National Central University, Taiwan

[2]Department of Geosciences, National Taiwan University, Taiwan

[3] Institute of Oceanography, National Taiwan University, Taiwan

[4] Fabulous Power CO., LTD., Taiwan

yichialu@cc.email.com

Keywords: *Tatun Volcano Group (TVG), carbonate clumped isotope (Δ47) thermometer, neutral hot fluids.*

ABSTRACT

The Liuhuangtzuping area, located in the northeastern part of the geothermally active Tatun Volcano Group (TVG), is situated adjacent to the She-Huang-Ping steaming ground(SHP) and Geng-Zi-Ping (GZP) steaming ground. Historically, SHP was deemed unsuitable for geothermal power generation due to its high corrosion potential with a pH value of hot springs ranging between 2-3. However, in recent years, Fabulous Power Co. has successfully drilled dry steam in SHP and is currently underway with the construction of a 1.4MW geothermal power plant. Liuhuangtzuping, in close proximity, presents an intriguing prospect for future Enhanced Geothermal Systems (EGS) development, featuring substantial layers of lava flows beneath.

In this study, we examined clumped isotope compositions for carbonates precipitating from near-neutral fluids in drilled cores of the Liuhuangtzuping area. The Δ47 values for five carbonate samples ranged from 0.434±0.012 ‰ to 0.512±0.020 ‰, corresponding to the estimated temperatures ranging from 184±6℃ to 114±7℃. Overall, these results suggest the existence of a subsurface reservoir where fluids are neutral in pH and sufficiently hot (180-185 ℃) for geothermal energy exploration.

1. INTRODUCTION

1.1 Geothermal policies and goals in Taiwan

To achieve the ambitious goal of reducing carbon emissions by 30% by 2030 and reaching net-zero carbon emissions by 2050, Taiwan, located within the Pacific Ring of Fire (Fig. 1a), recognizes geothermal energy as a critical focal point for future development. Geothermal power generation is expected to replace fossil fuels, leading to a substantial reduction of 1.8 to 6.2 million metric tons of CO_2 emissions annually.

The Tatun Volcanic Group (TVG) is situated to the northwest of the Taipei Basin, with a population of approximately 6.66 million people in the vicinity. While young volcanoes in the region pose potential future threats, it also offers abundant geothermal energy resources. The TVG is estimated to hold 80-200 MW for conventional geothermal resources (Chen, 1970; MRSO, 1969, 1970, 1971, 1973); When considering Enhanced or Engineered Geothermal Systems (EGS) or Advanced Geothermal Systems (AGS), the estimate rises to 1,405 MW and 1,481 MW inside and outside the Yangmingshan National Park, respectively (Tseng, 2012).

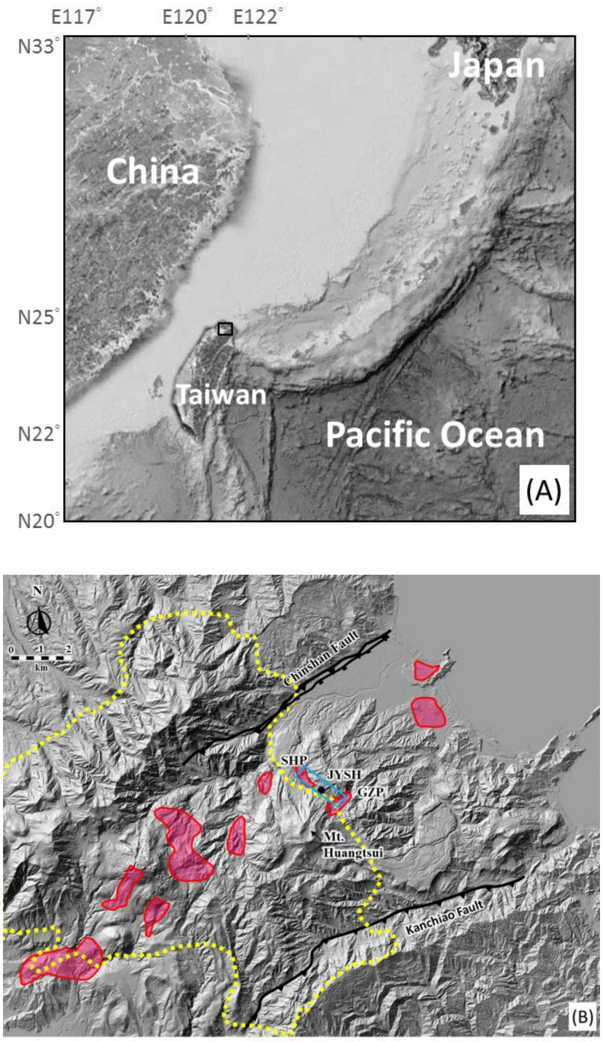

Figure 1: (A) Taiwan is situated within the Pacific Ring of Fire, with the TVG area highlighted within the black box. (B) The primary geothermal area of TVG (highlighted in red) exhibits a northeast-southwest orientation, with a significant portion located within the Yangmingshan National Park (indicated by the yellow dashed line). Within the Liuhuangtzuping Geothermal field, two main steaming grounds can be found: She-Huang-Ping (SHP) and Geng-Zi-Ping (GZP). The JYSH well, central to this study, is strategically positioned between these two steaming grounds.

However, despite its significant geothermal potential, most of the high-heat flow areas in the TVG are situated within national parks (Fig. 1b), making it challenging to develop geothermal projects under current regulations. Only the northeastern region, known as the "Liuhuangtzuping Geothermal Demonstration Park," lies outside the national parks. This area, designated by the New Taipei City, is being developed by Fabulous Power Co., covering an impressive area of nearly 20,000m^2.

1.2 Liuhuangtzuping Geothermal field

The heat source of the Liuhuangtzuping Geothermal field is derived from the southern Mt. Huangtsui (Fig.2). The eruption age of Mt. Huangtsui is estimated using different dating methods: plagioclase-groundmass U-Th age of 72±4 ka (Zellmer et al., 2016), zircon U-Pb age of 200 ka (Chu et al., 2018), and K-Ar ages of 190±30 ka (Tsao, 1994). According to the LiDAR terrain image, Mt. Huangtsui exhibits two lava flows that flow northward, resulting in the formation of two distinct steaming grounds: She-Huang-Ping steaming ground(SHP) and Geng-Zi-Ping (GZP) steaming ground.

During the 1960s and 1970s, more than 12 shallow exploration wells were drilled in the SHP and GZP (Table 1). The results indicated excellent geothermal potential here. For instance, G-302 reached a depth of only 104 m but encountered temperatures of up to 140°C. However, the subsequent drilling of two deep wells did not yield the expected high temperatures and encountered strong acidity. For instance, CPC-SHP-1T was drilled to a depth of 2025 m, but the temperature reached only 160°C, and E303, drilled to a depth of 1300 m, recorded a temperature of only 125°C. In 2020, Fabulous Power Co. achieved a successful drilling operation, obtaining dry steam at SHP. They are now preparing to launch a 1.4 MW geothermal power plant, which will utilize Omat company's Binary power generator and is scheduled to begin commercial operation in September 2023. Meanwhile, the dry steam from the GZP steaming ground is the next phase of the planned development.

The Liuhuangtzuping Geothermal field has short-term plans to utilize dry steam from the steaming ground for power generation. Furthermore, there are future intentions to employ EGS and AGS technologies for geothermal development. In order to better understand the subsurface characteristics and assess the feasibility of EGS and AGS, a geothermal well named JYSH exploration well is planned to be drilled in the lava plateau to a depth of 1500 m, it will be situated 0.4 km from SHP and 0.8 km from GZP, away from any steaming ground. The drilling operation into dense two-pyroxene andesite aims to focus on "temperature" and "non-acidity." The former directly impacts the efficiency and ultimate power output, while the latter is crucial to avoid corrosion issues that could complicate engineering efforts and significantly increase development costs. Consequently, the primary objective in site selection is to avoid areas with upward migration of volcanic gases through fractures.

1.3 JYSH exploration well

The JYSH exploration well started drilling in 2019 with an initial plan to reach a depth of 1500 m. However, drilling encountered a tricky strata at 1100 m, leading to a decision to perform sidetrack drilling. Currently, the well depth is approximately 1100 meters.

The notable feature in this area is the presence of lava flows overlying sedimentary bedrock. Based on neighboring geothermal wells, E-303 encountered sedimentary bedrock at a depth of 600 m, while CPC-SHP-1T encountered sandstone at a depth of 400 meters. According to inference, JYSH should encounter sedimentary bedrock at around 533 m. However, in this area, sedimentary and igneous rock sequences begin to alternate and appear between 650m and 700m, suggesting that this well might have been drilled on the boundary of an intrusion body.

Above 650 meters, the igneous rock shows two-pyroxene andesite, while below 650 meters, the sedimentary rock exhibits prominent silicification and often features black rock veins, which have been confirmed to be enargite.

In the JYSH exploration well, numerous calcite appears with andesite cuttings. These calcite veins can represent the products of deep fluids that ascended to shallow depths and subsequently precipitated. By utilizing the novel technique of carbonated Clumped isotope analysis, it is possible to estimate the precipiated temperature, and in combination with carbon and oxygen isotope analysis, it’s possible to know the original fluid $\delta^{18}O$ composition. This article focuses on these calcite veins in the hope of gaining a better understanding of the subsurface temperature and fluid characteristics in this region.

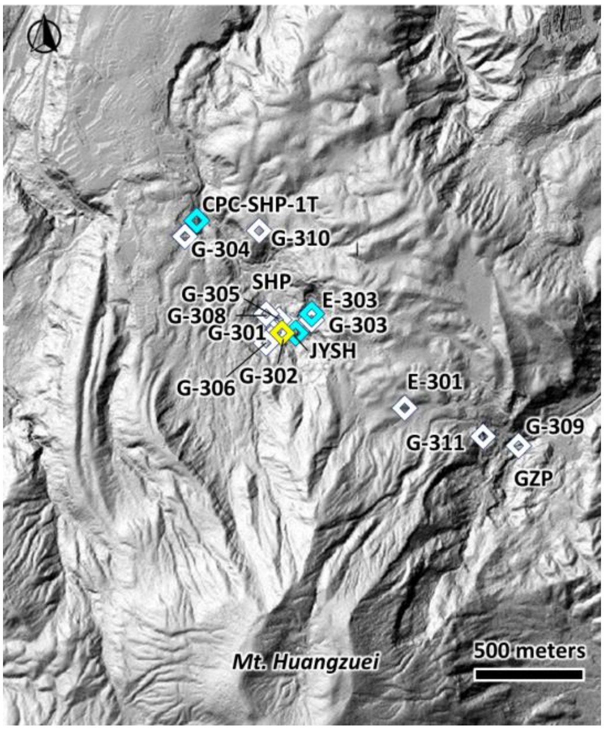

Figure 2: The geothermal fields formed by Mt. Huangtsui and the previously drilled geothermal wells (indicated by polygons) in this area. The yellow ones represent steam with a dryness exceeding 80%, while the blue ones indicate wells where cuttings have revealed calcite (representing the presence of neutral fluids).

Table 1: The well depth and bottom temperature of the Liuhuangtzuping Geothermal field

Well No.	Elevation (m)	TWD97(WGS84) longitude	TWD97(WGS84) latitude	Well depth(m)	T_{bottom} (℃)
E-301	629	121.6094795	25.18532688	474	103
E-302	430	121.6062403	25.19035966	60	no data
E-303	464	121.6077201	25.19266471	1300	125.2
G-301	406	121.6025879	25.19214404	147	134
G-302	424	121.6050639	25.19123115	104	140
G-303	439	121.6077363	25.19191534	150	28
G-304	415	121.5991166	25.19242897	132	23
G-305	359	121.6039836	25.19349252	89	98
G-306	460	121.6029736	25.18988551	100	38
G-308	367	121.6023026	25.19467299	144	116
G-309	388	121.6158694	25.18868333	136	29
G-310	354	121.6037976	25.19602107	124	102
G-311	437	121.6130333	25.18934722	138	63
CPC-SHP-1T	303	121.5994629	25.19831371	2025	160

2. METHOD

Five cutting samples were collected from the JYSH exploration well at depths of 200m, 355m, 380m, 385m, and 400m. These samples will undergo carbon and oxygen isotopic analyses, and carbonate clumped isotope analysis. The carbon and oxygen isotopic analyses using a Thermo Scientific MAT 253 Isotope Ratio Mass Spectrometer (IRMS) at the Institute of Oceanography, National Taiwan University. The isotopic compositions were normalized to the Vienna Pee Dee Belemnite (V-PDB) for $\delta^{13}C$ and the Vienna Standard Mean Ocean Water (V-SMOW) for $\delta^{18}O$. The δ notation is defined as:

• (‰) = [(Rsample⁄Rstandard) -1] × 1000

where R is the ratio of either $^{13}C/^{12}C$ or $^{18}O/^{16}O$. The analytical precision (1σ), based on replicate analyses of the carbonate standards, was 0.03 ‰ and 0.06 ‰ for carbon and oxygen isotopes, respectively.

For the carbonate clumped isotope analysis, powdered Samples were soaked in 3% hydrogen peroxide to remove organic matters for 10 hours, then dried out at 50 ℃ (Kluge et al., 2015). The 20 mg cleaned-up samples were digested in a 3 ml 105% phosphoric acid bath (H_3PO_4) set at 90 ˚C for 10 minutes to produce CO_2, which were then purified by cryogenic and Hayes separation traps. The CO_2 gasses were analyzed for masses 44 to 49 using a MAT 253 gas source mass spectrometer at the Institute of Oceanography, National Taiwan University. Carbonate clumped isotope compositions are expressed in Δ notation:

$$\Delta 47 = \left[\left(\frac{R47}{R47^*}-1\right)-\left(\frac{R46}{R46^*}-1\right)-\left(\frac{R45}{R45^*}-1\right)\right]\times 1000$$

where R^i = mass i/mass 44 and the * indicates ratios for isotopologues at stochastic abundance levels (Affek and Eiler, 2006). Mass 47 CO_2 contains the ^{13}C–^{18}O bond on which the thermometer is based (Ghosh et al., 2006b). All of the data were calibrated by "Easotope," software for processing complex isotopic corrections (John and Bowen, 2016). All carbonate clumped isotope values are presented on an absolute reference frame, herein referred to as the 'carbon dioxide equilibrium scale,' or CDES, which empirically corrects for instrumental nonlinearities and changes in the ionization environment during mass spectrometry (Dennis et al., 2011). The four ETH standards were routinely analyzed for data calibration. The Carrara marble, a carbonate reference material, was also analyzed to monitor system stability and precision, with the following long-term average: Δ47 is 0.384 ± 0.010.

The calcite precipitation temperature calculated from corrected Δ47 values was based on an experimental calibration curve between 25℃ and 250℃ by Kluge et al. (2015). The $\delta^{18}O$ values of fluids were estimated from $\delta^{18}O_{calcite}$ and T-Δ47 using the equation by Friedman and O'Neil (1977).

3. RESULTS

The carbon and oxygen isotopic values of calcite in JYSH ranged from -6.6 ‰ to -5.4 ‰ and 9.0 ‰ to 11.0 ‰ for $\delta^{13}C$ VPDB and $\delta^{18}O$ VSMOW, respectively (Table 2). The Δ47 values of down hole cuttings are 0.512±0.020 ‰, 0.485±0.019 ‰, 0.434±0.012 ‰, 0.489±0.019 ‰, and 0.437±0.016 ‰ (±1SE), which translates to clumped isotope temperatures of 114±7℃, 134±7℃, 184±6℃, 131±6℃ and 181±7℃, and the calculated $\delta^{18}O$ values of the original thermal water are -4.6 ‰, -3.9 ‰, -1.4‰, -3.4‰ and +0.1‰ for depths of 200m, 355m, 380m, 385m, and 400m respectively (Table 3).

Table 2: The carbon and oxygen isotope results

Sample name	$d^{13}C$ (‰,VPDB)	$d^{18}O$ (‰,VPDB)	$d^{18}O^a$ (‰,SMOW)
BLSH-200	-5.4	-19.3	11.0
BLSH-355	-5.7	-20.3	10.0
BLSH-380	-5.8	-21.3	9.0
BLSH-385	-6.6	-19.6	10.7
BLSH-400	-5.6	-19.6	10.7

Table 3: Clumped isotope data and the calculated $\delta^{18}O$ VSMOW of fluids

Sample name	Replicates (n)	Ave D47 (‰,CDES)	S.D. (‰,CDES)	T (˚C)^a	Error-	Error+	$d^{18}O_{H2O}$ (‰,SMOW)
BLSH-200	5	0.512	0.020	114	107	120	-4.6
BLSH-355	5	0.485	0.019	134	127	141	-3.9
BLSH-380	6	0.434	0.012	184	178	190	-1.4
BLSH-385	7	0.489	0.019	131	125	137	-3.4
BLSH-400	8	0.437	0.016	181	174	187	0.1

4. DISCUSSION

4.1 Neutral conduction geothermal fluid

Due to the lack of PT measurements in JYSH well, we are unable to know the temperature profile with depth. However, based on the drilling log, the return drilling mud temperature reached 91°C. We speculate that the temperature of the host rock inside the well should be close to the temperature ranges obtained from clumped isotope analysis: 114±7°C, 134±7°C, and 131±6°C. The temperature of 115-135°C also corresponds to the dry steam output of nearby SHP steaming ground at depths of around 200-400 meters. Because the host rock in this area lacks well-developed fractures connecting to the surface, and there is little to no fluid flow. Therefore, surface geothermal manifestations are not observable.

The calculated $\delta^{18}O_{fluid}$ values of the original thermal water are -4.6 ‰, -3.9 ‰, and -3.4‰, indicating a tendency towards meteoric water or groundwater composition (similar to the isotopic value of river in SHP streaming ground with values ranging from -4.6 ‰ to -3.7 ‰). Moreover, the presence of calcite precipitation suggests that the fluid is not strongly acidic and lacks significant volcanic gas dissolution. For future EGS or AGS projects in this area, simulations and feasibility assessments can be based on a temperature of around 130°C as a reference.

4.2 Deep neutral geothermal fluid in Liuhuangtzuping

It is worth noting that there are two clumped isotope temperature data from the BLSH exploration well, showing values of 184±6°C and 181±6°C, which are significantly higher than other calcium carbonate precipitation temperatures in this area. These two data points also exhibit more corrected calculated $\delta^{18}O_{fluid}$ values, reaching -1.4 ‰ and +0.1‰, implying the possibility of magma water contamination (magma water has $\delta^{18}O$ values of approximately 5.5‰ to +10.0‰, Taylor, 1974) or undergoing strong water-rock interactions and fractional processes. These indications suggest that the precipitated original water originates from deeper neutral water sources in the Liuhuangtzuping area, representing potential temperatures of deep neutral water contained in this region.

Because the deep magma fluid contains Cl and various volatile gases, the initial conditions are likely acidic. However, as it ascends and passes through sandstone layers, there might also be plagioclase present in the form of igneous dikes and to shollow andesite lava flows to provide neutralization.

$$\begin{aligned} CaAl_2Si_2O_8(\text{anorthite}) + H_2SO_4 + 2H_2O \\ \leftrightarrow CaSO_4(\text{anhydrite}) \\ + Al_2Si_2O_5(OH)_4(\text{kaolinite}) \end{aligned}$$

As long as there are no cracks with volcanic gases mixed in to provide H_2S, there is a possibility of having neutral fluids.

4.3 Carbon isotope values in TVG

The carbon isotopic values of calcite in JYSH ranged from -6.6 ‰ to -5.4 ‰ for $\delta^{13}C$ VPDB. Regarding the magmatic carbon sources, the $\delta^{13}C$ values of high-temperature CO_2 gases derived from island arc volcanoes have been reported as in the range of -5 ± 3‰ (Sano and Marty, 1995), which is slightly lower than that of mantle origin ($\delta^{13}C$ = -4.0 ± 2.5‰, a value from Kilauea volcano, Hawaii (Hurwitz et al., 2003)). Moreover, the $\delta^{13}C_{CO2}(g)$ of TVG is approximately -3.0 to -7.3‰ (Lee et al., 2005; Yang et al., 2003). By comparison, the carbon source of vein carbonates precipitated in JYSH are derived from the volcanic gas in the surrounding area.

5. CONCLUSION

For future geothermal development of EGS and AGS, this study aims to identify neutral geothermal fluids in the Liuhuangtzuping Area and utilize the clumped isotope (Δ47) thermometer to understand their temperatures. Calcite samples found in the JYSH exploration well at depths of 200-400 m indicate the presence of non-acidic fluids in the dense fractured host rock. Clumped isotope temperature data suggests that these conduction geothermal fluids have temperatures ranging approximately from 115°C to 135°C, representing meteoric fluid components. Furthermore, deeper neutral water temperatures can reach up to 180-185°C, with indications of magma water contamination based on the original water's oxygen isotope values (Fig.3). These temperature findings can serve as valuable references for numerical simulations during the injection and extraction processes in future EGS or AGS development in this area.

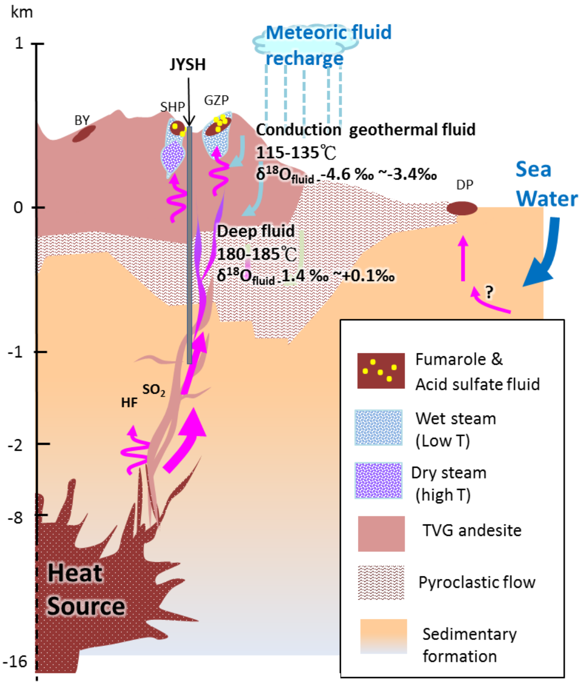

Figure 3: Conceptual model of neutral water formation in the Liuhuangtzuping geothermal field..

ACKNOWLEDGEMENTS

This work was supported by Ministry of Science and Technology (MOST), Taiwan [108-2116-M-002-009, 109-2116-M-002-034, 110-2811-M-002-611, and 112WFA0710019], and Institute of Earth Sciences, Academia Sinica.

REFERENCES

Chang, P.Y., (2012). National Energy Program: The Study of Chingshui Geothermal Field(3/3), National Science Council 2012-Final report (NSC 101-3113-M-002 -001).

Chen, C. H., (1970). Geology and geothermal power potential of the Tatun volcanic region. *Geothermics 2*, 1134-1143.

Chu, M. F., Lai, Y. M., Li, Q., Chen, W. S., Song, S. R., Lee, H. Y., 2018. Magmatic pulses of the Tatun Volcano Group, northern Taiwan, revisited: Constraints from zircon U-Pb ages and Hf isotopes. *Journal of Asian Earth Science*s 167, 209-217.

Dennis, K. J., Affek, H. P., Passey, B. H., Schrag, D. P., Eiler, J. W., (2011). Defining an absolute reference frame for 'clumped' isotope studies of CO_2. *Geochim. Cosmochim. Acta 75*, 7117–7131.

Friedman, I., O'Neil, J. R., (1977). Compilation of stable isotope fractionation factors of geochemical interests. In Fleischer, M.(ed.) Data of geochemistry, 6th edn., U. S. Geol. Surv., Prof. Paper 440-KK, Washington D.C., KK1–KK12.

Ghosh, P., Garzione, C.N., and Eiler, J.M., (2006b). Rapid uplift of the Altiplano revealed through ^{13}C-^{18}O bonds in paleosol carbonates. *Science*, 311, 5760, 511–515.

Hurwitz, S., Goff, F., Janik, C.J., Evans, W.C., Counce, D.A., Sorey, M.L., Ingebritsen, S.E., (2003). Mixing of magmatic volatiles with groundwater and interaction with basalt on the summit of Kilauea Volcano, Hawaii. *J. Geophys. Res*. 2028–2039.

John, C.M., Bowen, D., (2016). Community software for challenging isotope analysis: First applications of "Easotope" to clumped isotopes. Rapid Commun. *Mass Spectrom 30*, 2285–2300.

Kluge, T., John, C. M., Jourdan, A.L., Davis, S., Crawshaw, J., (2015). Laboratory calibration of the calcium carbonate clumped isotope thermometer in the 25–250℃ temperature range. *Geochim. Cosmochim. Acta. 157*, 213–227.

Lee, H.F., Yang, T.F., Lan, T.F., Song, S.R., Tsao, S.J., (2005). Fumarolic gas composition of the Tatun volcano group, Northern Taiwan. *Terr. Atmos. Ocean. Sci. 16*, 843–864.

MRSO, (1969). The Report on Geothermal Exploration of Tatun Volcano Group I. Mineral Research and Service Organization Report 90. (in Chinese).

MRSO, (1970). The Report on Geothermal Exploration of Tatun Volcano Group II. Mineral Research and Service Organization Report 102. (in Chinese).

MRSO, (1973). The Report on Geothermal Exploration of Tatun Volcano Group IV. Mineral Research and Service Organization Report 126. (in Chinese).

Taylor, H.P., (1974). The application of oxygen and hydrogen isotope studies to problems of hydrothermal alteration and ore deposition. Econ. Geol. 69, 843–883.

Tseng, H.C., (2014) 3D Geological Structure and Potentials of Geothermal Power in the Tatun Volcano Group, Master's thesis of National Taiwan University.

Tsao, S. J., (1994). Potassium-argon age determination of volcanic rocks from the Tatun Volcano Group, Bull. *Geol. Surv.*, 9, 137– 154. (in Chinese).

Yang, T.F., Ho, H.H., Hsieh, P.S., Lin, N.J., Chen, Y.G., Chen, C.H., (2003). Compositions and sources of fumarolic gases from Tatun Volcano Group, North Taiwan. *J. Nat. Park* 13, 127–156.

Zellmer, G.F., Rubin, K.H., Muller, C.A., Shellnutt, H.G., Belousov, A., Belousova, M., (2016). Resolving discordant U-Th-Ra ages: constraints on petrogenetic processes of recent effusive eruptions at Tatun Volcano Group, northern Taiwan. *Geol. Soc. Lond.*, Spec. Publ. 422. doi.org/10.1144/SP422.3.

ISSN 2703-4275