Applicability of the Na-K geothermometer in Slate Formations of Taiwan

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ABSTRACT

More than 2/3 of hot springs in Taiwan are located in the Central Range metamorphic terrane, where argillite, slate, phyllite and black schist are predominated. Rapid uplift and erosion generate a higher geothermal gradient. The meteoric water infiltrated downward, was heated, then rose to the surface as hot springs by regional faults or fractured systems.

The SiO_2 geothermometer has been proved to be suitable in the argillite/slate formations of Taiwan (Chen, 1985; Huang et al., 2018). However, the applicability of the Na-K geothermometer has been debated for a long time. The widely used formula proposed by Fournier and Truesdell (1973) isn't suitable in argillite/slate formations, because K-feldspar is absence. Chen (1985) proposed an albite-muscovite equilibrium formula of the Na-K geothermometer for argillite/slate formations. However, the 60-days argillite-fluid interactions showed that the Na-K geothermometer has a reverse relationship with experimental temperature (Huang et al., 2018).

In this paper, we advocate that the reverse relationships of Na-K geothermometer and experimental temperature in Huang et al. (2018) may be affected by reaction time and redox state. The good correlation of Na/K and silica temperatures from well fluids implies that the Na-K geothermometer is worth considering.

A new empirical formula of Na-K geothermometer is proposed by the fluids from deep production wells and based on quartz geothermometers above 180°C in this study.

$\log(Na/K)=2.474*10^3T^{-1}-3.7267$ $\quad R^2=0.71$

From which the $T_{Na/K}$ (°C)

$$227°C > T > 180°C, \quad T(°C) = \frac{2474}{\log\left(\frac{Na}{K}\right)+3.73} - 273.15$$

Most of the calculated errors between $T_{Na\text{-}K}$ and T_{quartz} we proposed are less than 8°C in the Chingshui, Tuchun, and Lushan geothermal fields. Poor coefficient of determination (R^2 value) may be due to the equilibrium involved with H^+ and complex clay mineral interactions.

1. INTRODUCTION

1.1 Geological setting

The island of Taiwan is formed by an active mountain building process along a complex convergent boundary between the Eurasian Plate and the Philippine Sea Plate. The Philippine Sea plate is moving toward WNW at about 70 mm/yr and colliding with the Eurasian continental margin (Seno and Maruyama, 1984; Tsai et al., 1981; Yu and Chen, 1994). Folding and fault thrusting exist everywhere in the central Taiwan, which cause rapid uplifting with the rate around 5-10 mm/yr in the past few million years (Chen, 1982; Ching et al., 2011; Lee, 1977; Liu et al., 1982) and create the island of Taiwan (Ho, 1986; Teng, 1990, 1987).

Rapid uplift and erosion generate an above-average geothermal gradient (Chen, 1975). Nisbet and Fowler (1982) calculated and showed that the erosion rate is high in comparison with other areas of the world. More than 100 hot springs spread out in a 300 km long and 40-70 km wide metamorphic terrane, including the Central Mountain Range and the Hsuishan Range (Chen, 1985).

One of the unique metamorphic terrane with several thousand meters thick of slate from early to middle Miocene, the Lushan Formation distributes widely in the Central Range. It consists largely of black to dark gray argillite, slate, and phyllite with occasionally interlayered with thin meta-sandstones (Chen, 1985). This formation is exposed in the northern Taiwan and extends southward along the crest zone of the Central Range (Chen, 2016) to the areas of Chihpen and Tawu in the southeastern Taiwan (Chen, 2016). The Chingshui geothermal field, Tuchang-Jentse geothermal field, the Lushan geothermal field, the Chihpon geothermal field, and the Chinlun geothermal field are among the most famous ones (Fig.1). To build a suitable and workable geothermometer in this terrane is critical for estimating reservoir temperatures and geothermal potentials.

1.2 Chemical characters of thermal waters in the slate formations

Hot springs in the Lushan Formation occur in deep valleys or depressions surrounded by elevated mountain peaks (Chen, 1985). Chen (1982) proposed that the heat source of hot springs in the slate formation originated from the residual heat of rock formations. The meteoric water infiltrated downward, was heated by the surrounded rocks with a high geothermal gradient, then rose to the shallower reservoirs or to the surface as hot springs through regional faults or fractured systems.

The hydrogen and oxygen isotopic compositions of natural hot springs and thermal water support the model mentioned above. Plots of H and O isotopic compositions of thermal water on the local Meteoric Water Line (MWL), 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; Yui et al., 1993). Liu et al. (1990), thus, suggested that the thermal fluids came from the deep circulation of meteoric water.

Geochemically, the hot fluids in the Lushan Formation belong to the sodium bicarbonate type, which are formed by reaction of carbonic acid in water with the albite or plagioclase in the rocks (Chen, 1985). The concentration of HCO_3^- is extremely high, ranging from 760-2800 mg/L, while the Cl^- and SO_4^{2-} concentrations are much lower than those of volcanic thermal waters, only 13-50 mg/L and 15-60 mg/L, respectively. It's because the volcanic gas, HCl and H_2S are rare in the metamorphic environments (Chen, 1985).

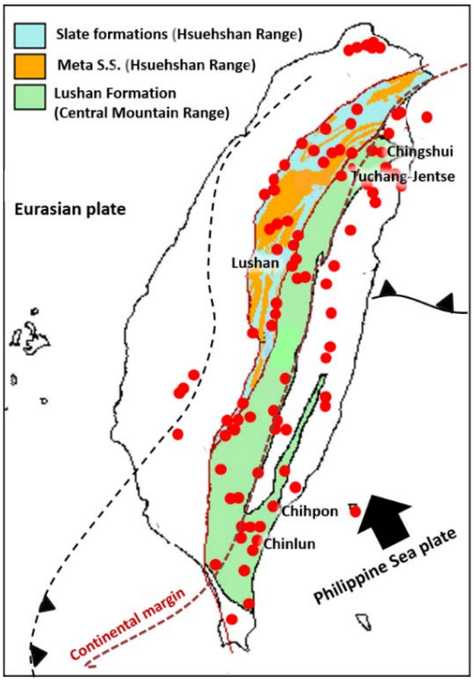

Figure 1: Geological setting and hot springs distribution in Taiwan.

1.3 Na-K geothermometer

The most common geothermometers to estimate the subsurface reservoir temperatures are using SiO_2, Na-K, Na-K-Ca or Na-K-Mg (White, 1970; Fournier and Rowe, 1966; Fournier and Truesdell, 1973, 1974; Fournier, 1977, 1979; Fournier and Potter, 1982; Giggenbach, 1988; Huang et al., 2018). Theoretically, the Na-K, Na-K-Ca or Na-K-Mg geothermometer would be better than silica geothermometer, since the Na/K ratio is independent of spring water evaporation or dilution (Ellis and Wilson, 1960; Ellis and Mahon, 1964).

Mineralogically, the slate in the Lushan Formation contains approximately 60% of quartz, 15% of feldspar, 9% of illite mixing with muscovite, and 16% of chlorite (Huang et al., 2018) without K-feldspar. Therefore, the equilibrium of albite and orthoclase for Na/K geothermometer (White, 1965; Ellis and Wilson, 1960; Giggenbach, 1988) seems to be not suitable for the Lushan Formation.

Chen (1985) proposed the albite-muscovite equilibrium for the Na-K geothermometer, which the silica temperature may represent reservoir one, and the formula is valid for 130-350°C:

$$\log(Na/K)=1.67*10^3T^{-1}-1.73 \qquad (1)$$

From which the Max $t_{Na/K}$ (Albite-Muscovite) (°C):

$$T(℃)=\frac{1670}{\log\left(\frac{Na}{K}\right)+1.73}-273.15 \qquad (2)$$

The albite-muscovite reaction formula:

$$3\ \text{Albite} + 2H^+ + K^+ \leftrightharpoons 3\ Na^+ + \text{Muscovite} + 6\ \text{Quartz}$$

Because the H^+ is involved in the reaction, the variation of pH-value may play a role of uncertainty (Chen, 1985). However, when using this formula, we obtain Na-K temperatures that are about 40-60 °C higher than well logging maximum temperatures.

The 60-days experiments of the argillite-fluid interactions show that the silica geothermometer got convinced results, and the Na/K and Na-K-Ca ratio didn't equilibrate with feldspar. It's mainly controlled by clay minerals such as illite/muscovite and chlorite (Huang et al., 2018). Huang et al. (2018) made conclusions that the Na-K geothermometer showed a reverse relationship from experimental temperatures and suggest that it is not applicable in the argillite/slate of the Lushan Formation.

In this paper, we use more than 120 datasets collected from the deep wells in various locations of the Lushan formation, calculate the Na/K ratios and silica temperatures, and discuss the suitability of the Na-K geothermometer. Then, we revisit the details of the assumptions and data selections in Chen (1985). Finally, the revised albite-muscovite reaction formula is proposed.

2. METHOD

A total of 134 deep well samples with Na^+, K^+, SiO_2 concentrations, pH values, and the highest well and enthalpy temperatures are collected for the feasibility test of Na-K geothermometer. Among them, 53 samples are from the Chingshui geothermal field, 71 are from the Tuchang-Jentse geothermal field, 5 are from the Lushan geothermal field, 5 are from the Chihpon geothermal field and 1 is from the Chinlun geothermal field.

For deriving an empirical Na/K geothermometer in slate formation, we use the silica temperatures in chalcedony and quartz instead of maximum downhole temperature for the following three reasons: (1) deep water temperature could be higher than that measured downhole one; (2) different water temperatures may come from different fractured systems in the same well, resulting the average temperature lower than maximum downhole temperature; and (3) the silica is dissolved in water, which records water temperature precisely.

The chalcedony geothermometer (Arnórsson, 1983):

100°C <T< 180°C, $T(°C) = \frac{1112}{4.91-\log(SiO2)} - 273.15$

The quartz geothermometer for boiling spring under condition of maximum steam (Fournier, 1977):

T >180°C, $T(°C) = \frac{1522}{5.75-\log(SiO2)} - 273.15$

The log(Na/K) is calculated to correlate the $10^3/T_{SiO2}$(K), and the relationship of log(Na/K) and $10^3/T_{SiO2}$(K) are also calculated.

3. RESULTS

Plots of log(Na/K) and $10^3/T_{SiO2}$(K) of deep well fluids are shown in Fig.2. Fluids from the Chingshui geothermal field have the highest silica temperatures.log(Na/K) and $10^3/T_{SiO2}$(K) show better correlations based on the quartz geothermometer above 180°C than those of chalcedony one below 180℃. The equilibrium temperature derived from log(Na/K) and $10^3/T_{quartz}$(K) can be described by the equation:

$$\log(Na/K)=2.474*10^3T^{-1}-3.7267 \quad R^2=0.71 \tag{3}$$

From which the Max $t_{Na/K}$ (°C)

$$T>180°C, \quad T(℃)=\frac{2474}{\log(\frac{Na}{K})+3.73} - 273.15 \tag{4}$$

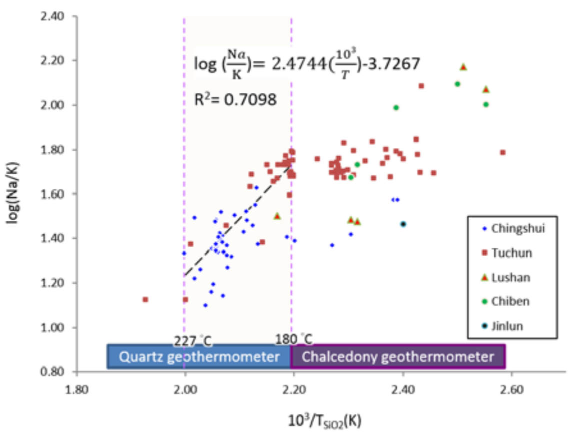

Figure 2: Plots of log(Na/K) and $10^3/T_{SiO2}$(K) of deep well fluids.

4. DISCUSSIONS

4.1 Is Na-K geothermometer applicable in the slate formations?

The 60-days experiments of the argillite-fluid interactions show that the Na-K geothermometer has a reverse relationship from the experimental temperature (Huang et al., 2018). It infers that the Na-K geothermometer is not suitable to estimate the reservoir temperature for the slate formations. However, the field data, including the hot springs (Chen, 1985) and the well fluids (Chen, 1985 and this study) showed the Na/K ratio has good correlation with well and silica temperatures.

We proposed that the reaction time and the redox state correlated to pH value play a dominated role for the differences. Firstly, the Na/K geothermometer is generally thought to take a longer time to reach equilibrium than other commonly used geothermometers (Fournier, 1989). It is debatable that such equilibrium can be reached within 60 days.

Huang et al. (2018) described that there was secondary silicate mineral with a curled flake morphology deposited during the slate-rock interaction products, and the EDS results revealed that the Si: Al: Fe ratios of silicate minerals that grew in temperature ranges of 200 °C–300 °C were closed to clay minerals, i.g. chlorite. According to the dissolved experiment of alumino-silicate parent rocks, the clay dissolved faster than feldspar (Lo et al., 2017), implying that clay minerals are easier to equilibrate with aqueous solution than feldspar in a hydrothermal system. We wondered the pyrites in argillite/slate are oxidized and result in the growth of the Fe-rich secondary silicate minerals and strong acid fluids. If this reaction was occurred, it would be much different from those of deep reservoir in slate formations. The euhedral or framboidal pyrite crystals are widely distributed inside the argillite/slate, even inside the calcite/quartz veins, indicating a reducing environment in the reservoir. The oxidizing condition in hydrothermal systems only occurs in the surface steaming grounds. Therefore, the reverse relationships from Na-K geothermometer and experimental temperature can't represent the reservoir situation.

The insignificant mineral alterations were found in deep cores raised from production wells in the argillite/slate formations, even the host-rock being surrounded by the veins (Lu et al., 2017). This observation could attribute to weak alkaline characteristics of hot fluids in the slate formation. Therefore, it's difficult to identify the minerals affecting the system of Na-K equilibrium. However, the good correlation of Na/K and well and/or silica temperatures implies that the Max $t_{Na/K}$ is still worth to be considered.

4.2 The empirical formula of Na-K geothermometer

Chen (1985) combined the hot springs and well data from Chingshui, Tuchang, and Chihpen to propose the albite-muscovite equilibrium for the Na-K geothermometer in the slate formation. However, the calculated Na-K temperatures according to Chen (1985) were much higher than maximum well temperature, and silica temperatures, i.e., the measured maximum temperatures in the production wells of Chingshui are 215-225°C; while the reservoir temperatures calculated from the silica and Na-K geothermometers are 196-227 °C and 224-318 °C, respectively, based on the Chen's empirical formula .

The higher calculated Na-K temperatures of Chen (1985) may be caused by the data selections, which they not only included the well data, but also combined the data from hot springs. Chen (1985) proposed that most of the shallow water often has its maximum $t_{Na/K}$ being higher than its t_{sio2}; while the deep water directly from the deep sources has a silica temperature very close to the maximum $t_{Na/K}$. It implies that the Na/K ratio is not easily re-equilibrated in ascending thermal water, which used to estimate the temperature of source water. On the other hand, the SiO_2 is more easily re-equilibrated in ascending thermal water, and records temperature change more effectively than the Na/K ratio. However, if the empirical formula included those data with extremely low t_{sio2}, the large error would be occurred.

Chen (1985) used the quartz geothermometer to derive an empirical formula of Na/K geothermometer for slate formation from 130-350 °C. However, the quartz geothermometer is only applicable above 180 °C (i.e. $10^3/T_{SiO2}(K)<2.2$) (Fournier, 1977). Those data, thus, produce higher uncertainty from the empirical formula of Na-K geothermometer.

Here we propose a new empirical formula of Na-K geothermometer, which the data contributed in this formula were only selected from deep production wells. We use the chalcedony and quartz geothermometers to calculate the temperatures of thermal waters with below and above 180°C separately. The results show that the log(Na/K) has better correlations with T_{quartz}, than $T_{chalcedony}$. It is not surprised, according to the water-slate interaction experiment by Huang et al. (2018), the deviation is only 1 °C–6 °C in the quartz geothermometer, but 20–30 °C in the chalcedony due to its polymorph phase transition. For more precise calculation, the empirical formula of Na-K geothermometer was only evaluated above 180 °C, based on the quartz geothermometer temperature (equation 4).

Most of the calculated errors between $T_{Na\text{-}K}$ we proposed and T_{quartz} are less than 8°C (Fig.3). Notably, the R^2 of this formula is only 0.71. It is because either the albite or clay minerals in the water-rock interaction of slate formations with H^+ in the systems, pH value would affect the results. It is also much complex than those of Na-K geothermometer equilibrated with orthoclase and plagioclase in the volcanic systems.

In summary, this empirical formula of the Na-K geothermometer is applicable to the thermal water with temperature higher than 180 °C. The geothermal fields in Taiwan with well temperature higher than 180 ℃ are predominantly distributed in Chingshui, Tuchun and Lushan, and thus are suitable to use this formula to estimate reservoir temperature.

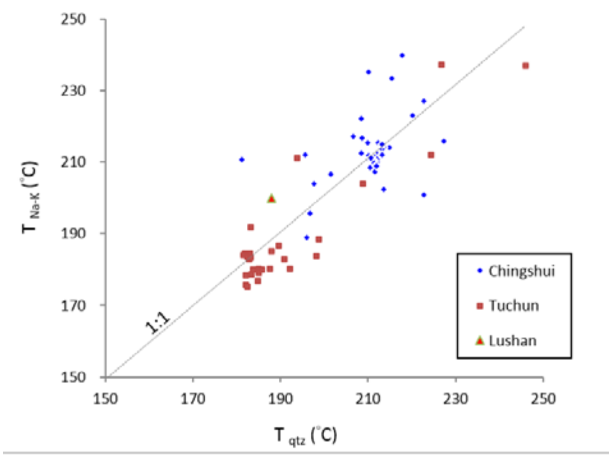

Figure 3: Plots of quartz geothermometer and Na-K geothermometer.

4. CONCLUSION

In this paper, we advocate that the reaction time and the redox state are the two main factors on Na-K equilibrium during argillite-fluid interactions, and can explain that the reverse relationships of Na-K geothermometer and real temperature described in Huang et al. (2018), as well as the good correlation of Na/K and silica temperatures from the well fluids.

A new empirical formula of the Na-K geothermometer is proposed by the fluids from deep production wells in terms of the quartz geothermometer being higher than 180°C.

$$T>180°C, \quad T(℃)=\frac{2474}{\log\left(\frac{Na}{K}\right)+3.73}-273.15$$

Most of the calculated errors between $T_{Na\text{-}K}$ and T_{quartz} by our formula are less than 8°C in the Chingshui, Tuchun, and Lushan geothermal fields. The equilibrium involved H^+ and complex clay mineral interaction would result from the poor R^2 value.

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REFERENCES

Arnórsson, S., Gunnlaugsson, E., Svavarsson, H.: The chemistry of geothermal waters in Iceland. III: Chemical geothermometry in geothermal investigations. *Geochim. Cosmochim. Acta* 47, 567–577. (1983).

Chen, C.H.: Thermal waters in Taiwan, a preliminary study. Proc. Grenoble Symp., Aug. 1975, *Int. Assoc. Hydrol. Sci., Publ.* No. 119, pp. 79-88. (1975).

Chen, C.H.: Analysis of topographic effect on ascending thermal water in the Central Range of Taiwan. *Proc. Natl. Sci. Counc.*, Part A, 6: 241--249. (1982).

Chen, H.F.: Crustal uplift and subsidence in Taiwan: an account based upon retriangulation results. *Spec. Publ. Cent. Geol. Surv. Taiwan* 3, 127–140. (1984)

Chen, W.S.: An introduction to the geology of Taiwan explatory text of the geologic map of Taiwan (1/400000). *Geological Society Located in Taipei, Taipei.* (2016).

Chen, C.H.: Water-Rock Interaction Chemical characteristics of thermal waters in the Central Range of Taiwan. R.O.C. *Chemical Geology* 49, 303–317. (1985).

Ching, K.E., Hsieh, M.L., Johnson, K.M., Chen, K.H., Rau, R.J., Yang, M.:. Modern vertical deformation rates and mountain building in Taiwan from precise leveling and continuous GPS observations, 2000–2008. Jour. Geophy. Res. 116. doi:10.1029/2011JB008242. (2011).

Ellis, A.J., Mahon, W.A.J.: Natural hydrothermal systems and experimental hotwater rock interactions. *Geochim. Cosmochim. Acta* 28, 1323–1357. (1964).

Ellis, A.J., Wilson, S.H.: The geochemistry of alkali metal ions in the Wairakei hydrothermal system. N. Z. J. *Geol. Geophys.* 3, 593–617. (1960).

Fournier, R.O., Potter, R.W.: Revised and expanded silica (quartz) geothermometer. *Geotherm. Res. Council Bull.* 11, 3–12. (1982).

Fournier, R.O., Rowe, J.J.: Estimation of underground temperatures from the silica content of water from hot springs and wet-steam wells. *Am. J. Sci.* 264, 685–697. (1966).

Fournier, R.O., Truesdell, A.H.: An empirical Na-K-Ca geothermometer for natural waters. *Geochim. Cosmochim. Acta* 37, 1255–1275. (1973).

Fournier, R.O., Truesdell, A.H.: Geochemical Indicators of Subsurface Temperature: Part II Estimation of Temperature and Fraction of Hot Water Mixed with Cold Water 2. *U.S. Geological Survey*, pp. 263–270. (1974)

Fournier, R.O.: Chemical geothermometers and mixing models for geothermal systems. *Geothermics* 5 (1-4), 41–50. (1977)

Fournier, R.O.: A revised equation for the Na/K geothermometer. *Geotherm. Res. Council Transac*. 3, 221–224. (1979).

Fournier, R.O.: Lectures on geochemical interpretation of hydrothermal waters. *UNU Geothermal Training Programme.* (1989).

Giggenbach, W.F.: Geothermal solution equilibria. Derivation of Na-K-Mg-Ca geoindicators. *Geochim. Cosmochim. Acta* 52, 2749–2765. (1988).

Ho, C.S.: A synthesis of geologic evolution of Taiwan. *Tectonophysics* 125, 1–16. (1986).

Huang, Y.H., Liu, H.L., Song, S.R., Chen, H.F.: An ideal geothermometer in slate formation: A case from the Chingshui geothermal field, Taiwan. *Geothermics* 74, 319–326. (2018).

Lee, P.Y.: Rate of the Early Pleistocene uplift in Taiwan. *Mere. Geol. Soc. China,* 2: 71--76. (1977).

Liu, K.K., Yui, T.F., Shieh, Y.N., Chiang, S.C., L.H., C., Ho, J.Y.:Hydrogen and oxygen isotope compositions of meteoric and thermal waters from the Chingshui geothermal area, northeastern Taiwan. *Proc. Geol. Soc. China* 33, 143–165. (1990).

Liu, T.K.:Tectonic implication of fission track ages from the Central Range, Taiwan. *Proc. Geol. Soc. China*, No. 25, pp. 22--37. (1982).

Lo, F.L., Chen, H.F., Fang, J.N.: Discussion of suitable chemical weathering proxies in sediments by comparing the dissolution rates of minerals in different rocks. *J. Geol.* 125 (1), 83–99. (2017).

Lu, Y.C., Song, S.R., Wang, P.L., Wu, C.C., Mii, H.S., MacDonald, J., Shen, C.C., John, C.M.: Magmatic-like fluid source of the Chingshui geothermal field: NE Taiwan evidenced by carbonate clumped-isotope paleothermometry. *J. Asian Earth Sci.* 149, 124–133. (2017).

Nisbet, E.G. and Fowler, C.M.R.: The thermal background to metamorphism, 1. Simple onedimensional conductive models. *Geosci. Can*., 9: 161--164. (1982).

Seno, T., Maruyama, S.: Paleogeographic reconstructionand origin of the Philippine sea. *Tectonophysics* 102, 53–84. (1984).

Teng, L.S.: Geotectonic evolution of late Cenozoic arc-continent collision in Taiwan. *Tecionophysics* 183, 57–76. (1990).

Teng, L.S.: Stratigraphic records of the late Cenozoic Penglai orogeny of Taiwan. *Acta Gwl. Taiwan.* 25, 205–224. (1987).

Tsai, Y.B., Liaw, Z.S., Lee, T.Q., Lin, M.T., Yeh, Z.H.:. Seismological evidence of an active plate boundary in the Taiwan area. *Mem. Geol. Sot. China* 4, 143–154. (1981).

White, D.E.: Saline waters of sedimentary rocks. In: In: Young, P., Galley, J.E. (Eds.), Fluids in Subsuface Environments, American Association of Petroleum Geologists Memories 4. pp. 342–365. (1965).

White, D.E.: Geochemistry applied to the discovery, evaluation, and exploitation of geothermal energy resources. In: Proceedings of the United Nations Symposium on the Development and Utilization of Geothermal Resources. *IIRG, CNR, Pisa, Italy*. pp. 58–80. (1970)

Yu, S.B., Chen, H.Y.: Global Positioning System measurements of crystal deformation in the Taiwan arc-continent collision zone. *Terr. Atom. Ocean.* 5, 477–498. (19