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Magmatic-like fluid source of the Chingshui geothermal field, NE Taiwan evidenced by carbonate clumped-isotope paleothermometry

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Abstract

The Chingshui geothermal field, a moderate-temperature and water-dominated hydrothermal system, was the site of the first geothermal power plant in Taiwan. Many geological, geophysical and geochemical studies using more than 21 drilled wells have been performed since the 1960s. However, there are still controversies regarding the heat and fluid sources due to the tectonically complicated geological setting. To clarify the heat and fluid sources, we analyzed clumped isotopes with carbon and oxygen isotopic compositions of calcite scaling in geothermal wells and veins on outcrops and calculated the $\delta^{18}O$ values of the source fluids. Two populations of $\delta^{18}O$ values were calculated: -5.8±0.8 ‰ VSMOW from scaling in the well and -1.0±1.6 ‰ to 10.0±1.3 ‰ VSMOW from outcropping calcite veins, indicative of meteoric and magmatic fluid sources, respectively. Meanwhile, two hydrothermal reservoirs at different depths have been identified by magnetotelluric (MT) imaging with micro-seismicity underneath this area. As a result, we propose a two-reservoir model: the shallow reservoir provides fluids from meteoric water for the

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scaling sampled from wells, whereas the deep reservoir provides magmatic fluids from deep marble decarbonization recorded in outcropping calcite veins.

Keywords: Chingshui Geothermal field, clumped isotopes, calcite veins, magmatic fluid

1. Introduction

Understanding of the heat source for a geothermal field is critical for developing and maintaining a long-term sustainable power plant. Therefore, the quantity and stability of the thermal fluids supply are basic information for designing and constructing a commercial geothermal power plant.

The origin of the heat source that generates thermal fluids underneath the Chingshui geothermal field has long been debated (Chen, 1982; Liu et al., 1990, 1982; Tong et al., 2008; Tseng, 1978; Yeh et al., 1989; Yu and Tsai, 1979; Yui et al., 1993). The field is located in a rapidly uplifting metamorphic argillite/slate formation of the Taiwan orogenic belt. The hydrogen and oxygen isotopic compositional data of natural hot springs and thermal water support a model where the fluids come from a meteoric origin with a recharge area located at an altitude above 1,000 m (Liu et al., 1990, 1982). Liu et al. (1990), thus, suggested that the thermal fluids came from deep heated circulation of meteoric water controlled by regional fault systems. In this model, the heat source of the Chingshui geothermal system originated from the

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residual heat of rock formations in the Central Range of the Taiwan orogeny that have been rapidly uplifted since 5 Ma (Chen, 1982; Liu et al., 1990, 1982). The meteoric water infiltrated into, and was heated by, deep rocks with a high geothermal gradient and then rose to the shallower reservoir or to the surface as hot springs (Chen, 1982; Yui et al., 1993). This scenario with deep convective water circulation has long been accepted as the thermal fluids origin for the Chingshui geothermal field.

However, based on geophysical data and borehole information, several researchers (Tong et al., 2008; Yeh et al., 1989; Yu and Tsai, 1979) proposed that the high heat flow and geothermal gradient may result from the existence of a magma chamber within the shallow crust or from shallow intrusive dikes underneath the Chingshui geothermal field. There is an E-W-trending magnetic anomaly onshore and a low-velocity zone underneath the offshore crust that indicate possible magmatic intrusion related to the back-arc opening of the Okinawa Trough (Tong et al., 2008; Yu and Tsai, 1979).

To distinguish between the aforementioned heat sources for the Chingshui geothermal field, more evidence are needed. The stable isotope analysis of fluid-derived materials serves as a powerful technique for tracing the origin of geothermal fluids. In this study, we apply the carbonate clumped isotopic technique to directly reconstruct the formation temperature and fluid source of calcite veins. In a second step, the oxygen isotopic compositions of the parent thermal fluids for the calcite veins can be calculated. Finally, combining geophysical data and other geochemical lines of evidence, such as the He and C isotopic ratios of the waters, we identify the probable fluid sources and propose a genetic model for the Chingshui geothermal system.

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2. Geologic background

Taiwan is well-known for active orogenesis, with the Philippine Sea plate moving northwestward and colliding with the Eurasian continental margin. South of Taiwan, the Eurasian plate subducts beneath the Philippine Sea plate to form the northernmost part of the Luzon arc (Fig. 1-a). The Philippine Sea plate subducts underneath the Eurasian plate, leading to the formation of the Ryukyu arc in northern Taiwan (Fig. 1-a). The Okinawa Trough is a back-arc basin in the Ryukyu arc-trench system, which extends from southwestern Kyushu Island of Japan to the Ilan Plain of northeastern Taiwan (Kimura, 1985). Three stages of opening since 15 Ma have been recognized, and the latest phase of extension that occurred in the southwestern part of the Okinawa Trough is characterized by normal faults with vertical offsets since the late Pleistocene (Furukawa et al., 1991; Kimura, 1985; Sibuet et al., 1998). The Ilan Plain (Fig. 1-b) of northeastern Taiwan is situated at the southwesternmost tip of this trough. The age of the normal stress affecting the Ilan Plain is not known. However, a thermoluminescence (TL) age of 7.0±0.7 ka obtained from a siltstone xenolith found at Kueishantao, an offshore volcanic island 10 km away from the coast of Ilan Plain (Chen et al., 2001), may suggest the probable timing for the extensional event.

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The Chingshui geothermal field is located in the valley of the Chingshui River, southwest of Ilan Plain (Fig. 1-b). The rock hosting the geothermal field is the Miocene Lushan Formation, consisting of argillite/slate with intercalated thin meta-sandstones of the Jentse Member (Hsiao and Chiang, 1979; Tseng, 1978). Several faults, including the Xiaonanao and Chingshuishi Faults and a few small unnamed ones, cut through rock bodies in this area. The Xiaonanao Fault is a thrust fault with wide damage zones that are rich in quartz veins with euhedral pyramidal crystals on the outcrops along the Chilukeng River (Fig. 1-c). The fault stretches to the east where an upside-down sequence of strata appears at the Shimen River (Tseng, 1978). The Chungshuishi Fault is a south-north strike-slip fault, inferred from geophysical data such as micro-seismicity and magnetotelluric (MT) images as it is not exposed at the surface (Tong et al., 2008; Yu and Tsai, 1979).

3. Sampling and Methods

3.1 Sampling

Carbonate scaling samples were collected from abandoned produced wells IC-13 and IC-19 (Fig. 1-c). The IC-13 well was drilled to a depth of 2,020 m in 1978 and produced hot fluids in the Chingshui geothermal power plant during 1981-1993. In comparison, the IC-19 well was drilled to a depth of 901.5 m in 1986 and produced

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hot fluids for the power plant during 1986-1993. The scaling samples analyzed in this study were retrieved by Industrial Technology Research Institute of Taiwan(ITRI) in 2009, which obtained an assignment to restart the Chingshui geothermal power plant and washed the obsolete wells. The washed-out materials are composed of scaling and slates mixed with micas from the drilling muds and iron oxides from the casing. We selected the scaling with well-defined precipitation layers (Fig. 2), which indicated rapid nucleation and precipitation interspersed with crystal growth (Jones and Peng, 2012).

Abundant white veins (FS-1 to FS-32) crop out at the confluence of the Chingshui River and the Chilukeng River. They occur in the gouge zones of several parallel normal faults with strike-slip components (inferred by slickenside direction), plus fractures and joints in an area approximately 200 m long along the Chingshui River bank (Fig. 1-c). The mineral assemblage for these white veins is predominantly composed of calcite with minor quartz. The thickest gouge, approximately 2 m wide with a steep dip, contains blocks of quartz veins (Fig. 3-a). Thicknesses for most of the fault gouge zones vary between 10 cm and 1.5 m, with strikes ranging from N55°E to N75°E and dips from 30°N to 80°N (Fig. 3-b).

3.2 Methods

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3.2.1 Carbon and oxygen isotopic analysis

A total of 47 samples were selected for carbon and oxygen isotopic analyses, including 35 samples from outcrops in damage zones and 12 samples from scaling inside obsolete wells (9 samples from IC-13 and 3 samples from IC-19).

The carbon and oxygen isotopic compositions of carbonates were analyzed by a Thermo Scientific MAT 253 Isotope Ratio Mass Spectrometer (IRMS) equipped with an automatic Carbonate Device (Kiel) 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:

δ (‰) = $[(R_{sample}/R_{standard}) - 1] \times 1000$, 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.

3.2.2 Carbonate clumped-isotope thermometry

An innovative method called the "clumped-isotope" thermometer has emerged as an alternative for determining crystallization temperatures of carbonate minerals (e.q. Affek and Eiler, 2006; Eiler and Schauble, 2004; P. Ghosh et al., 2006). Unlike

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traditional carbonate $\delta^{18}O$ thermometry, which requires the $\delta^{18}O$ values of fluids for absolute temperature calculation, clumped-isotope thermometry depends only on the degree to which the heavy isotopes (^{13}C and ^{18}O) bond to each other. The abundance of the isotopologues of CO_2 gas with mass 47 ($^{13}C^{18}O^{16}O$) compared to a stochastic distribution is denoted as the $\Delta47$ value. Because $\Delta47$ is independent of the oxygen isotopic composition of the fluid and depends only on the formation temperature of carbonates (Ghosh et al., 2006), both the temperature of carbonate formation and the $\delta^{18}O$ value of the fluid can be reconstructed (Eiler, 2007). This method is a major breakthrough for revealing the fluid oxygen isotopic composition even in the absence of fluid inclusions or other independent temperature estimates.

Clumped isotope analysis was conducted in the Qatar Stable Isotope Laboratory at Imperial College London. Samples for clumped-isotope analysis were powdered and soaked in 3 % hydrogen peroxide to remove organic matter and then dried in an oven at 50°C overnight. The clean samples were digested in 2 ml of a 105 % orthophosphoric acid (H_3PO_4) held at 90°C and stirred for 10 minutes to produce CO_2, which was then purified by cryogenic and Porapak Q traps. The CO_2 gases were analyzed for masses 44-49 using a Thermo MAT 253 gas source isotope ratio mass spectrometer. The details of the analytical procedure were the same as those described

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in Kluge et al. (2015), and all of the data processing was performed using “Easotope”, a software program designed for complex isotope analysis (John and Bowen, 2016). The parameters used for processing the data followed procedures highlighted in Schauer et al. (2016) and in Daëron et al. (2016) to avoid problems with the ^{17}O correction.

The calcite growth temperatures calculated from corrected Δ47 values were based on experimental calibrations from Kluge et al. (2015) adapted for the new ^{17}O correction. The $\delta^{18}O$ values of fluids were estimated using the equation of Friedman & O’Neil (1977).

3.2.3 U-Th dating

The carbonate veins collected in the field and identified as having formed in a single event (by inspection of SEM images) were selected for U-Th dating. The U-Th dating was performed in the High-Precision Mass Spectrometry and Environment Change Laboratory (HISPEC) of the Department of Geosciences, National Taiwan University (NTU). The subsamples were cleaned with ultrasonic methods (Shen et al., 2002) and analyzed on a Thermo Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) with single secondary electron multiplier protocols. The detailed chemistry and instrumentation are described in Shen et al. (2003) and

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Shen et al. (2012), respectively. The half-lives of U and Th nuclides used for the ^{230}Th age calculation are given in Cheng et al. (2013). Uncertainties in the U-Th isotopic data and ^{230}Th dates are given at the two-sigma (2σ) level or two standard deviations of the mean ($2\sigma_m$) unless otherwise noted.

4. Results

4.1 Mineral assemblage of scaling and veins

Most of the scaling samples from the IC-13 and IC-19 production wells are composed of pure calcite, with a few samples containing subsidiary quartz. Approximately half of outcrop vein samples (17/32) consist of mixtures of calcite and quartz, while the others (15/32) are composed of pure calcite near the fault zones. Based on the mosaic textures observed in microscopic and back-scattered detector (BSE) images (Fig. 4), these veins from outcrops and cores show that calcite and quartz were precipitated at the same time.

4.2 Carbon and oxygen isotopic ratios

Carbon and oxygen isotopic analyses indicate that the samples from outcrops and scaling in geothermal wells possess the highest and lowest values, respectively. The δ^{13}C and δ^{18}O values of outcrop samples range from -1.9 ‰ to -0.3 ‰ VPDB and 8.3

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‰ to 17.8 ‰ VSMOW, respectively (APPENDIX A. SUPPLEMENTARY DATA-1), and the scaling in production wells shows values ranging from -7.9 ‰ to -7.0 ‰ VPDB and 2.8 ‰ to 4.9 ‰ VSMOW for $\delta^{13}C$ and $\delta^{18}O$, respectively (APPENDIX A. SUPPLEMENTARY DATA-1) (Fig. 5).

4.3 Clumped-isotope (Δ47) analysis

The Δ47 value of the IC-13 scaling collected at a depth of 939 meters is 0.411±0.002 ‰, the precipitation temperature estimated using the equation of Kluge et al. (2015) is 214±16℃, and the calculated $\delta^{18}O$ value of fluid is -5.8±0.7 ‰ VSMOW.

Three outcrop veins were analyzed for their clumped-isotope compositions, and the Δ47 values are 0.383±0.006 ‰, 0.482±0.022 ‰ and 0.386±0.009 ‰ (Table 1). Based on Kluge et al., (2015), the precipitation temperatures of the calcite veins are 264±30℃, 136±20℃ and 259±32℃. The calculated $\delta^{18}O$ values of the fluids are 8.0±1.1 ‰ VSMOW, -1.0±1.6 ‰ VSMOW and 10.0±1.3 ‰ VSMOW, respectively.

4.4 Vein carbonate ages

U-Th isotopic concentration data and uncorrected ages are listed in Table 2. The ^{238}U contents range between 3 and 53 ppb. $^{230}Th/^{238}U$ activity ratios range between

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0.061 and 2.8. The ^{230}Th contents consist of two parts. The first is the radiogenic amount that decayed from parent nuclides ^{238}U and ^{234}U. The other is the initial ^{230}Th ($^{230}Th_0$) associated with detrital material incorporated into the carbonate crystal matrix, which should be corrected for in the age equation (Broecker, 1963) to obtain accurate ^{230}Th ages. A speculative initial $^{230}Th/^{232}Th$ ($^{230}Th/^{232}Th_{ini}$) atomic value of 4-5 × 10^{-6}, based on a bulk-earth crustal Th/U atomic ratio of 3.6-3.8 (Taylor and McLennan, 1995) and an assumed secular equilibrium between ^{230}Th and ^{238}U, was generally used to calculate ^{230}Th dates (Cheng et al., 2000; Shen et al., 2002). The natural variability of this $^{230}Th/^{232}Th_{ini}$ can be more than 100 % (Richards and Dorale, 2003; Shen et al., 2012). The determined $^{230}Th/^{232}Th$ atomic ratios are only as low as 1-43 x 10^{-6}, which suggests a significant amount of $^{230}Th_0$. Isochron techniques, used to obtain reliable estimates for the $^{230}Th/^{232}Th_{ini}$ ratio and the ^{230}Th age for a matrix with a single thorium source, cannot successfully be applied to our vein carbonate samples, which indicate complicated input of detrital isotopes. The uncorrected ages in Table 2 represent their maximal formation ages. The maximal age of the youngest vein carbonate, sample FS-2 near the fault zone (Fig. 3-c), is 4,174±743 yr, and the oldest, sample FS-8, is 202±35 kyr (Table 2).

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5. Discussion

5.1 Clumped-isotope thermometry in geothermal systems

Applications of clumped isotopes at high temperatures, such as basin fluids, hydrothermal systems and metamorphism, are few but increasing in number (e.q. Bergman et al., 2013; Cruset et al., 2016; Dale et al., 2014; Kele et al., 2015; Luetkemeyer et al., 2016; MacDonald et al., 2016; Shenton et al., 2015; Sumner et al., 2015). Most of the experimental and empirical clumped-isotope $\Delta47$-temperature relationships have mainly been determined for paleoclimate applications (e.q. Daëron et al., 2011; Eiler, 2011; Ghosh et al., 2006; Tripati et al., 2010; Zaarur et al., 2011) However, a recent calibration using precipitation experiments mixing $CaCl_2$ and $NaHCO_3$ in a pressurized reaction vessel at pressures of up to 80 bars established a calibration curve between 25˚C and 250˚C (Kluge et al., 2015). This calibration is the most appropriate for high temperature applications of clumped isotopes, such as the geothermal calcite precipitates in this study.

The scaling samples in this study can be used to validate the $\Delta47$-T calibration curve of (Kluge et al., 2015). Much scaling occurred inside the pipes during the productions of thermal fluids for the power plant, and the well temperatures were recorded directly down to a depth of 1,275 meters. The temperatures at the well

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bottom (1,500 m) and head of IC-13 were 210˚C and 183.9˚C, respectively, under a pressure of 14.6 Kg/cm^2 (Tong et al., 1978). The scaling samples of IC-13 were collected at the depth interval of 939-1,067 m, where the temperature of the thermal fluids ranged from 187˚C to 191˚C measured by Chinese Petroleum Corporation, Taiwan (CPC) (Tong et al., 1978). These results indicate that the temperature for precipitated calcite scaling in the IC-13 well may have ranged from 187˚C to 210˚C.

The calculated clumped-isotope temperature of the IC-13 scaling using the equations of Kluge et al. (2015) is 214±16˚C. The temperature of precipitated scaling directly measured from well logging ranges from 187˚C to 210˚C. Accordingly, the Δ47-T equation calibrated by Kluge et al. (2015) yields a temperature that is within error of the well temperature, validating the use of this calibration for the well conditions. However, given the error on clumped-isotope measurements (±15˚C at this high temperature), we acknowledge that we cannot completely exclude that the temperatures are perhaps slightly higher than the well temperatures.

One possibility with scaling deposits is the effect of degassing on the clumped-isotope values, similar to what is observed for speleothems (Affek and Zaarur, 2014; Daëron et al., 2011). For geothermal scaling, rapid depressurization leads to the release of exsolution CO_2 gases, causing a rapid oversaturation of the

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solution with bicarbonate accompanied by a pH increase. This causes carbonate minerals to precipitate from the thermal water immediately. The calibration of Kluge et al. (2015) was performed at isotopic equilibrium, without depressurizing the cylinder. Previous work on speleothems had already highlighted the effect of rapid CO_2 degassing on the clumped-isotope value of precipitated calcite, resulting in a temperature recorded in the mineral approximately 6˚C warmer than ambient conditions (Affek et al., 2014; Daëron et al., 2011). In a similar fashion, the clumped isotope temperatures of the scaling in this study is slightly higher than the measured well temperature and so may reflect a similar process, although the error on the clumped isotope temperatures preclude stating this with any certainty .

5.2 Two End Members for Fluid Sources

Thermal waters from drilling wells and surface outcrops have been collected for oxygen and hydrogen isotope analyses to understand their origin (Liu et al., 1990, 1982). The δD and $\delta^{18}O$ values of thermal water ranged from -58 ‰ to -47 ‰ and from -7.4 ‰ to -5.7 ‰, respectively, which are considerably lower, by 20 ‰ in δD, than those of the local river and creek waters. Such results suggested that the recharge area for the thermal water could be located at higher altitude (Liu et al., 1990, 1982). In addition, the circulation of thermal water might be shorter than the 20 years

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determined by tritium dating (Chiang et al., 1984). Based on these data, many researchers concluded that thermal fluids from the Chingshui and Tuchang geothermal fields may have come from deep circulation of meteoric water, which infiltrated into the deep crust and was heated by the high geothermal gradient due to rapid uplift during the Taiwan orogeny (Chen, 1982; Yui et al., 1993).

A previous study analyzing calcite cuttings in core IC-16 showed $\delta^{18}O$ and $\delta^{13}C$ values ranging from -7.3 ‰ to -0.9 ‰ and 0.0 ‰ to 15.1 ‰, respectively (Yui et al., 1993). Apparently, these data are intermediate between the values of scaling and outcrops in our study (Fig. 5). Several of these calcite cuttings with higher $\delta^{18}O$ values (9.4-15.1 ‰) and $\delta^{13}C$ values (-4.8~-0.9 ‰) in core IC-16 were considered as the result of strong water-rock interaction at 230˚C, when meteoric water interacted with Lushan Formation argillite/slate (the $\delta^{18}O$ values were estimated to be 12.2 ‰ by Chu and Shieh (1981) (Liu et al., 1986)). However, no significant hydrothermal alterations have been found in cuttings and short cores of IC-16 (Liu et al., 1986). The higher isotopic ratios of calcite cuttings may result from isotopic exchange between marine authigenic carbonates and thermal fluids at temperatures that are progressively increasing during metamorphism (Yui et al., 1993).

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On the basis of the clumped-isotope analyses in this study, different fluid sources can be distinguished. The $\delta^{18}O$ value of thermal fluid precipitating the calcite scaling in well IC-13 is -5.8±0.8 ‰ (calculated using Friedman & O'Neil, 1977), which is similar to the $\delta^{18}O$ values of -7.4 ‰ to -5.7 ‰ measured from the thermal waters and consistent with that from local meteoric water (Liu et al., 1990). These results imply that the thermal water inside well IC-13 may come from very shallow circulation with little water-rock interaction or without mixing with other deeper fluids. On the other hand, the $\delta^{18}O$ values of fluids precipitating calcite veins in and near surface outcrops of fault zones are -1.0±1.6 ‰ to 10.0±1.3 ‰ (calculated using Friedman & O'Neil, 1977). These oxygen isotopic ratios are totally different from that of local meteoric water and suggest that the thermal fluids may be generated by either magmatic or metamorphic processes (Taylor, 1974). The results strongly indicate that two end members of fluids can be identified in terms of oxygen isotopic compositions. One comes from meteoric water with lower $\delta^{18}O$ values, while the other originates from either magmatic or metamorphic fluids with higher $\delta^{18}O$ values.

Two geothermal reservoirs have been proposed underneath the Chingshui geothermal field according to magnetotelluric (MT) images (Chiang et al., 2014; Song, 2012). One is shallower at a depth of less than 3,000 m, while the other is

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deeper at depths ranging from 4,000 m to 8,000 m. Moreover, abundant micro-seismicity occurred at the top of the deep reservoir, which was detected by seismometers deployed between 2010 and 2012 (Liu, 2013). This result leads us to infer that the deep reservoir may be a high-temperature hydrothermal system with frequent hydraulic fracturing that induces micro-seismicity.

Our isotopic data combined with these lines of evidence suggest that the scaling in geothermal wells could be derived from fluids originating from the shallower reservoir, which contains heated meteoric water. In contrast, the veins with larger $\delta^{18}O$ values on outcrops could be formed from the deeper reservoir with ^{18}O-enriched, deeply sourced fluids related to either metamorphic dehydration or magmatic processes. The samples from IC-16 (Liu et al., 1986) could be mixed in different percentages beneath the Chingshui geothermal field. Thus, deep faults with wide damage zones could provide a conduit for upwelling from the deeper reservoir to precipitate calcite veins near the faults.

According to the maximum age of U-Th dating (uncorrected age) on these outcrop veins, the deeper reservoir and normal faults were active from 0.2 myr and continued until fairly recently (< 4.172 kyr). It is noteworthy that the youngest vein occurring

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near the fault shows the highest temperature (264±30°C) and the largest $\delta^{18}O$ value, which suggests that the deeper reservoir is still active today.

The mixing of various fluids with significantly different isotopic compositions to form thermal water is common in geothermal systems. Such characteristics have been recognized in many famous hydrothermal fields all over the world, such as the Larderello and Sicily of Italy, the Geysers of the USA, the Showashinzan volcano of Japan, and Tongonan of the Philippines (Alvis-Isidro et al., 1993; Geyh, 2000; Giggenbach, 1989). The thermal fluids were formed by magmatic and/or metamorphic fluids mixing with locally recharged meteoric water in a fractured geothermal reservoir, and then the meteoric water was heated with a $\delta^{18}O$ shift; meanwhile, water-rock interaction and mineralization occurred in a deeper reservoir.

5.3 Magmatic or metamorphic fluid source for the deeper fluid reservoir?

A double reservoir model is proposed here to interpret the geological and geochemical evidence in the Chingshui geothermal system (Fig. 6). In this model, the upper reservoir with a meteoric water source is heated by the deeper one, which supplies heat and fluids for the Chingshui geothermal system. However, the deepest well in the Chingshui area is only approximately 3,000 meters deep, which is

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shallower than the depth of the deeper reservoir identified by the MT images. It is not possible to obtain fluid samples directly from the deeper reservoir; thus, sampling and analyses on volatile gases and on veins precipitated from the deeper fluids are the probable ways to recognize its properties and origin.

Helium isotope data from Cheng (2014) provided strong evidence of magmatic fluids from the deeper reservoir in the Chingshui geothermal field. Two runs of gases were collected from well IC-19 at a depth of 500 m for helium isotopic measurements. The ratios of $^{3}He/^{4}He$ were 3.8-4.0 R_A and 0.8 R_A for the first and second runs, respectively. These results indicated the existence of a mantle-derived component in the Chingshui area, which may be derived from magmatic degassing; however, the lower helium isotope ratio of the other sample also implied a mixing between such a deeper, magmatic-related reservoir and a shallower, crustal-related one (Cheng, 2014).

Establishing the existence of a magmatic-related reservoir with certainty requires further evidence. In general, deeper reservoirs derived from magma intrusions may be composed of abundant hot fluids. Fluids dissolved in magma increase with pressure and depth and affect the mechanics of magma intrusion (Burnham and Barnes, 1979). When magma rises up from deep to shallow depths, fluids can be separated from the

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magma and accumulated near the top of intrusive bodies. The whole process may induce micro-seismicity around intrusive bodies. Abundant micro-seismicity induced by hydrothermal activity or natural hydraulic fracturing has been observed on the top or around the margins of the deeper reservoir in the Chingshui area (Liu, 2013). On the other hand, the Chingshui geothermal field is located at the southwesternmost tip of the triangular Ilan Plain, which is the western extension of the opening Okinawa Trough. A series of normal faults and opening joints have been recognized to support the extensional regional stresses occurring in this area. These faults may provide conduits or stress fields for magma to rise up easily and erupt at the surface as a volcano, the Kueishantao, and to intrude underneath the Chingshui area and Ilan Plain (Tong et al., 2008). Higher ratios of $^{3}He/^{4}He$ with values of 7.3~8.4 R_A have been observed in the Kueishantao (Yang et al., 2005), and the values are comparable to that of the sample from the drilling well in the Chingshui geothermal field. Thus, geochemical and geophysical evidence along with the tectonic setting strongly support a model where magma intrusions may have occurred and provided abundant thermal fluids underneath the Chingshui geothermal field.

The result of oxygen isotopic analyses of vein carbonates from the outcrop must be assessed in view of the proposed model. The $\delta^{18}O$ values of fluids estimated from the

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outcrop carbonate samples indicate that thermal fluids of the deeper reservoir is rich in ^{18}O with $\delta^{18}O$ values up to 10.0 ‰. Most volcanic and plutonic rocks show uniform $\delta^{18}O$ values ranging from +5.5 ‰ to +10.0 ‰ (Taylor, 1974), but a few may be as high as +13 ‰, such as the Pleistocene volcano in north Rome, Italy (Turi and Taylor, 1976). However, wide ranges of $\delta^{18}O$ values from +5 to +25 ‰ have been recognized in most regional metamorphic fluids and dehydration waters from metamorphosed shale, limestone, and chert (Taylor, 1974). Thus, it is difficult to distinguish metamorphic dehydration from magmatic degassing with only the oxygen isotopic composition of thermal fluids in the Chingshui geothermal field. In addition, the dominant rock formation of the Chingshui area is the Lushan Formation, which is composed of argillite or slate formed during the Late Cenozoic Penglai Orogeny. Abundant pore water would have been released as thermal fluids during metamorphism with ambiguous oxygen isotopic compositions due to various fluid origins and complex water-rock interactions (Phillips, 1993; Yardley et al., 2013). Therefore, we cannot completely exclude the possibility of metamorphic fluids being involved in the deep reservoir in the Chingshui geothermal field based on oxygen isotopes alone.

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Carbon isotopic compositions of vein carbonates may provide more information in terms of fluid sources. The $\delta^{13}C$ values of outcrop calcite veins in the Chingshui area range from -1.9 ‰ to -0.2 ‰, which is heavier than those of calcareous meta-sandstone in the Lushan Formation, which range from -3.2 ‰ to -2.5 ‰, and those of dissolved inorganic carbon (DIC) in geothermal water from the upper reservoir, which range from -8.5 ‰ to -7.5 ‰ (Liu et al., 1982). 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 Tatun Volcano Group (TVO, Fig. 1-b), Taiwan, is approximately -3.0~-7.3 ‰ (Lee et al., 2005; Yang et al., 2003). By comparison (Fig. 7), the carbon source of vein carbonates precipitated from the deeper reservoir could not be derived only from the Lushan Formation or volcanic gas in the surrounding area. A carbon source with higher $\delta^{13}C$ values should be included in the deeper reservoir. So far, only marine carbonates could possibly inherit ^{13}C-enriched carbon reservoirs. Many marbles that crop out in the Tongau area are several to tens of kilometers away from the Chingshui area (Chu and Shieh, 1981; Yui and Lan, 1991). The rock formation underneath the

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Lushan Formation is a pre-Tertiary basement that is predominantly composed of marble (Ernst, 1983). Carbon isotope compositions of this marble have been analyzed, and the $\delta^{13}C$ values range from +0 ‰ to +4.0 ‰ (Chu and Shieh, 1981; Yui and Lan, 1991). It seems probable that the thermal fluids of the deeper reservoir in the Chinghsui area may partially come from or mix with fluids derived from marble decarbonization.

On the basis of multiple lines of evidence noted above, the fluid source of the deeper reservoir in the Chinghsui geothermal field may be regarded as likely related to magmatic intrusion with a subsidiary input of metamorphic decarbonization.

6. Conclusions

The carbon, oxygen and clumped-isotopic compositions of calcite scaling in wells and veins on outcrops were analyzed, and the formation temperatures of calcites were estimated to examine the fluids and carbon sources in the Chingshui geothermal area. The calculated $\delta^{18}O$ values of hot fluids with the growth of calcite veins on the outcrop are varied and significantly different from those of local meteoric water, while the $\delta^{18}O$ values of fluids derived from scaling are close to the calculated values. This result implies that the oxygen isotopic compositions of hot fluids may have

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different sources for the calcite veins and scaling in the Chingshui geothermal field. Previous study of magnetotelluric (MT) images of this area identified two possible fluid reservoirs with different depths underneath Chingshui (Chiang et al., 2014; Song, 2012), and the He isotopic composition of thermal water suggested a deep magmatic source (Cheng, 2014). Consequently, the shallow reservoir may provide heated meteoric water for the precipitation of scaling in well IC-13, while the deep reservoir could supply magmatic-like fluids for the growth of veins on the outcrops. Considering the larger $\delta^{13}C$ values of outcrop samples, the DIC in the deep reservoir may also involve deep marble dissociation.

7. Acknowledgments

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Fig. 1. (a) The plate tectonic context in which Taiwan sits, where is famous for the young orogenic belt where the Philippine Sea plate collides with the Eurasian continental margin. (b) The Chingshui geothermal field is located in the valley of Chingshui River, which is in the southwestern Ilan Plain. (c) The sample locations of fields and wells in the Chingshui geothermal field.

Fig. 2. The scaling of IC-13 showing precipitated layers (Black arrows), which indicate rapid nucleation and precipitation interspersed with crystal growth.

Fig. 3. (a) A normal fault (red line), located at the confluence of Chingshui River and Chilukeng River is approximately 2 m wide with a steep dip and contains blocks of quartz veins. (b) A series of normal faults is found along the river (Fig. 3-a) with strikes N55-75°E and dips 30-80°N. (c) The white arrowhead indicates sample FS-2 in the damage zone of the fault in Fig. 3-b.

Fig. 4. The BSE image of FS-7 from the outcrop shows calcite (lighter) and quartz (darker) intergrown together.

Fig. 5. The plots of carbon and oxygen isotopes of calcite veins and calcareous meta-sandstone in outcrops, scaling from well IC-13 and well IC-19, and calcite from well IC-16 (Liu et al., 1986). The results show that calcites from outcrops and the well IC-13/IC-19 scaling represent two isotopic end members and those from well IC-16 are mixtures.

Fig. 6. The geothermal conceptual model to interpret the geological and geochemical evidence in the Chingshui geothermal system. The calculated $\delta^{18}O$ values of hot fluids associated with the

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growth of calcite veins on the outcrop are much heavier and significantly different from that of the local meteoric water, while the $\delta^{18}O$ values of fluids derived from scaling are close to that. This result implies that the shallow reservoir provided heated meteoric water for the precipitation of scaling in well IC-13, while the deep one could supply magmatic-like fluid for the growth of veins on the outcrops. The $\delta^{13}C$ values of outcrop samples range from -1.9 to -0.2 ‰, which are higher than the $\delta^{13}C_{DIC}$ values in meteoric water, calcareous meta-sandstone, and gas of mantle origin. They imply the possibility that the deep reservoir might also be involved in deep marble decarbonization.

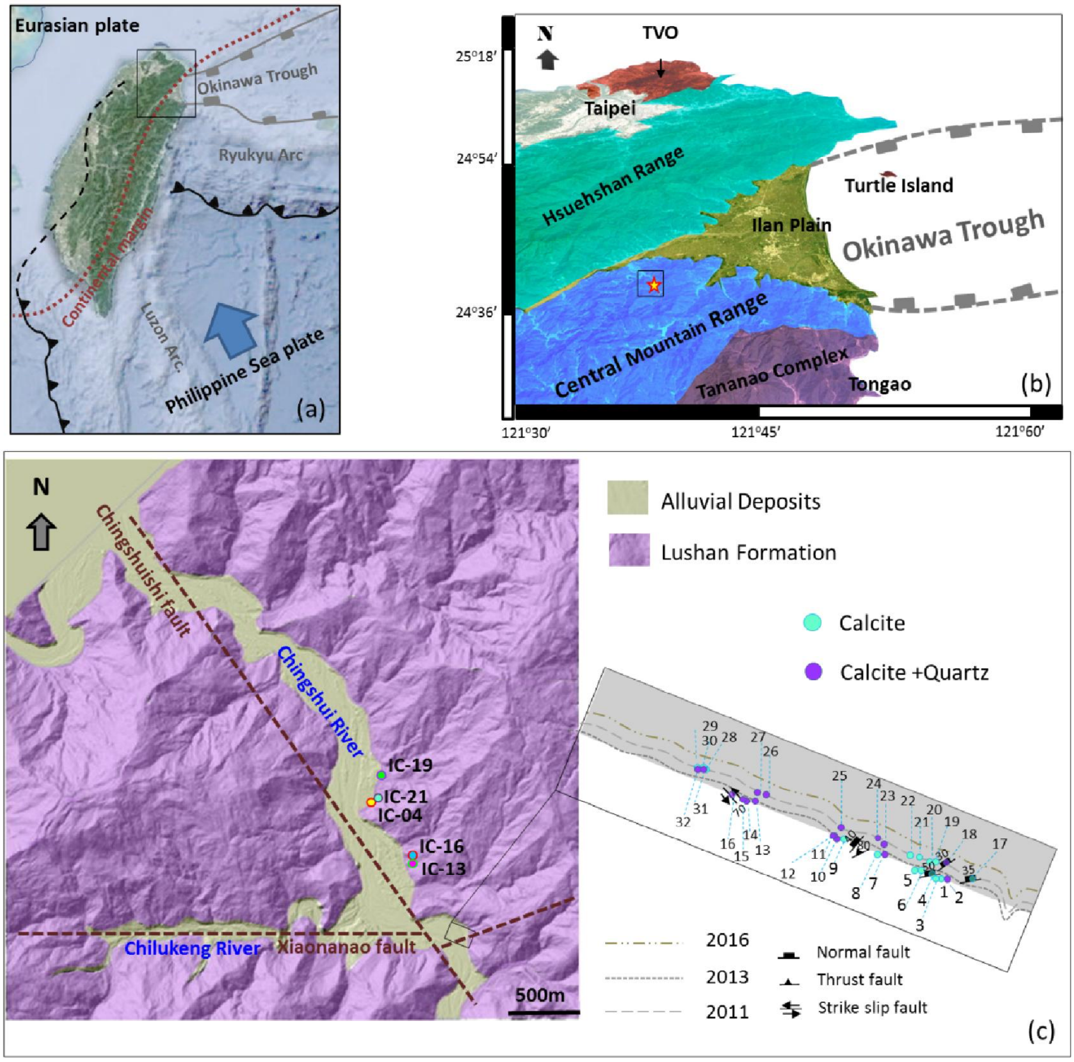
Fig. 7. The comparison of $\delta^{13}C$ values of outcrop calcite veins in the Chingshui field, DIC in geothermal water from the upper reservoir (Liu et al., 1982), calcareous meta-sandstone in the Lushan Formation, CO_2 gas from TVO (Lee, 2005; Yang et al.,2003), CO_2 gas of mantle origin (Hurwitz et al., 2003), CO_2 gas from an island arc volcano (Sano & Marty, 1995), and the marble from Tongau (Chu and Shieh, 1981; Yui and Lan, 1991). This comparison implies implies that the thermal fluids of the deeper reservoir in the Chinghsui area may partially come from or mix with fluids derived from marble decarbonization.

Table 1. Clumped-isotope data and the calculated $\delta^{18}O$ values of fluids.

Table 2. The uncorrected /maximal ages by uranium-series dating.

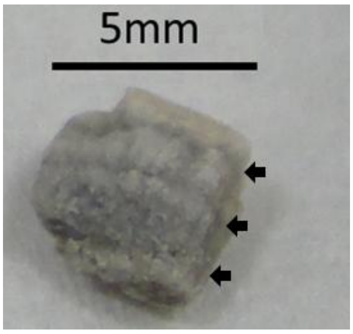
APPENDIX A. SUPPLEMENTARY DATA 1. Carbon and Oxygen Isotopic data

APPENDIX A. SUPPLEMENTARY DATA 2. Clumped-isotopic data


Eurasian plate
Okinawa Trough
Ryukyu Arc
Continental margin
Luzon Arc
Philippine Sea plate
(a)
N
TVO
Taipei
Hsuehshan Range
Turtle Island
Ilan Plain
Okinawa Trough
Central Mountain Range
Tananao Complex
Tongao
(b)
25°18′
24°54′
24°36′
121°30′
121°45′
121°60′
N
Chingshuishi fault
Chingshui River
IC-19
IC-21
IC-04
IC-16
IC-13
Chilukeng River
Xiaonanao fault
500m
Alluvial Deposits
Lushan Formation
Calcite
Calcite +Quartz
2016
2013
2011
Normal fault
Thrust fault
Strike slip fault
(c)

707

708

709 

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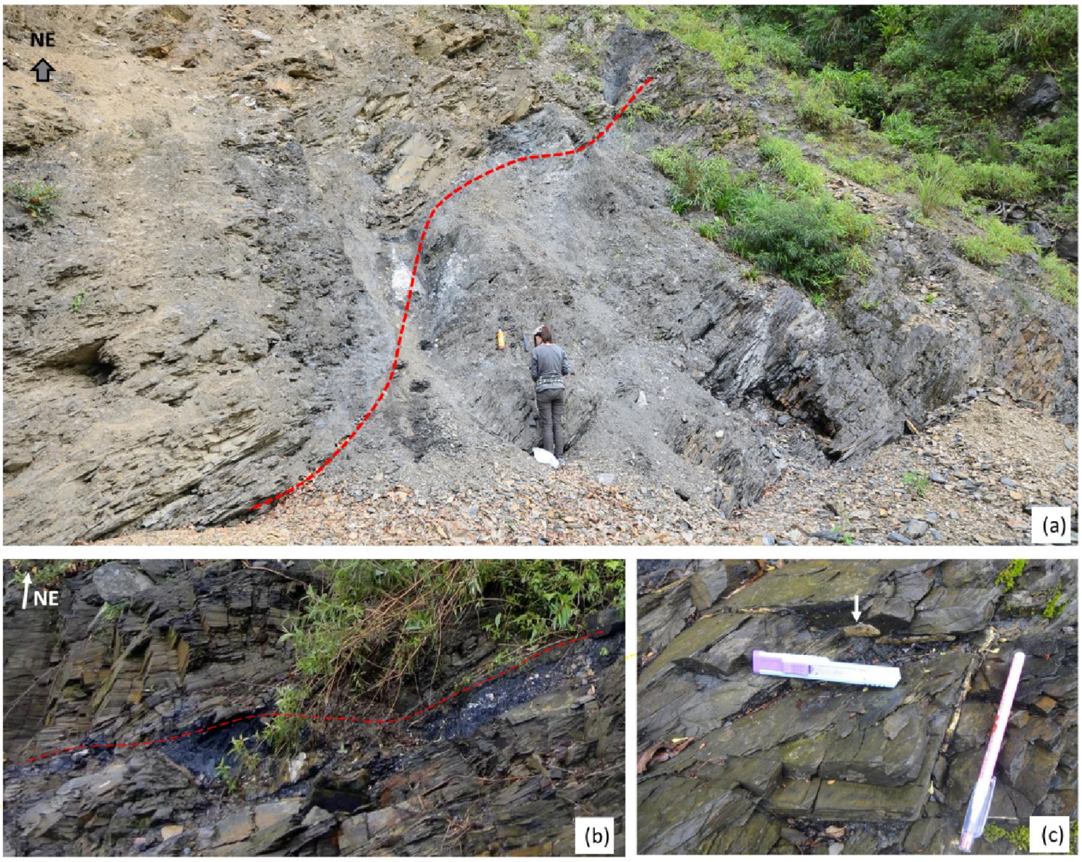

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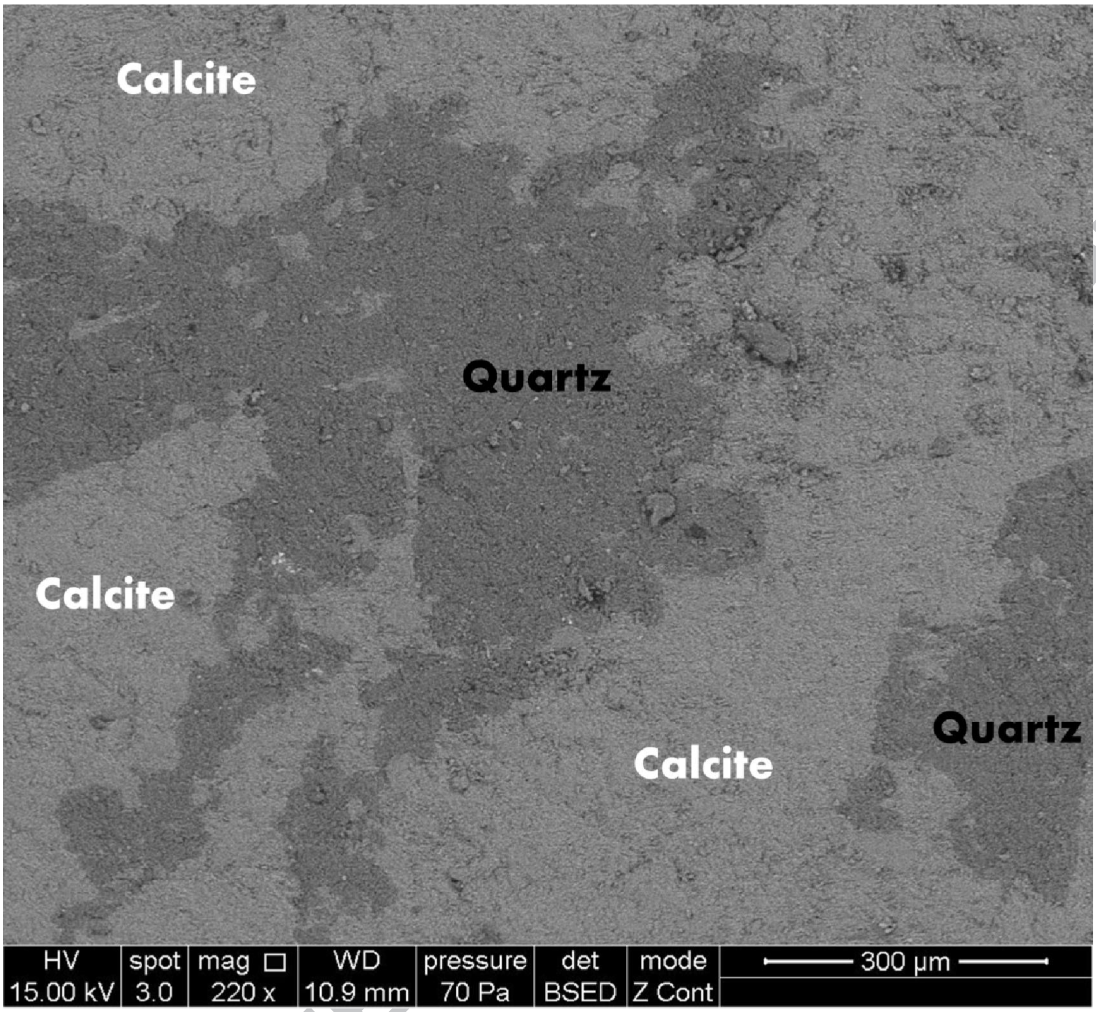

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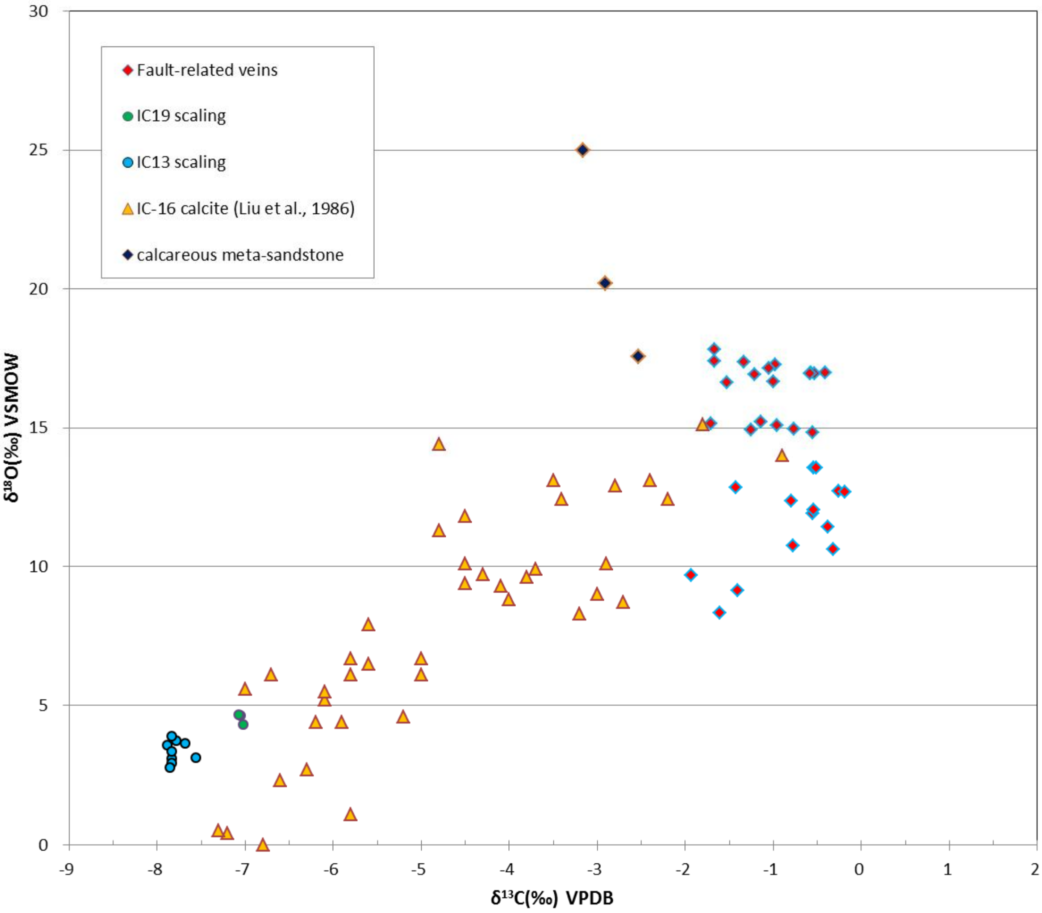

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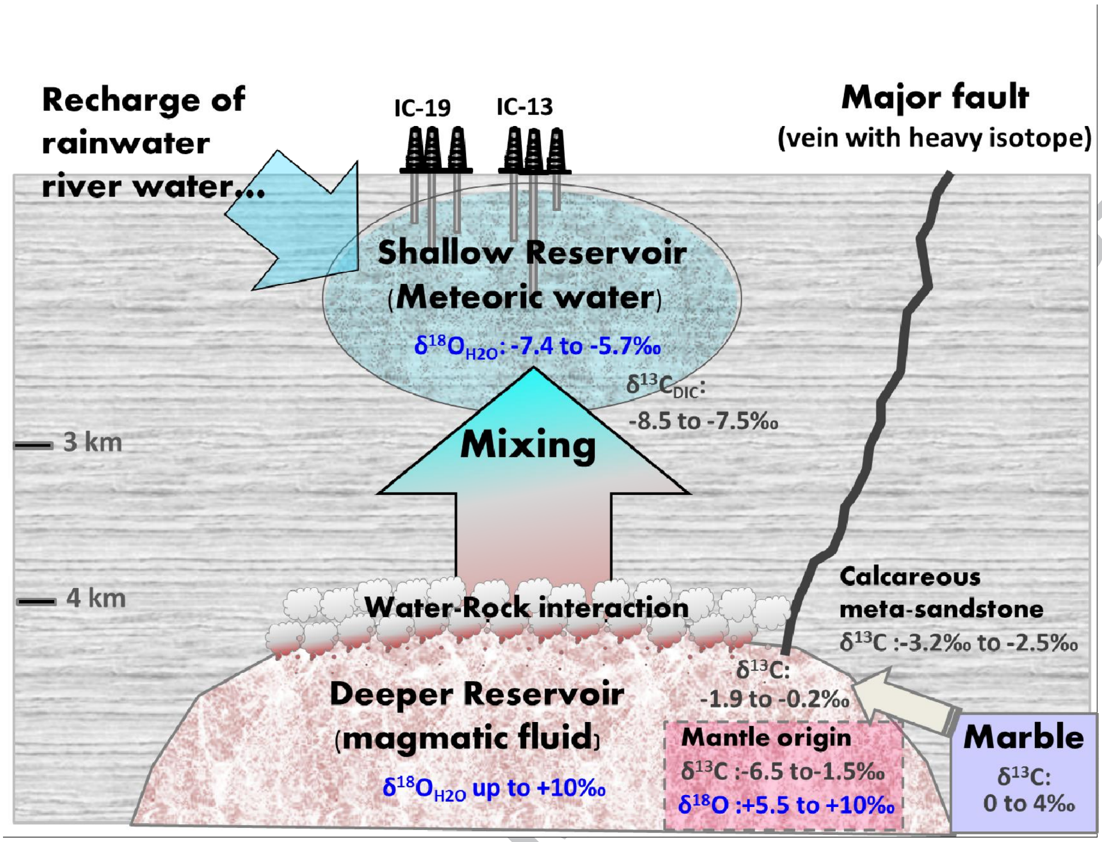
717 

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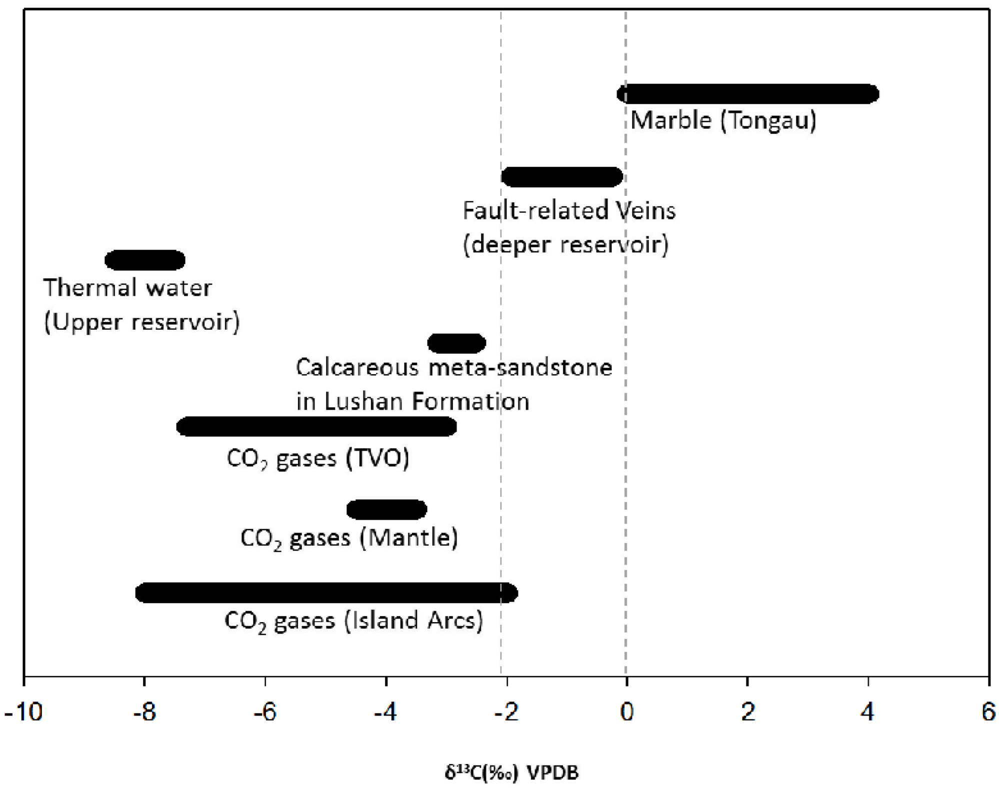

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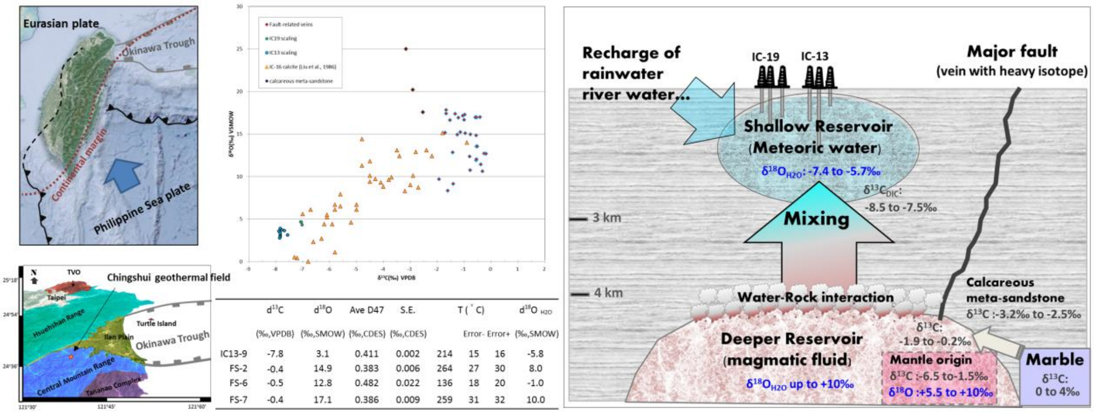

	$d^{13}C$	$d^{18}O$	Ave D47	S.E.	T (°C)			$d^{18}O_{H2O}$
	(‰,VPDB)	(‰,SMOW)	(‰,CDES)	(‰,CDES)		Error-	Error+	(‰,SMOW)
IC13-9	-7.8	3.1	0.411	0.002	214	15	16	-5.8
FS-2	-0.4	14.9	0.383	0.006	264	27	30	8.0
FS-6	-0.5	12.8	0.482	0.022	136	18	20	-1.0
FS-7	-0.4	17.1	0.386	0.009	259	31	32	10.0

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	Replicates	$\delta^{13}C$	$\delta^{18}O$	$\delta^{18}O$[a]	Ave $\Delta47$	S.E.	T (˚C)[b]			$d^{18}O_{H2O}$ (‰,SMOW)[c]		
	(n)	(‰,VPDB)	(‰,VPDB)	(‰,SMOW)	(‰,CDES)	(‰,CDES)		Error-	Error+	min.	max.	ave.
IC13-09	2	-7.8	-27.0	3.1	0.411	0.002	214	15	16	-6.5	-5.1	-5.8
FS-2	3	-0.4	-15.5	14.9	0.383	0.006	264	27	30	7.0	9.0	8.0
FS-6	3	-0.5	-17.6	12.8	0.482	0.022	136	18	20	-2.6	0.5	-1.0
FS-7	2	-0.4	-13.4	17.1	0.386	0.009	259	31	32	8.8	11.1	10.0

[a.] δ18Ocalcite (‰ SMOW). Calculated with a formula of Friedman & O'Neil, 1977.

[b.] The calcite growth temperatures calculated from corrected $\Delta47$ values are based on various theoretical and experimental calibrations derived by revised Kluge et al.(2015).

[c.] The $\delta^{18}O$ of fluids were estimated by Friedman & O'Neil (1977), synthetic calcite.

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Sample	Weight	^{238}U	^{232}Th	$d^{234}U$	$[^{230}Th/^{238}U]$	$[^{230}Th/^{232}Th]$	Age
name	g	ppb	ppt	measured[a]	activity[c]	ppm[d]	uncorrected
FS-2	0.2793	15.188 ± 0.022	15409 ± 258	621.1 ± 3.9	0.061 ± 0.011	0.99 ± 0.17	4,172 ± 743
FS-3	0.0077	8.12 ± 0.06	24953 ± 219	3747 ± 34	2.8825 ± 0.1003	15.49 ± 0.55	88,581 ± 4333
FS-6	0.0052	3.98 ± 0.03	4745 ± 135	1882 ± 39	2.3227 ± 0.0906	32.18 ± 1.54	1,39,957 ± 10001
FS-7	0.0019	45.12 ± 0.33	76750 ± 966	533 ± 16	0.3331 ± 0.0293	3.23 ± 0.29	26,367 ± 2608
FS-8	0.0046	4.66 ± 0.05	7419 ± 157	422 ± 30	1.2843 ± 0.0813	13.32 ± 0.88	2,02,385 ± 35499
FS-9	0.0019	5.47 ± 0.02	22202 ± 279	1449 ± 30	2.348 ± 0.1542	9.54 ± 0.64	2,00,580 ± 30832
FS-10	0.0008	71.09 ± 0.23	40416 ± 610	407 ± 16	0.545 ± 0.0332	15.81 ± 0.99	52,031 ± 4033
FS-12	0.0018	20.5 ± 0.27	60097 ± 586	368 ± 28	0.9227 ± 0.0626	5.2 ± 0.35	1,14,207 ± 13627
FS-14	0.0018	52.97 ± 0.64	18894 ± 389	111 ± 19	0.9299 ± 0.0244	43.04 ± 1.34	1,86,269 ± 15740
FS-15	0.0019	48.82 ± 0.55	63055 ± 802	150 ± 20	0.9078 ± 0.0340	11.6 ± 0.44	1,60,352 ± 14905
FS-16	0.0043	23.21 ± 0.21	53608 ± 522	510 ± 19	1.1868 ± 0.0452	8.48 ± 0.32	1,47,083 ± 11459

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1. It's the first time to use clumped isotope thermometry in a geothermal system of Taiwan.
2. Two-reservoir model was proposed for the Chingshui geothermal system based on new geochemical and geophysical data.
3. The heat sources of the Chingshui geothermal system have been predominantly identified as magmatic origin, which is different from previous studies.
4. The deep fluids may be derived from mixed magmatic fluid and marble decarbonization according to the carbon, oxygen and clumped-isotopic data.

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