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## Variations of geothermometry and chemical-isotopic compositions of hot spring fluids in the Rehai geothermal field, southwestern China

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### Abstract

Geothermal variations, origins of carbon-bearing components and reservoir temperatures in the Rehai geothermal field (RGF) of Tengchong volcanic area, Yunnan Province, southwestern China, are discussed on the basis of carbon isotope compositions, combined with helium isotope ratios and geothermal data from 1973 to 2000.  $\delta^{13}\text{C}$  values of  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and travertine in the hot springs range from  $-7.6\text{‰}$  to  $-1.18\text{‰}$ ,  $-56.9\text{‰}$  to  $-19.48\text{‰}$ ,  $-6.7\text{‰}$  to  $-4.2\text{‰}$ ,  $-6.4\text{‰}$  to  $-4.2\text{‰}$  and  $-27.1\text{‰}$  to  $+0.6\text{‰}$ , respectively. The carbon dioxide probably has a mantle/magma origin, but  $\text{CH}_4$  and He have multiple origins.  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  in RGF thermal fluids are predominantly derived from igneous carbon dioxide, but other ions originate from rocks through which the fluids circulate. The  $^{13}\text{C}$  values of  $\text{CO}_2$ ,  $\text{HCO}_3^-$  (aq) and  $\text{CO}_3^{2-}$  (aq) illustrate that isotopic equilibria between  $\text{CO}_2$  and  $\text{HCO}_3^-$  (aq), and  $\text{CO}_3^{2-}$  (aq) and between DIC and travertine were not achieved, and no carbon isotope fractionation between  $\text{HCO}_3^-$  (aq) and  $\text{CO}_3^{2-}$  (aq) of the hot springs in RGF was found. Using various geothermometers, temperatures of the geothermal reservoirs are estimated in a wide range from  $69\text{ °C}$  to  $450\text{ °C}$  that fluctuated from time to time. The best estimate of subsurface reservoir temperature may be  $250\text{--}300\text{ °C}$ . Contributions of mantle fluids and shallow crust fluids in Rehai geothermal field varied with time, which resulted in variations of chemical and isotopic compositions and reservoir temperatures.

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**Keywords:** carbon isotopes; geothermal fluids; geothermometry; geochemistry; Tengchong volcanic area; Southwest China

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## 1. Introduction

Chemical and isotopic geochemistry plays an important role in researching origins of hot-spring fluids and temperature of geothermal reservoir. Carbon isotope compositions of various carbon-bearing components in a geothermal system differentiate each other (Bergfeld et al., 2001) and  $^3\text{He}/^4\text{He}$  ratios of different gases are obviously dissimilar (Mamyurin and Tolstikhin, 1984; Du, 1994; Du et al., in press) because of the isotope fractionation and different origins. In addition, it was reported that observed carbon isotope ratios in geothermal discharges were likely to represent frozen in compositions attained after minimum residence times of 20 ka at 400 °C and 10 Ma at 300 °C (Giggenbach, 1982). Therefore, the origins of fluid components and heat, temperature of reservoir and geothermal resources can be investigated by the isotopic geochemical technique. Molecular compositions of spring gases were employed to trace origins of gases (Xu et al., 1994; Goff and Janik, 2002) and to estimate temperature of geothermal reservoir (D'Amore and Panichi, 1980; Arnorsson and Gunnlaugsson, 1985). The helium isotope ratios of hydrothermal fluids in volcanic areas usually are concordant with those of mantle helium and/or show mixture of different amount crust helium (Xu et al., 1994; Du et al., 1999). However, hydrothermal fluids in the region of lack Quaternary volcano have a lower  $^3\text{He}/^4\text{He}$  value, for example, the observed mean  $^3\text{He}/^4\text{He}$  ratios of hot spring gases from Yangbajin district and some northern sites in the southern Tibetan plateau are  $0.12 R_A$  ( $R_A=1.4\times 10^{-6}$ ) and  $0.22 R_A$ , respectively, indicated more crustal gas contribution to hot springs (Yokoyama et al., 1999). Additionally, isotopic ratios of oxygen and hydrogen of waters, combined with dissolved ion concentration, are widely used in studying water origins and water–rock reaction (Liao and Zhao, 1999; Minissale et al., 2003).

The many contributions have also been done in researching the geothermal resource in southwest Yunnan Province since the beginning of 1970s in order to reduce timber consumption for domestic using (Tong and Zhang, 1989; Liao and Zhao, 1999). The stable isotopic compositions of carbon dioxide and helium of gases in the Tengchong volcanic area were conducted for tracing origins of gases and heat (Li,

1991; Wang et al., 1994; Xu et al., 1994; Shangguan et al., 2000). In early 1990s, magnetotelluric sounding was conducted for exploring geothermal reservoir, which revealed that high conductivity layers exist, one at depth from 2 to 3 km which may indicate reservoir and another from 7 to 20 km which may hint a cooling magma chamber (geothermal source) under Rehai geothermal field (RGF) (Liao and Zhao, 1999). Recently, Lou et al. (2002) showed a three-dimensional (3-D) diagram of a low-velocity body at depth from 3 to 12 km under in RGF. However, the geothermal resource is used for bathing now and was used for power supplying with some small factories that were closed several years ago because of water pollution, but no geothermal power plant was established. One of the main reasons is that potential of geothermal reservoir is not clear enough. So far, although detailed chemical and isotope investigations have been made of waters and gases of hot springs, as mentioned before, carbon isotope distribution in coexisting carbon dioxide,  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$ , methane and deposits (travertine) of the hot springs in RGF and temporal chemical variations of the geothermal fluids are not described in the literature.

In this paper, we present systematically the variations of geochemical features and carbon isotopic compositions of coexisting carbon-bearing pieces of the hot springs in the Rehai geothermal field. Our objectives are to discuss the causes for time-variation of chemical components, origins of fluids and reservoir temperature.

## 2. Geological and geothermal setting

Rehai (meaning Hot Sea) geothermal field, located about 11 km southwest of Tengchong town, is the biggest and hottest geothermal system in the Tengchong volcanic area. Tengchong volcanic area is located in Yunnan Province, southwest China, and is one of several active volcano areas in China (Fig. 1; Jiang et al., 1998; Wei et al., 2003). Tengchong volcanic area is tectonically situated in the mini-Tengchong block that is located in the eastern collision boundary between the India and Eurasia plates. To the west, the mini-Tengchong block is connected with the Tibetan plateau, which is the highest mountainous region induced by the India–Eurasia collision, and to

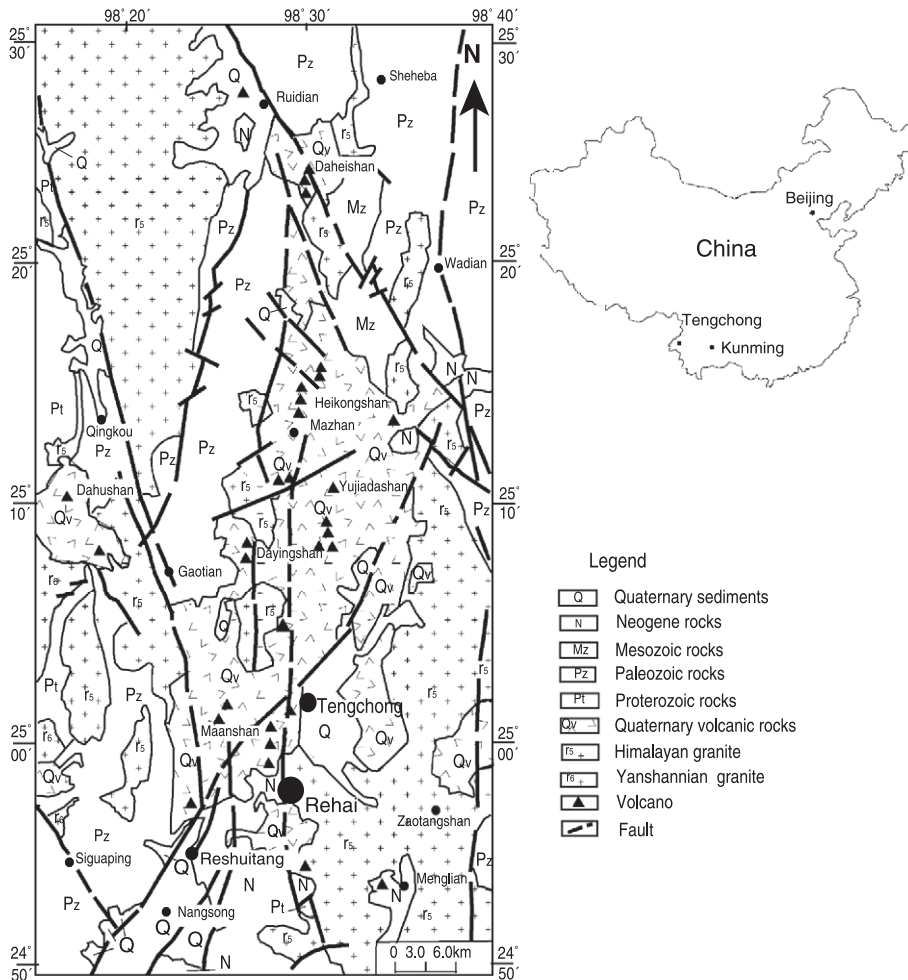


Fig. 1. Geological map of the Tengchong volcanic area Yunnan Province, southwestern China (modified after Jiang et al., 1998) showing the locations of Rehai geothermal field with large circle, upper right diagram shows the location of Tengchong in China.

the east it borders with the southern China plate and the Indo-China block. The mini-Tengchong block developed from a micro continent between Gondwanaland and Eurasia since the Late Paleozoic, tectonic activity became very intense up to the early Cenozoic. Quaternary volcanoes and fault structures are presently the most conspicuous features of this region. The active faults (faulting movement occurred since 100 ka BP) with strikes of NNE, NS, NW and NE have been well developed in the region (Liao and Guo, 1986; Jiang et al., 1998).

The Tengchong volcanic area is characterized by several dozen basalt and andesitic craters and cones formed during Late Tertiary–Quaternary. The 68

different volcanoes, of which three are Holocene volcanoes (namely Dayingshan, Maanshan and Heikongshan), have been identified in a region of 24°40′–25°30′ N and 98°15′–98°45′ E, and about 140 sites of hot spring activity have been found (Fig. 1). The volcanic activity can be divided into four periods: (1) middle–late Pliocene to Middle Pleistocene basalt ( $3.83 \pm 0.72$ –0.9 Ma), (2) middle–late Pleistocene silicic pyroclastic rocks (0.8–0.01 Ma) and (3) Holocene basaltic andesites (0.01–<0.007 Ma), the latest eruption occurred in Qing Dynasty (1609) (Jiang, 1998; Wei et al., 2003). Detailed 3-D P-wave velocity structure of the lithosphere reveals strong low-velocity zones in the upper

crust with a width of about 30 km under RGF (Lou et al., 2002). The low-velocity zones extend to depths of 85 km into the mantle with a lateral extent of about 100 km under Tengchong volcanic area (Huang et al., 2002), suggesting the possibility of subjacent existence of magma chambers and/or bodies of partial melt.

Beneath the Quaternary volcanic rocks, strata of RGF consist primarily of Quaternary sediments, Tertiary sandstone and conglomerate, Pliocene olivine-bearing basalt and Yanshannian (66–205 Ma) granite and andesite. Rocks encountered in the boreholes in the studied area are mainly sandy conglomerate, sandstone, siltstone, clay, basalt, andesite, granite and migmatite (Table 1; Liao and Zhao, 1999). Surface hydrothermal minerals in the geothermal system consist predominantly of sulfates (gypsum, alunogen, halotrichite), carbonates (calcite, trona, thermonatrite), clay minerals (kaolinite, illite-smectrite mixed layer mineral) and silica minerals (opal, chalcedony) (Zhu and Tong, 1987).

Several geothermal systems occur in the Tengchong volcanic area and the most important geothermal system is RGF. The hydrothermal activity can be divided in four periods according to the isotopic dating of hot spring sediment: (1) about 380–300 ka, (2) 300–180 ka, (3) 40–80 ka and (4) since 20–30 ka (Liao and Zhao, 1999). Hydrothermal manifestations, such as hot springs, geysers, fumaroles and steaming ground can be found throughout RGF. Dozens of hot spring waters in RGF have been analyzed and can be classified into three chemical groups. The first are Na–Cl–HCO<sub>3</sub> waters discharged from the hottest springs. The second are Na–HCO<sub>3</sub>–Cl waters mainly found in the hot springs adjacent to springs of the first type and the third are Na–HCO<sub>3</sub>

waters mainly found in lower temperature springs (Zhang et al., 1987).

More than 20 boreholes in RGF were drilled for exploring core deposits (Au and U) and geothermal resource during 1976–1993 (Table 2; Liao and Zhao, 1999). The higher temperature measured at depth of 380 m in drill hole (ZK1607) deep to 400 m was 142 °C, and temperatures measured at depths of 210–220 m in holes of CK1840 and CK1921 were 60 °C at southern RGF, accordingly estimated temperature gradients are 23.68 to 100.00 °C/100 m; and the lower temperature gradients obtained in some shallow boreholes were 2.46 to 43.86 °C/100 m. In addition, measured values of heat flow in Huaguaqing–Liu-huangtang district range from 74.2 to 147.3 mW/M<sup>2</sup> (Liao and Zhao, 1999).

Hydrothermal activity in RGF has become more frequent since 1993. According to observed data of the Tengchong Station of Seismology and Volcanology (TSSV), more than 20 hydrothermal explosions or mud volcanic eruptions have occurred in RGF since then. The very severe hydrothermal eruptions occurred near Hamazhui on 13 May 1994, near Huantaijing in November 1996, at Xipoxia on 7 June 1999, at east Xipoxia on the south bank of Zhaotanghe River on 20 September 1999 and near Shizitou on 10 October 2001 (Shangguan et al., 2004). The eruptions caused landslides, fortunately, which did not cause any life loss and building damages because no people live nearby there.

### 3. Sampling and analytical methods

During fieldwork of August 2000 in Yunnan Province, we surveyed the volcanoes and the geo-

Table 1  
Rocks revealed by drilling in Rehai geothermal field (Liao and Zhao, 1999)

Age		Rocks
Holocene (Q <sub>4</sub> )		Fluvial sediment
Middle Pleistocene (Q <sub>2β</sub> )		Olivine basalt (0.87 Ma)
Lower Pleistocene (Q <sub>1α</sub> )		Pyroxene-biotite andesite, basaltic hornblende andesite
Lower Miocene (N <sub>1</sub> )	Upper	Gravel, coarse sandstone, bedded thin-bed siltstone and coal lamella; 85.5 m thick
	Middle	Granitic microconglomerate and grit stone, bedded siltstone and gravel; about 350 m thick
	Lower	Granitic sandy gravel, bedded muddy siltstone and conglomerate; about 50 m thick
Cretaceous (K <sub>2γ</sub> )		Granite (68.8 Ma)
Protozoic (Pt)	Gaoligong Group (PCm)	Gneiss and migmatite

Table 2  
Temperatures in the boreholes in the Rehai geothermal field (Liao and Zhao, 1999)

No.	Position	Strata	MD (m)	DMT (m)	T (°C)	TG (°C/100m)
CK1	Southern Wenhuaishi	Nanlin group, migmatite	149.72	32.56 136.00	26.72 43.60	16.34
CK2	Langpuzhai	Andesite, Nanlin Group	400.59	60.00 400.00	19.00 45.40	7.76
CK3	Lijiachun	Nanlin Group	151.33	30.00 150.00	18.10 22.80	9.15
CK4	Labahekou	Quaternary sandy gravel	250.13	93.00 246.00	24.70 38.70	9.15
CK5	Firework plant	Nanlin Group, migmatite	400.63	33.70 400.00	19.68 34.80	4.13
CK6	Xiaqiluo	Migmatite	150.49	30.50 150.00	21.50 25.20	2.46
CK8	Guanzhang	Quaternary sandy gravel	150.26	30.00 145.00	21.50 25.20	3.22
CK9	Dawozitianfang	Quaternary sandy gravel	100.46	38.42 100.00	21.00 23.30	3.73
CK11	Dazhai	Basalt, Nanlin Group	164.48	30.00 140.00	21.75 70.00	43.86
CK13	Bangeshan	Andesite, Nanlin Group	151.25	32.00 150.00	18.50 24.80	5.34
ZK01	NW Reshuitang	Quaternary sandy gravel	19.29	4.75 19.29	23.0 27.6	31.64
ZK02	Eastern CK9	Quaternary sandy gravel	25.28	5.50 19.30	23.0 24.9	11.59
ZK03	Wenhuaishi	Quaternary sandy gravel	20.29	5.50 20.29	17.20 22.60	36.51
ZK05	Langpuzhai	Weathered andesite	21.86	5.00 18.00	24.0 27.0	23.08
ZK1607	South end of Songmuqing	Nanlin Group, migmatite	390.75	350.00 380.00	112.0 142.0	100.00
ZK1505	Middle part of Songmuqing	Nanlin Group, migmatite	280.00	100.00 239.00	38.0 86.0	27.00
ZK2303	North end of Songmuqing	Nanlin Group	180.05	80.00 130.00	38.0 50.0	19.36
ChG01	Nangsongguanzhen	Quaternary sandy gravel	25.50	25.50	20.0	
CK1840	Shapo	Nanlin Group		210.00	60	23.68
CK1920	Shapo	Nanlin Group		210.00	60	23.68
CK1921	Shapo	Nanlin Group		220.00	60	22.50
CK2025	Shapo	Nanlin Group		288.00	57	15.67
CK2027	Shapo	Nanlin Group		334.00	51	11.46
CK2048	Shapo	Nanlin Group		122.00	36	20.59

MD—the maximum depth, DMT—depth measuring temperature, TG—temperature gradient.

thermal fields in Tengchong County and collected samples of spring deposits (carbonate, sulfate and silica minerals), and water and gas from hot springs of RGF (Fig. 2) in order to investigate the carbon isotope compositions of CO<sub>2</sub>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, CH<sub>4</sub> and travertine. Spring gases and waters were collected using glass bottles (250 mL) in order to avoid carbon isotope contamination. The glass bottles were first

filled with spring water and then positioned upside down in the spring outflow for collecting gas bubbles. The filled spring water was partially replaced by gas and a gas sample was collected. Water samples were collected with glass bottles that were directly put into the hot spring water and sealed with a rubber block in the water in order to avoid air contamination.

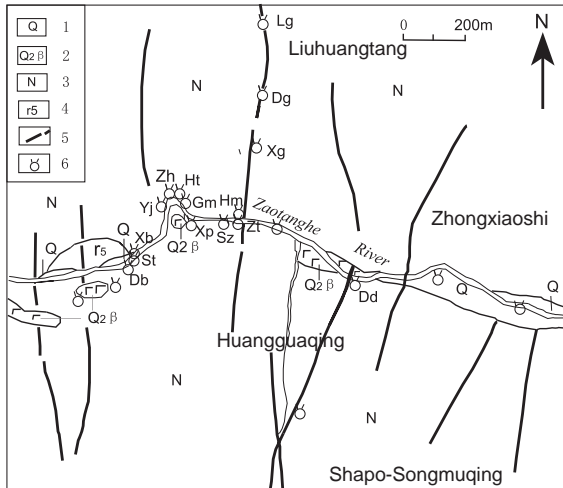


Fig. 2. Figure showing positions of samples in the Rehai geothermal field, Tengchong: 1, Quaternary sediments; 2, middle Pleistocene basalt; 3, Neogene arenaceous conglomerate; 4, Yanshanian granite; 5, Holocene fault and 6, Hot springs (Dg: Dagunguo, Lg: Laogunguo; Xg: Xiaogunguo, Ht: Huaitaijing, Zt: Zaozangshe, Zh: Zhenzhuquan, Sz: Shizitou, Yj: Yanjingquan, Gm: Gumingquan, Hm: Hamazhui, Xb: Xiaobaiyan, Db: Dabaiyan, St: Shizitang, Xp: Xipoxia).

The molecular compositions of gaseous samples were determined with Finnigan MAT 271 mass spectrometer (MS) in Lanzhou Institute of Geology (LIG), Chinese Academy of Sciences. Five-microliter gas was taken from the sample bottle with a mini injector, and injected into the sample entrance line connected to the MS.

Concentrations of  $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$  in hot spring waters were chemically analyzed by acid titration in the field. The carbon-bearing species ( $\text{CO}_3^{2-}$  and  $\text{HCO}_3^-$ ) in hot spring waters were separately precipitated with  $\text{Ba}(\text{OH})_2$  and  $\text{NaOH}$ . The  $\text{BaCO}_3$  deposits were filtered from the liquids and dried at about  $50^\circ\text{C}$  in the laboratory at TSSV on the same day of sampling water. Carbon isotopic analyses of DIC were conducted with an MS of Finnigan MAT 252 installed at the Laboratory Center of the Research Institute of Petroleum Exploration and Development (RIPED) after the traditional treatment of precipitates with phosphoric acid, and one sample (Lg) was verified at LIG because of the very negative value.  $\delta^{13}\text{C}$  values of carbon dioxide in the gas samples were determined at LIG. Methane in the geothermal gas samples was separated and combusted, the carbon dioxide product

was purified and the carbon isotope identification was confirmed on the line of GC-C-MS (MAT 252) at LIG (Du et al., 2003). The  $\delta^{13}\text{C}$  values were normalized to PDB. The  $\delta^{13}\text{C}$  values of the geothermal methane have an error of less than 0.1 per mil, and those of the travertine and DIC have errors less than 0.2 per mil.

## 4. Results and discussion

### 4.1. Geochemistry of the geothermal waters

The chemical compositions of the hot spring waters in RGF have been analyzed many times by different researchers. We selected some data for the same sites to study chemical variations of hot springs (Table 3; Tong and Zhang, 1989; Li, 1991; Liao and Zhao, 1999). Total dissolved solid (TDS) of the water samples of the high temperature ( $>40^\circ\text{C}$ ) springs has a range of 930 to 3628 mg/L. Temperature and pH values of the high temperature springs are in the ranges of 78 to  $96^\circ\text{C}$  and 7 to 9.45, respectively.  $\text{HCO}_3^-$ , Cl and  $\text{SiO}_2$  were prevalent in the hot springs, and concentrations range from 512 to 1280 mg/L, 269 to 712 mg/L and 97.5 to 491.25 mg/L, respectively. Nevertheless, carbonate ion was not detected in all water samples of Dagunguo spring (Big Boiling Pool) and three water samples of Laogunguo spring. Concentrations of Na are much higher than those of K, Ca, Mg and Li. Lithium concentrations are between 2.1 and 8.3 mg/L. Hot spring waters in RGF are chemical type of Na–Cl– $\text{HCO}_3^-$  waters that were diluted and mixed with different amounts of deep geothermal waters (Table 3; Fig. 3). This is responsible for higher concentrations of  $\text{SiO}_2$ , Cl and Li, but lower Ca and Mg, which are usually found in the high temperature geothermal system (D'Amore et al., 1987; Goff and Janik, 2000). As mentioned by Liao and Zhao (1999), the deep source water of the hot springs in RGF may be Na–Cl water, and mix with shallow fresh waters to different extents during upward migration. The concentrations of main cations and anion in the spring waters fluctuated distinctively with time (Fig. 3). Variations of  $\text{HCO}_3^-$ , K and Mg concentrations are larger than those of  $\text{SO}_4$  and Na with time, and Cl concentration in waters of the four hot springs changed slightly. The concentrations of main ions in the studied springs decreased from 1973

Table 3  
Chemical compositions and variations of geothermometry of hot spring waters in the Rehai geothermal field of Tengchong volcanic area, China

Sample no.	Location	Sampling date	T/°C	pH	Na	K	Ca	Mg	Li	SiO <sub>2</sub>	Cl	F	CO <sub>3</sub>	HCO <sub>3</sub>	SO <sub>4</sub>	TDS	T <sub>(SiO<sub>2</sub>)</sub>	T <sub>(Na/Li)</sub>	T <sub>(Na/K)</sub>	T <sub>(K/Mg)</sub>	T <sub>(Na-K-Ca)</sub> (β=1/3)
Dg	Dagunguo	1973	96.6		925	141	1.5	0.14			710	26.3	0	1186	28.5	2526			245	173	277
		1980	88	8.0	840	120	0.10	0.02	8.3	450	698	20	0	1168	31	2811	247	271	238	268	303
		1990	92	7.7	1000	161	1.20	0.75	7.0	491	712	nd	0	1256	nd	3628	256	232	251	193	283
		1994	94		857	125	0.08	0.03		438	673	19.4	0	1183	18.5	2794	244		241	259	308
Rs	Reshuitang	1973	96.2		700	58	3.7	1.1		156	325	12.5	0	1233	16.2	1889	164		190	146	210
		1980	96	7.5	640	50	1.14	0.80	2.1	150	307	10.5	0	984	35	1703	161	163	186	147	209
		1990	90	8.2	845	74	29.00	15.80	1.5	144	315	nd	0	1280	nd	2704	159	119	194	112	200
		1994	87		644	54	0.39	0.92		125	307	11.4	19	1247	21.4	1835	150		191	147	237
Yj	Yanjingquan	1973	94.5		725	110	1.5	0.08			742	32.5	193	738	39	2423			245	227	267
		1980	95	8.0	680	110	0.29	0.02	6.2	340	559	14	261	700	11	2379	221	261	252	263	292
		1990	92	9.3	701	107	16.00	2.15	4.5	386	610	nd	150	900	nd	2876	232	223	245	156	238
		1994	94		735	95	0.09	0.04		350	567	17.2	208	608	18.9	2348	223		229	237	292
Dd	Dadijiao	1973	80.3		425	36	2.0	0.26			335	7.5	0	503	25.8	1180			191	155	211
		1980			450	42	0.86	0.17		118	372	9.7	22	522	27	1325	147		200	169	230
		1994	82		501	68	0.82	0.14		185	365	10.1	0	780	15.7	1617	175		233	192	256

Concentration data (mg/L) are selected from different references but at the same sampling positions; data of 1973 and 1994 after Liao and Zhao (1999); those of 1980 after Tong and Zhang (1989) and those of 1990 after Li (1991). Analytical methods employed by the authors were flame-photometry for Na and K, atomic absorption spectrophotometry for Ca, Mg and Li, titration and colorimetry for CO<sub>3</sub>, HCO<sub>3</sub>, Cl, F and SiO<sub>2</sub>, and titration and turbidimetry for SO<sub>4</sub>; nd, not determined. Calculated temperatures in °C, the employed geothermometers of T<sub>SiO<sub>2</sub></sub> and T<sub>Na/Li</sub> after Verma and Santoyo (1997), T<sub>Na/K</sub> after Can (2002), T<sub>K/Mg</sub> after Giggenbach (1988) and T<sub>Na-K-Ca</sub> after D'Amore et al. (1987) and Fournier and Truesdell (1973), the formula shown in the text.

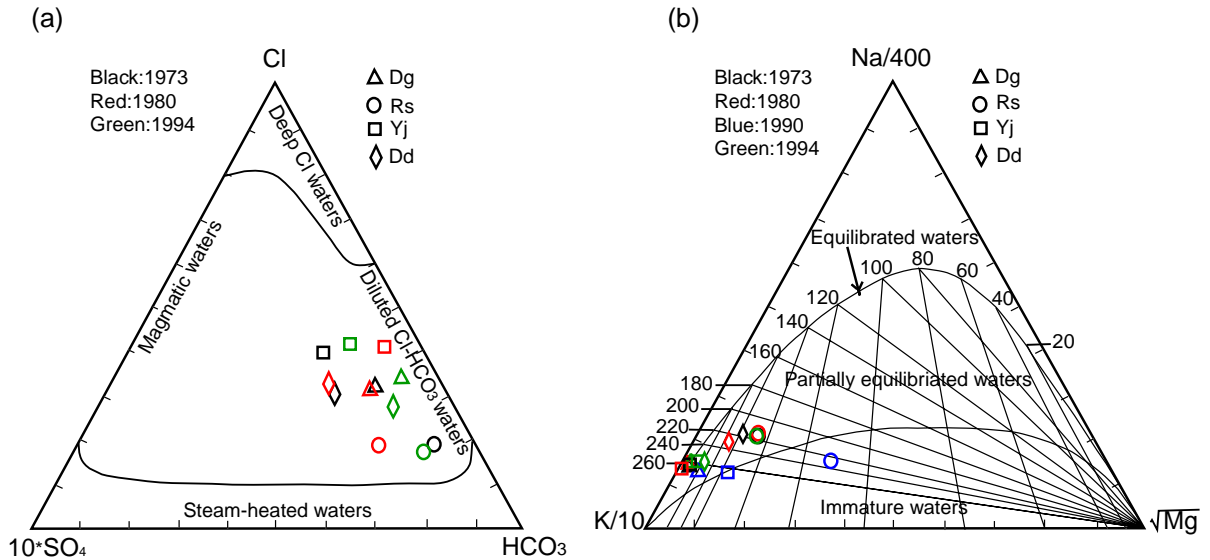


Fig. 3. (a) Ternary diagram of Cl–SO<sub>4</sub>–HCO<sub>3</sub>, (b) ternary diagram of Na/400, K/10 and (Mg)<sup>0.5</sup>, in mg/L (Modified from Shevenell and Goff, 1995).

to 1980, increased from 1980 to 1990 and dropped from 1990 to 1994 with the exception of Li and SiO<sub>2</sub>. However, SO<sub>4</sub> and F concentrations show a decreasing trend from 1973 to 1994. The chemical variations of the springs with time could be caused by seasonal variations of shallow groundwater mixture. Temperature of Reshuitang spring decreased with time, indicating decrease of heat derived from deep geothermal fluids and/or increase of mixture with cool groundwater.

Dissolved ions in the sample waters in the study area could be mainly derived from reactions of geothermal fluids with rocks and from contributions of magmatic degassing. Concentrations of Cl<sup>-</sup> and SiO<sub>2</sub> have a positive correlation (Fig. 4a), which was considered as an index of mixture of deep-hot water and shallow-cold water (Arnorsson, 1985). Another evidence for the mixture of different waters is that δ<sup>18</sup>O of water directly corresponds with Cl<sup>-</sup> concentration (Fig. 4b). Probably, the DIC is predominantly

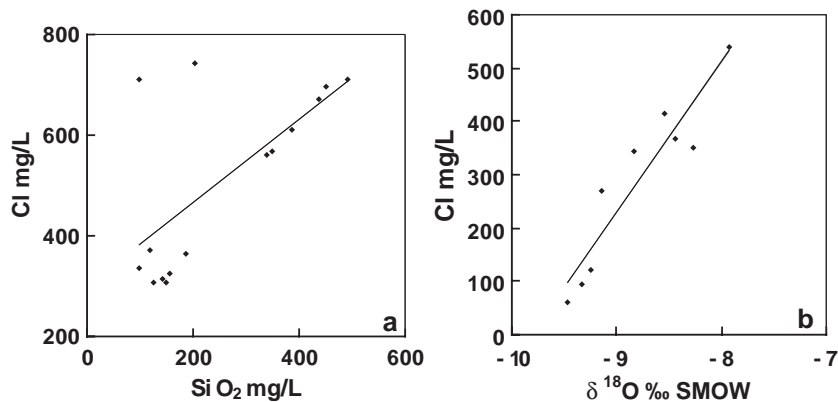


Fig. 4. Plots of Cl vs. SiO<sub>2</sub> (a) and Cl vs. δ<sup>18</sup>O (b). Showing correlations between ion concentrations and oxygen isotopic compositions of waters in RGF, data after Liao and Zhao (1999).



derived from magmatic carbon ( $\text{CO}_2$ ) because the hot spring waters are supersaturated with  $\text{CO}_2$  and limestone does not exist in the subsurface of Tengchong volcanic area.

Spring water in the study area was derived from meteoric water. Annual value of regional precipitation is 1425 mm that is plenty to supply water to the springs in the Tengchong district where active faults are very developed (Figs. 1 and 2). Most of spring waters in Tengchong district were classified as fresh water (Tong and Zhang, 1989). However, waters from high-temperature springs in RGF show higher values of TDS (Table 3), which may be caused by deep circulation of water and interaction between water and rocks. The isotopic ratios of hydrogen and oxygen of hot spring waters show characteristics of meteoric water and with different degrees of shift caused by water–rock reaction and/or magmatic fluid addition (Fig. 5). Five points of steam-condensed waters are scattered along the low part of the meteoric water line (triangles in Fig. 5), which can be explained by the processes of vaporization and condensation because

water vaporization results in heavy isotope (D and  $^{18}\text{O}$ ) depletion in vapor, and consequently condensed water from the vapor depletes more in D and  $^{18}\text{O}$  than the source water. The points of hot spring waters in RGF depart from the lines of global and local (Tengchong district) meteoric waters, which resulted from water–rock reaction or magmatic fluid mixture. Data of samples collected in November 1993 (Ohsawa et al., 1995), in the active period of hydrothermal explosion, are plotted between those of steam-condensed waters and hot spring waters collected before 1989 (Tong and Zhang, 1989), indicating a change in isotopic composition caused by contribution of deep steam condensation.

#### 4.2. Geochemistry of the hot spring gases

Molecular concentrations and helium isotopic ratios of gases from the hot springs changed with time (Table 4). In a triangle plot of  $\text{CH}_4\text{--CO}_2\text{--N}_2/(\text{Ar}+\text{O}_2)$  (Fig. 6a), it is evident that the points of a same spring in different times scattered widely,

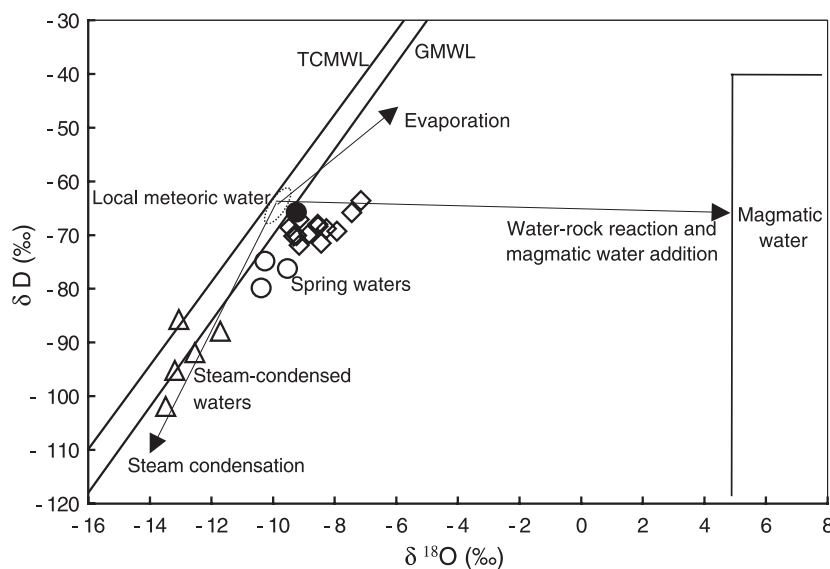


Fig. 5. Diagram of  $\delta\text{D}$  vs.  $\delta^{18}\text{O}$  of waters in Rehai geothermal field, Yunnan Province, southwestern China. Showing spring-steam-condensed water (triangle), hot spring waters (diamond), river water (solid circle) (data from Liao and Zhao, 1999); open circle: hot spring waters (data from Ohsawa et al., 1995); the lines: GMWL, global meteoric water ( $\delta\text{D}=8\delta^{18}\text{O}+10$ ) and TCMWL, meteoric water in Tengchong district ( $\delta\text{D}=7.8\delta^{18}\text{O}+14.9$ , Tong and Zhang, 1989); dashed circle, supposed local meteoric water; the arrow lines illustrate the isotopic shifting tendencies caused by different factors. Note the isotopic values for the hot springs scattered on the right of GMWL and between the arrow lines of steam condensation and water–rock reaction and magmatic water addition, indicating the contributions of deep steam and magmatic water and effect of water–rock reaction on the hot spring waters.

Table 4  
Gas compositions,  $^3\text{He}/^4\text{He}$  and geothermometry of spring gas in the Rehai geothermal field of Tengchong volcanic area, China

No.	Spring	Date	H <sub>2</sub> S	H <sub>2</sub>	He	CH <sub>4</sub>	CO	CO <sub>2</sub>	Ar	O <sub>2</sub>	N <sub>2</sub>	$^3\text{He}/^4\text{He}$	$T_{\text{CHS}}$	$T_{\text{CO}_2}$	$T_{\text{H}_2\text{S}}$	$T_{\text{H}_2}$	$T_{\text{H}_2\text{S}/\text{H}_2}$	$T_{\text{CO}_2/\text{H}_2}$	$T_{\text{CO}_2/\text{N}_2}$		
Dg	Dagongguo	1980				0.25		49.7		6.55	29.46			166						158	
		1990		0.014	0.0041	0.33		35.26	0.61			54.75	3.86		160		227		244	135	
		1994			0.042	1.36		97.35				1.24	3.26		239						280
		1998	0.21	0.23	0.013	1.22		94.86	0.052	0.03	2.18	4.19		167	201	188	250	305	267		260
		2000			0.011	1.43		79.31	0.3	4.61	14.32				196						200
Lg	Laogongguo	1990		0.0023	0.0039	0.33		55.2	0.4		38.08	3.90		180		209			217	160	
		1994			0.014	0.50		99.09	0.088		0.31	3.37		203							322
		1998	0.23	0.063	0.0047	0.64		96.17	0.065		3.12	4.24		142	202	190	239	282	251		252
		2000			0.0029	0.61		93.53	0.13	0.39	5.34				200						235
Ht	Huaitaijing	1990		0.022	0.0005	0.04		42.38	0.56	11.68	47.67	2.35		169		231			248	145	
		1994				0.13		99.66			3.2	3.80		203							252
		1998	0.077	0.063	0.0003	0.02		93.58	0.042		3.05	2.92		160	200	168	239	300	251		252
		2000		0.27		0.0092	0.14	28.85	1.27	21.91	47.46				148		254		284		134
Rs	Reshuitang	1990		0.0086	0.0004			10.33	0.87	17.53	71.23	2.29		79		111 <sup>b</sup>			106	90	
		1992		0.0076	0.0031	0.34		32.41	0.63			56.33	3.27		155		110 <sup>b</sup>		69		132
		2000			0.0004	0.23	0.051	68.02	0.57	5.02	26.09				189						178
Zz	Zhaozhichang	2000			0.06	0.061	88.8	0.22	2.95	7.88			199							222	

Data are selected from different references but at the same sampling positions, Data of 1998 after Shangguan et al. (2000); 1994: Dai et al. (1995); 1992: Wang et al. (1994); 1990: Li (1991); 1980: Tong and Zhang (1989) and others: this study. Date was the sampling years. Gas compositions in volume percent,  $^3\text{He}/^4\text{He}$  normalized to  $R_A$ . Employed gas geothermometers:  $T_{\text{CO}_2} = -44.1 + 269.25 \log(\text{CO}_2) - 76.88 (\log \text{CO}_2)^2 + 9.52 (\log \text{CO}_2)^3$ ,  $T_{\text{H}_2\text{S}}^a = 246.7 + 44.81 \log(\text{H}_2\text{S})$  and  $T_{\text{H}_2\text{S}}^b = 173.2 + 65.04 \log(\text{H}_2\text{S})$ ,  $T_{\text{H}_2}^a = 277.2 + 20.99 \log(\text{H}_2)$  and  $T_{\text{H}_2}^b = 212.2 + 38.59 \log(\text{H}_2)$ ,  $T_{\text{H}_2\text{S}/\text{H}_2} = 304.1 - 39.48 \log(\text{H}_2\text{S}/\text{H}_2)$ ,  $T_{\text{CO}_2/\text{H}_2}^a = 341.7 - 28.57 \log(\text{CO}_2/\text{H}_2)$  and  $T_{\text{CO}_2/\text{H}_2}^b = 311.7 - 66.72 \log(\text{CO}_2/\text{H}_2)$  (Arnorsson and Gunnlaugsson, 1985; Zhao and Armannsson, 1996);  $T_{\text{CHS}} = [24775/(\alpha + \beta + 36.05) - 273]$  ( $\alpha = 2 \log(\text{CH}_4/\text{CO}_2) - 6 \log(\text{H}_2/\text{CO}_2) - 3 \log(\text{H}_2\text{S}/\text{CO}_2)$ ,  $\beta = -7 \log P_{\text{CO}_2}$ ) (D'Amore and Panichi, 1980);  $T_{\text{CO}_2/\text{N}_2} = 148.5 + 64.35 \log(\text{CO}_2/\text{N}_2) + 5.239 \log(\text{CO}_2/\text{N}_2)^2 - 1.832 \log(\text{CO}_2/\text{N}_2)^3$  (Zhao and Armannsson, 1996).

showing concentration variations of gas components of hot spring gases from RGF and air contribution to the hot spring gases is less in 2000. The time variations of gas concentrations resulted from contribution changes of gases from mantle, crust and atmosphere. The variations of helium isotope ratios (Table 4) indicate amount change of mantle gas contribution temporally. Samples of 1998 were collected after a big hydrothermal explosion of 1997 in RGF, having the largest helium isotope ratios. CO<sub>2</sub> and CH<sub>4</sub> concentrations and increase of <sup>3</sup>He/<sup>4</sup>He ratios of hot spring gas released from Unzen volcanic area, Japan also varied from 1983 to 1992, which was most likely due to addition of magmatic gases (Notsu et al., 2001). In a plot of relative N<sub>2</sub>–He–Ar contents (Fig. 6b), hot spring gases in RGF fall on the trends between He-rich component derived from mantle and/or crust and an Ar-rich component derived from air. Therefore, it can be deduced that N<sub>2</sub> and Ar, the hot springs of RGF, were largely derived from air with mixture of lithosphere gas.

For researching origins of He and CO<sub>2</sub> of the hot springs in Tengchong volcanic area, we plotted the values of <sup>3</sup>He/<sup>4</sup>He vs. δ<sup>13</sup>C<sub>CO2</sub> (Fig. 7), along with values from different locations around the world

(Taylor, 1986; Du et al., 1999). The data from springs in RGF (in solid symbols) are largely plotted in the area of gases from volcanoes and geothermal fields such as Merapi, Ardoukoba, Momotombo, Hakone, Pinchincha, Pozzuoli Solfatare, Yellowstone and Casa Diablo and Hot Creek in Long Valley. The open triangles and open semicircles stand for data from other springs in the Tengchong district. One with the highest R/R<sub>A</sub> value, 7.54, from Heshun north of RGF is comparable to the values from the regions of Coso Hot Springs, Casa Diablo, Long valley, California and Uzon volcano, in which He and CO<sub>2</sub> were derived from mantle. Two samples with lower R/R<sub>A</sub> ratios from Xiposhang in RGF are near the value of air. It is obvious that helium of hot springs in Tengchong district is depleted in <sup>3</sup>He relatively to typical mantle gases that have <sup>3</sup>He/<sup>4</sup>He ratio (R/R<sub>A</sub>) larger than 8 and gases from some geothermal areas (Mamyryn and Tolstikhin, 1984; Goff and Janik, 2002).

Carbon isotope ratios from RGF are in the range of carbon dioxide derived from mantle and consistent with those from other geothermal systems in magmatic environments. Isotopic compositions of helium and carbon dioxide demonstrate that helium is derived

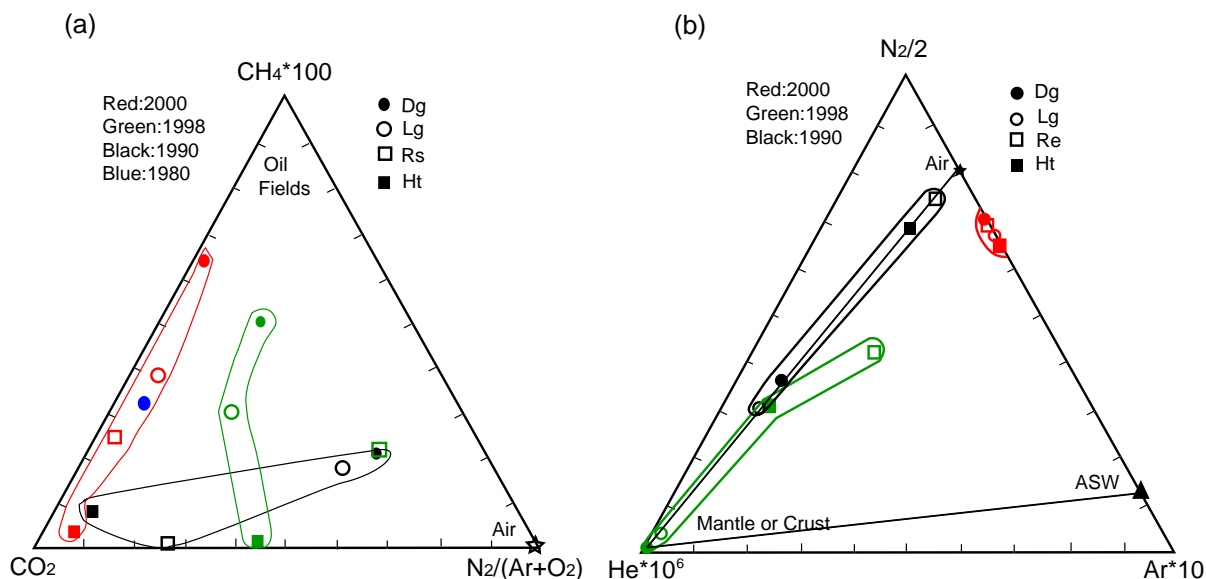


Fig. 6. (a) Ternary diagram of CH<sub>4</sub>×100–CO<sub>2</sub>–N<sub>2</sub>/(Ar+O<sub>2</sub>), (b) ternary diagram of He–Ar–N<sub>2</sub>. Showing gas components variation of some hot springs in RGF with time.

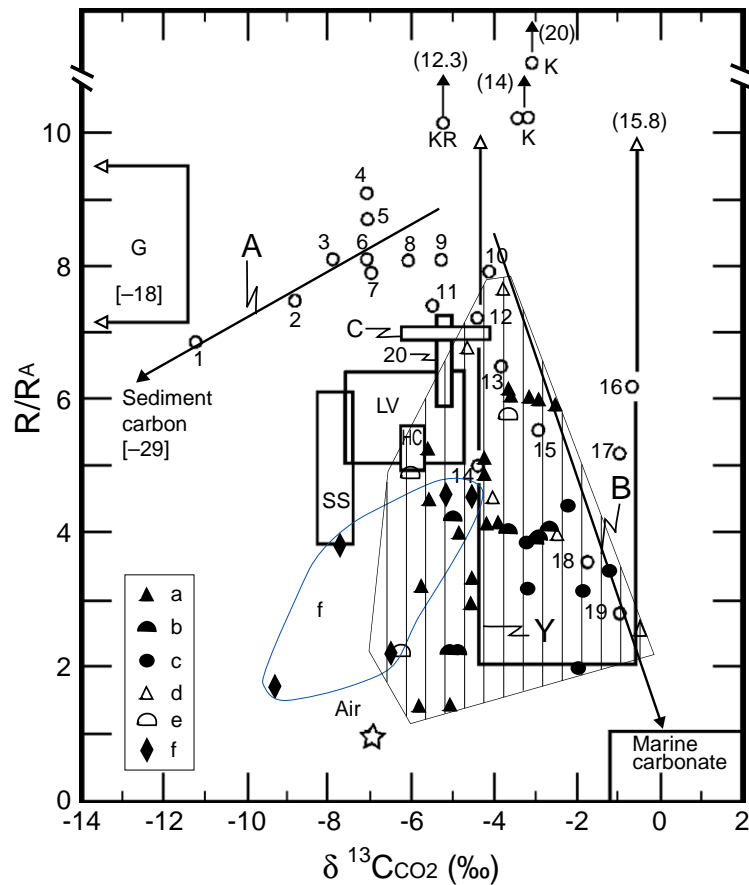


Fig. 7. Carbon and helium isotope correlations for volcanic and volcanic-geothermal gases (modified after Taylor, 1986). Rectangular fields indicate ranges of analyses. Numbers in round brackets,  $R/R_A$ ; in square brackets,  $\delta^{13}\text{C}$  of  $\text{CO}_2$ ; A, mixing line of mantle-organic carbon; and B, mixed line of mantle-marine carbonate. Locations: G, Geysers, Ca; KR, Krafla, Iceland; K, Kilauea, Hawaii; C, Coso Hot Springs, Ca; SS, Steamboat Springs, Nev.; LV, Casa Diablo, Long Valley, Ca; HC, Hot Creek, Long Valley, Ca; Y, Yellowstone (Taylor, 1986); number-marked circle: 1, Nagauruhoe; 2, Kuju; 3, Mt. Lassen; 4, Mid-Atlantic Ridge; 5, Ebeko, 6, East Pacific Rise (21°N); 7, Famous Vesicles; 8–9, Galapagos; 10, Soufriere de Guadeloupe; 11, Showashinzan; 12, Usu; 13, Merapi; 14 Ardoukoba; 15, Momotombo; 16, Hakone; 17, Vulcano; 18, Pinchincha; 19, Solfatare Pozzuoles; 20, Uzon (Taylor, 1986); f, Wudalianchi volcanic area (Du et al., 1999). Data of Tengchong volcanic area scattered in the shadow area: a (Shangguan et al., 2000), b (Li, 1991) and c (Dai et al., 1995) present data for the Rehai geothermal field; d (Shangguan et al., 2000) and e (Li, 1991) for other places in Tengchong district.

from mantle, atmosphere and crust, and  $\text{CO}_2$  is dominantly of magmatic origin. Using  $^3\text{He}/^4\text{He}$  and  $^4\text{He}/^{20}\text{Ne}$  ratios, Xu et al. (1994) estimated that contributions of mantle helium to hot spring gases in RGF range from 27 to 52%, crustal gas contributions range from 25 to 49% and atmosphere gas from 0 to 48%. It is worth mentioning that higher  $^3\text{He}/^4\text{He}$  ratios ( $>5 R_A$ ) were obtained from the samples of 1998 (Shangguan et al., 2000), which indicates fluctuating contributions of gases derived from mantle

after 1990. Observation of TSSV shows that hydrothermal explosion did not occur from July 1978 to January 1993, and more than 20 hydrothermal explosions occurred from 1993 to 2001.

Biogenic/immature gases have very low concentrations of ethane and higher alkanes, but predominant methane enriched in lighter carbon isotope ( $\delta^{13}\text{C} < -55\text{‰}$ ); methane in mature and post-mature gases is isotopically heavier than in immature gases, typically with  $\delta^{13}\text{C}$  values from  $-50\text{‰}$  to  $-25\text{‰}$ ; abiogenic

methane has  $\delta^{13}\text{C}$  value larger than  $-20\text{‰}$  (Stahl, 1977; Du et al., 2003). However, methane generated from sedimentary organic matter at high temperature and high pressure can have the features of such heavier carbon isotope ratio and reverse isotope distribution among gaseous hydrocarbons, which means that methane produced by sedimentary organic matter subducted into deep-earth can also have heavier carbon isotopic composition (Du et al., 2003). Methane of the hot spring in RGF has a wider range of  $\delta^{13}\text{C}$  values,  $-56.9\text{‰}$  to  $-19.5\text{‰}$  (Table 5). Methane, with  $\delta^{13}\text{C}$  value from  $-44.5\text{‰}$  to  $-24.0\text{‰}$ , in the hot springs of RGF would be generated from organic matter in the mature and post-mature stages on the basis of carbon isotope compositions, but abiogenic methane was considered as another source of methane (Dai et al., 1995). With an exception, methane in the sample of August 2000 from Huaitaijing spring with a value of  $-56.9\text{‰}$  would be generated by bacterial process, otherwise Dai et al. (1995) reported a larger value of  $-20.97\text{‰}$  and concluded that methane in their sample would be abiogenic. Wang et al. (1994) proposed that  $\text{CO}_2$  and  $\text{CH}_4$  from hot springs in RGF were derived from mantle based on heavier carbon isotopic compositions. Therefore, the molecular and isotopic variations of methane in the hot springs may result from varying contributions of methane in different periods. In any case, higher concentration  $\text{CO}_2$  with small amount of  $\text{CH}_4$  derived from deep-earth may reach isotopic equilibrium between them under high temperature, which is supposed to be precondition for carbon isotopic geothermometer.

### 4.3. Chemical and gas geothermometry

Dissolved chemical species and gas concentrations were widely used to obtain information on subsurface temperatures using multiple fluid–mineral equilibrium calculations. Some chemical geothermometers have been proposed and applied to many geothermal systems (Fournier and Truesdell, 1973; D’Amore and Panichi, 1980; D’Amore et al., 1987; Giggenbach, 1988; Verma and Santoyo, 1997; Goff and Janik, 2000; Can, 2002). We selected some chemical geothermometers to calculate subsurface temperatures in RGF in order to explore subsurface temperature variations with time. The calculated results are listed

Table 5  
Concentrations and carbon isotope ratios of carbon-bearing components in hot springs of the Rehai geothermal field Yunnan Province, Southwest China

Sample no.	Location	T (°C)	HCO <sub>3</sub> (mg/L)	CO <sub>3</sub> (mg/L)	CH <sub>4</sub> (%)	CO <sub>2</sub> (%)	$\delta^{13}\text{C}_{\text{HCO}_3}$ (‰)	$\delta^{13}\text{C}_{\text{CO}_3}$ (‰)	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	$\delta^{13}\text{C}_{\text{C}_{10}\text{H}_{16}}$ (‰)	$\delta(\text{CO}_2\text{--CH}_4)$ (‰)	T $\delta(\text{CO}_2\text{--CH}_4)$ (°C) <sup>a</sup>
Dg	Dagunguo	88.1	1254.78	–	1.43	79.31	-5.0	–	-24.1	-4.5	-3.0	19.6	389
	Dagunguo <sup>D</sup>				1.36	97.35			-19.48	-1.99		17.49	434
Lg	Laogunguo	69	192.3	–	0.61	93.53	-4.2	–	-37.7	-2.4	-27.1	35.3	183
	Laogunguo <sup>D</sup>				0.50	99.09			-20.58	-1.18		19.4	393
Ht	Huaitaijing	97.2	843.29	63.07	0.01	28.85	-6.7	-6.4	-56.9	-7.6	0.6	49.3	93
	Huaitaijing <sup>D</sup>				0.13	99.66			-20.97	-3.24		17.73	446
Rs	Reshutang	97.2	1198.4	82.52	0.23	68.02	-4.2	-4.2	-36.4	-6.0	0.6	30.4	231
Zz	Zaozhichang	88.1	1250	53.64	0.06	88.8	-4.4	-4.2	-44.5	-4.4	–	40.1	138

Data after D: Dai et al., 1995; others, this study.

<sup>a</sup>  $t = 221.66 / (\delta + 13.86) - 273.15$  (Giggenbach, 1982; Bottinga, 1969).

<sup>b</sup>  $t = \exp[(143.36 - \delta) / 20.75]$  calculated with  $\beta$  factors (Richtel et al., 1977).

in Table 3. The employed geothermometers are as following:

$$T_{\text{SiO}_2} = C_1 + C_2S + C_3S^2 + C_4\log S$$

( $S$  is  $\text{SiO}_2$  concentration, if  $\text{SiO}_2 < 295$  ppm,  
 $C_1 = -44.119$ ,  $C_2 = 0.24469$ ,  
 $C_3 = -1.7414 \times 10^{-4}$ ,  $C_4 = 79.305$ )  
 or  $T = C_1 + C_2S$  (1)

(if  $210 < T < 330$  °C,  $\text{SiO}_2 > 295$ ,  $C_1 = 140.82$ ,  
 $C_2 = 0.23517$ , Verma and Santoyo, 1997),

$$T_{\text{Na/Li}} = \frac{1049}{\log\left(\frac{\text{Na}}{\text{Li}}\right) + 0.44} - 273.15$$

(if  $\text{Cl} < 0.3$  m, (up to 10,650 ppm),

Na, Li in molal units) or

$$T_{\text{Na/Li}} = \frac{1267}{\log\left(\frac{\text{Na}}{\text{K}}\right) + 0.07} - 273.15$$
 (2)

(if  $\text{Cl} \geq 0.3$  m, Verma and Santoyo, 1997),

$$T_{\text{Na/K}} = \frac{1052}{1 + e^{(1.714\log(\frac{\text{Na}}{\text{K}}) + 0.252)}} + 76$$
 (3)

( $50 < T < 350$  °C, Can, 2002),

$$T_{\text{K/Mg}} = \frac{4410}{14.0 - \log\left(\frac{\text{K}^2}{\text{Mg}}\right)} - 273.15$$
 (4)

(Giggenbach, 1988),

$$T_{\text{Na-K-Ca}} = \frac{1647}{\log\left(\frac{\text{Na}}{\text{K}}\right) + \beta\left(\log\left(\frac{\sqrt{\text{Ca}}}{\text{Na}}\right) + 2.06\right) + 2.47}$$
 (5)

[Use  $\beta = 4/3$  if  $T < 100$  °C and  $(\log(\frac{\sqrt{\text{Ca}}}{\text{Na}}) + 2.06) > 0$ , but if  $T$  with  $\beta = 4/3$  is  $> 100$  °C, or the above function is negative, use  $\beta = 1/3$  (D'Amore et al., 1987; Fournier and Truesdell, 1973)], and seven gas geothermometers are employed from literature (Table 4; Arnorsson and Gunnlaugsson, 1985; Zhao and Armannsson, 1996; D'Amore and Panichi, 1980).

The calculated reservoir temperatures by different geothermometers for the same hot spring cover a wide

range (Tables 3 and 4), which is due to the errors of calculating coefficients of geothermometric equations, analyzing chemical species of samples, sampling and errors related to the geologic and thermodynamic processes of the chemical equilibria involved in the reactions (Verma and Santoyo, 1997, Zhao and Armannsson, 1996). This is not discussed in detail because it exceeds the subject of this paper. The temperature values calculated by chemical geothermometers, especially values of  $T_{\text{Na-K-Ca}}$ , are generally larger than those calculated by gas ones. For chemical geothermometry, correlation coefficients among the calculated reservoir temperatures ranging from 0.4682 ( $T_{\text{SiO}_2} - T_{\text{K/Mg}}$ ) to 0.8257 ( $T_{\text{K/Mg}} - T_{\text{Na-K-Ca}}$ ) indicate that there are positive correlations between the employed chemical geothermometers.  $T_{\text{Na-K-Ca}}$  gives the highest values (average of 254 °C and deviation of 37 °C) of the calculated values, but  $T_{\text{K/Mg}}$  and  $T_{\text{SiO}_2}$  give lower values. Values of  $T_{\text{Na/K}}$  have a mean of 222 °C and the smallest deviation of 26 °C. For the gas geothermometry, few values of  $T_{\text{CH}_4}$ ,  $T_{\text{H}_2\text{S}}$ ,  $T_{\text{H}_2}$  and  $T_{\text{H}_2\text{S}/\text{H}_2}$  were computed because of lack of  $\text{H}_2\text{S}$  and  $\text{H}_2$  data. Values of  $T_{\text{CH}_4}$  are smaller, but those of  $T_{\text{CO}_2/\text{N}_2}$  and  $T_{\text{H}_2\text{S}/\text{H}_2}$  are higher. Mean value of  $T_{\text{CO}_2}$  is 180 °C and with a smaller deviation of 34 °C and those of  $T_{\text{H}_2}$ ,  $T_{\text{CO}_2/\text{H}_2}$  and  $T_{\text{CO}_2/\text{N}_2}$  are 208, 215 and 200 °C with larger deviations of 57, 75 and 62 °C, respectively. It was reported that  $T_{\text{CO}_2}$  values tend to be slightly lower than measured temperatures and that  $T_{\text{H}_2\text{S}}$  and  $T_{\text{H}_2}$  geothermometers need improvement when reservoir temperatures are higher than 220 °C because of steam condensation during upflow and addition of carbon dioxide from a different source (Zhao and Armannsson, 1996). In addition, Zhang et al. (1987) obtain an average value of  $215 \pm 28$  °C of reservoir temperatures calculated with  $\text{SiO}_2$ -quartz, Na/K and Na-K-Ca geothermometers, and the maximum value of 276 °C estimated with chloride-enthalpy diagram of Fournier (1979) for 20 geothermal manifestations in RGF. According to the calculated values, therefore, it seems reasonable to estimate the average reservoir temperature to be about 250–300 °C.

It is interesting that temperatures of the same spring calculated by the same geothermometer fluctuate from 1973 to 200 (Fig. 8). Chemical geothermometry of Dd, Dg and Yj shows a slight increase trend from 1973 to 1994, but that of Rs is not clear.

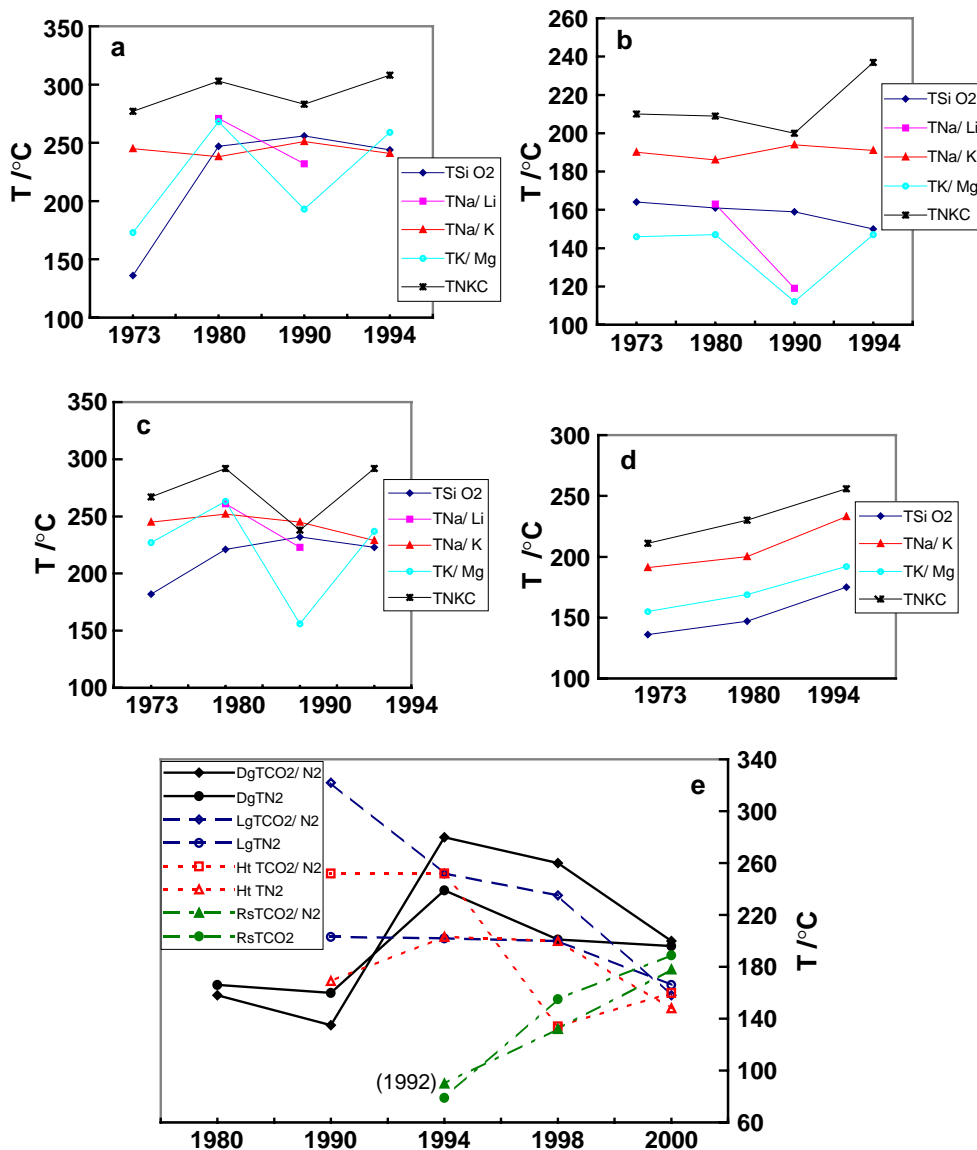


Fig. 8. Temporal variations of reservoir temperatures calculated with chemical geothermometers (a–d) and gas geothermometers (e). (a) Temperatures of Dg, (b) Rs, (c) Yj, (d) Dd and (e) for Dg, Rs, Lg and Ht.

Data of Dg and Yj display high temperatures in 1980 and lower ones in 1990, and those of Rs show lower values in 1990 (Fig. 8a–d). In Fig. 8e, the gas geothermometry data of Dg show an increase trend from 1980 to 2000 and higher temperatures in 1994; data of Rs increase directly from 1992 to 2000; but curves of Lg and Ht show decrease trends. In 1990, amount of cool water contributed to the hot springs is

more than those in other years (Fig. 3), and more air is mixed with spring gases in 1990 (Fig. 6). Those agree with lower temperatures in 1990 (Fig. 8a–c). Higher temperatures in 1994 and 1998 (Fig. 8) correspond with higher  $^3\text{He}/^4\text{He}$  ratios (Table 4), shifting of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  to direction of mixing of steam-condensed water derived from deep lithosphere (Fig. 5) and occurrences of many hydrothermal explosions, which

indicate that more deep fluids are contributed to the hot springs. Mantle and magmatic fluids act as the heat transmitter. Heat derived from upper mantle and lower crust is likely to be predominantly transmitted by upward migration of deep-earth fluids in geothermal and Quaternary volcanic areas because variation of conductivity of middle and upper crust in the area is small. It can be considered, therefore, that variations of contributions of deep fluid and cool waters are the main cause of reservoir temperature variations with time, which affect chemical reactions related to geothermometers and the processes reaching equilibria.

#### 4.4. Carbon isotope geothermometry

Carbon isotope ratios of carbon-bearing pieces in five hot springs of RGF were listed in Table 5. Water samples Dg and Lg have no measurable carbonate anion in solution so that no carbon isotope value was obtained. Water sample Zz was collected from a “new” hot spring on the road to a paper factory, and no travertine was collected.  $\delta^{13}\text{C}$  values of bicarbonate and carbonate anions are in the narrow ranges of  $-6.7\text{‰}$  to  $-4.2\text{‰}$  and of  $-6.4\text{‰}$  to  $-4.2\text{‰}$ , respectively, which is concordant with those of total dissolved inorganic carbon in RGF ( $-5.17\text{‰}$  to  $-3.13\text{‰}$ , Tong and Zhang, 1989).  $\delta^{13}\text{C}$  values of travertine have a wide range from  $-27.1\text{‰}$  to  $0.6\text{‰}$ , which may hint that travertine may be originally formed in different processes of chemical and biochemical deposition. Carbon isotope fractionation ( $\Delta^{13}\text{C}$ ) between  $\text{CO}_2$  and  $\text{HCO}_3^-$  in the hot springs is small ( $\Delta^{13}\text{C}_{(\text{CO}_2-\text{HCO}_3)}$  from  $-1.8\text{‰}$  to  $1.8\text{‰}$ ), but values of  $\Delta^{13}\text{C}_{(\text{CO}_2-\text{HC}_4)}$  and  $\Delta^{13}\text{C}_{(\text{CO}_2-\text{Trav})}$  are larger, with wide ranges from  $18.5\text{‰}$  to  $40.1\text{‰}$  and  $-24.7\text{‰}$  to  $7.0\text{‰}$ , respectively.  $\Delta^{13}\text{C}_{(\text{Trav}-\text{HCO}_3)}$  values range from  $-6.0\text{‰}$  to  $23.9\text{‰}$ , but  $\Delta^{13}\text{C}_{(\text{CO}_3-\text{HCO}_3)}$  values in the hot springs are negligible.

Carbon isotope ratios of coexisting  $\text{CH}_4$ ,  $\text{CO}_2$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and travertine provide thermal information of hydrothermal reservoir. On the assumption of equilibrium of isotopic exchange between  $\text{CH}_4$  and  $\text{CO}_2$  at subsurface reservoir, temperature of the reservoir can be estimated with calculation of Bottinga (1969) (Giggenbach, 1982; Bergfeld et al., 2001) and  $\beta$  factors (Richet et al., 1977) based upon carbon isotope fractionation between  $\text{CH}_4$  and  $\text{CO}_2$ .

The temperatures of reservoirs, estimated with  $t=22166/(\Delta+13.86)-273.15$  (Giggenbach, 1982; Bottinga, 1969), are in the range from about 78 to 450 °C, and those calculated with  $t=\exp[(143.36-\Delta)/20.75]$  corrected using  $\beta$  factors (Richet et al., 1977) range from 93 to 446 °C (Table 5). Carbon isotope data of  $\text{CO}_2$  and  $\text{CH}_4$  of sample Ht produced a lower temperature that is unreliable because equilibrium between magmatic  $\text{CO}_2$  and bacteria  $\text{CH}_4$  was not reached. The differences ( $|\Delta t|$ ) between the calculated temperatures using the two equations are 0 to 7 °C. Our data of Rs, Lg, Dg, Ht and Zz result in reservoir temperatures about 138 to 389 °C, and data from Dai et al. (1995) gave temperatures ranging from 393 to 450 °C. Calculated temperatures of 1994 are higher than those of 2000 for the same hot springs (Table 5), which is concordant with higher temperatures calculated by chemical and gas geothermometers in 1990 and 1994 (Fig. 8). Temperatures of larger than 260 °C, up to 450 °C, may indicate deep high temperature reservoir existence in RGF and/or variation of reservoir temperature that caused by varying contributions of mantle/magma fluids with time. The highest temperature of 450 °C might indicate that fluids from deep high temperature aquifer migrated quickly up to the surface, which is strongly supported by the fact that hydrothermal explosion or mud volcanic activities have been more frequent since 1990 as mentioned above, and that higher helium isotopic ratios were detected in the eruption sites (Shangguan et al., 2004). In addition, strong low-velocity zones, high heat flow, the negative gravity anomaly and low electric resistivity suggest the existence of magma chambers in the shallow crust (about 7 km) and upper mantle (85 km) under the Tengchong volcanic area (Sun et al., 1989; Huang et al., 2002; Lou et al., 2002) from which plenty of heat and volatiles are derived. Therefore, there may be higher temperature fluid layers at depth of more than 3000 m. Consequently, it can be inferred that reservoir temperatures in RGF possibly range from 222 to 450 °C that varies temporally as the temperature pulsation of the hot springs, as a consequence of recent severe hydrogeothermal activity and variation of mantle fluid supply. Other causes for variation of calculated temperatures may be that chemically calculated temperatures of the reservoirs would be lower than actual ones because the chemical compo-



sitions of the hot spring waters are easily modified by incorporation of shallow cool water. However, in the case of  $\text{CO}_2$  and  $\text{CH}_4$  which have reached isotopic equilibrium, carbon isotope compositions of  $\text{CH}_4$  and  $\text{CO}_2$  seem to be affected slightly by shallow water addition during upward migration, and obvious mixture of bacteria methane can be eliminated in calculation. Therefore, the reservoir temperatures estimated by carbon isotope geothermometer of  $\text{CH}_4$ – $\text{CO}_2$  would be rather close to the substantial temperatures of geothermal reservoirs in RGF. Carbon isotopic equilibrium between  $\text{CO}_2$  and  $\text{CH}_4$  may reach in some hot springs in the studied area because the lower concentration  $\text{CH}_4$  and high concentration  $\text{CO}_2$  show signatures of abiogenic/mantle origins (Dai et al., 1995; Wang et al., 1994), even though isotopic equilibria between  $\text{CO}_2$  and  $\text{CH}_4$  in geothermal systems are usually not obtained (Bergfeld et al., 2001).

Dissolved inorganic carbon ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ) in geothermal fluids results from solution of  $\text{CO}_2$  and dissolution of carbonate minerals.  $\delta^{13}\text{C}$  values of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  are a function of  $\delta^{13}\text{C}$  values of such  $\text{CO}_2$  and carbonate minerals, which are controlled by temperature, water–rock interaction, carbonate precipitation from fluid and equilibrium process.  $\delta^{13}\text{C}$  values of dissolved bicarbonate and carbonate in RGF are in a narrow range except for sample Lg (Table 5), which are concordant with data (–10.18‰ to –2.70‰) of total dissolved inorganic carbon in Tengchong volcanic area (Tong and Zhang, 1989). Deposit sample Lg is predominantly consisted of silica sinter, and contains much lower concentration of carbonate with very negative values (–27.1‰, Table 5). The  $^{13}\text{C}$  depleted carbonate in the sample Lg may be biochemically formed. Using the formulations of Halas et al. (1997) and Szaran (1997) and  $\delta^{13}\text{C}$  values of  $\text{CO}_2(\text{g})$ ,  $\text{HCO}_3^-(\text{aq})$  and  $\text{CO}_3^{2-}(\text{aq})$ , temperatures of the hot springs in RGF are estimated between 60 and 70 °C which are much lower than those measured in the field and calculated by other geothermometers (Tables 3–5). This result from that isotopic equilibria between  $\text{CO}_2(\text{g})$  and  $\text{HCO}_3^-(\text{aq})$  and  $\text{CO}_3^{2-}(\text{aq})$  at the hot springs was not achieved because water and carbon dioxide discharge/escape immediately from the springs and the magnitude of carbon isotope equilibrium in the system  $\text{HCO}_3^-(\text{aq})$ – $\text{CO}_2(\text{g})$  was directly proportion to isotopic exchange time (Szaran,

1997). Therefore, it would be caution to estimate reservoir temperature by the carbon isotope geothermometers of  $\text{HCO}_3^-(\text{aq})$ – $\text{CO}_2(\text{g})$ ,  $\text{CO}_2(\text{g})$ – $\text{CO}_3^{2-}(\text{aq})$ ,  $\text{HCO}_3^-(\text{aq})$ – $\text{CO}_3^{2-}(\text{aq})$  and  $\text{HCO}_3^-(\text{aq})$ – $\text{CO}_3^{2-}$  (travertine).

## 5. Summary

Combining with helium isotope compositions, isotopic compositions of carbon dioxide indicate that  $\text{CO}_2$  of the hot springs in RGF is predominantly derived from mantle/magmatic sources and partially from sedimentary carbonate. Dissolved inorganic carbon is mainly derived from mantle carbon dioxide, and other ions in the studied geothermal water originate from rocks through which the fluids circulate. Excess  $^3\text{He}$  from the hot springs in RGF is derived from mantle with crustal helium dilution and atmospheric addition, and hot spring water is originated from meteoric water. Methane in the hot springs is derived from mantle (Dai et al., 1995) and decomposition of organic matter, and the magnitude of  $\text{CH}_4$  concentrations changes periodically because the groundwater and mantle gas inputs changed temporally.

The geothermal and geochemical data indicate that reservoir temperatures varied from 1973 to 2000, which was resulted from time variations of contributions of mantle fluids and shallow crust fluids in Rehai geothermal field. The temperatures for the geothermal reservoirs of RGF the Tengchong volcanic area, Yunnan Province, Southwest China, estimated by the various geothermometries, range from about 220 to 450 °C. The shallow reservoirs may have temperature about 250–300. A temperature of 450 °C may present temperature of the deep fluid aquifer or the upper limit of reservoir temperature.

The  $^{13}\text{C}$  values of  $\text{CO}_2$ ,  $\text{HCO}_3^-(\text{aq})$  and  $\text{CO}_3^{2-}(\text{aq})$  show that isotopic equilibria between  $\text{CO}_2$  and  $\text{HCO}_3^-(\text{aq})$ ,  $\text{CO}_2$  and  $\text{CO}_3^{2-}(\text{aq})$  and between DIC and travertine were not achieved, and no carbon isotope fractionation between  $\text{HCO}_3^-(\text{aq})$  and  $\text{CO}_3^{2-}(\text{aq})$  in the hot springs of RGF was found. Therefore, it is hard to estimate temperature of reservoir by the carbon isotope geothermometers of  $\text{HCO}_3^-(\text{aq})$ – $\text{CO}_2(\text{g})$ ,  $\text{CO}_2(\text{g})$ – $\text{CO}_3^{2-}(\text{aq})$ ,  $\text{HCO}_3^-(\text{aq})$ – $\text{CO}_3^{2-}(\text{aq})$  and  $\text{HCO}_3^-(\text{aq})$ – $\text{CO}_3^{2-}$  (travertine).

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