APPLICATION OF ISOTOPE AND GEOCHEMICAL TECHNIQUES TO GEOTHERMAL EXPLORATION ----THE ZHANGZHOU CASE

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ABSTRACT

Zhangzhou Geothermal system, an inter-medium temperature geothennal system of convective type in the southeast of China is used as an example to demonstrate the problems and improvements in the application of isotope and geochemical techniques to the exploration of the saline geothermal waters in a granite terrain. It is found that deuterium, ^{18}**O** and tritium contents of water are good tracers for the **origin** of the water and of the salinity in it. Fluid / mineral equilibrium modeling is an important data interpretation scheme as to assist the selection and use of chemical geothermometers. Isotopic composition of dissolved sulfate was used not only as a tracer of the origin of salinity, particularly in the case of marine sulfate, but also as a geothermonmeter and a dating method. Carbon-14 is a good dating tool for thermal waters in granite terrain, but for thermal water of marine origin, **difficulty** arises ftom the limited amount of carbon in it. Alteration minerals found in the drill-holes helped the reconstruction of the thermal history of the system.

Key words: Isotope hydrology; Hydrogeochemistry; Geothermal systems; Methodology; Southeast China; Zhangzhou Basin

1. INTRODUCTION

Hot springs are widely distributed in the southeastern coastal area of China including Fujian, Guangdong and Hainan Provinces, which is a granite terrain. Zhangzhou geothermal system is the highest in temperature (122 °C at a depth of 90 meters, 114 °C at the well-head) and one of the highest in flow-rate and salinity, There has long since been intensive dispute on the genesis and energy potential of these systems. In this context, since 1985, the present authors and others have carried out a multi-discipline program (Wang, et al., 1989) to study Zhangzhou geothermal system and its surrounding systems (Figure 1) in order to improve the understanding of similar geothermal systems in other places of the region. In this process, a number of geochemical and isotope methods have been applied, most of them proved to be very useful, but some presented problems. This paper is a brief review of the hydrogeochemical and isotope studies

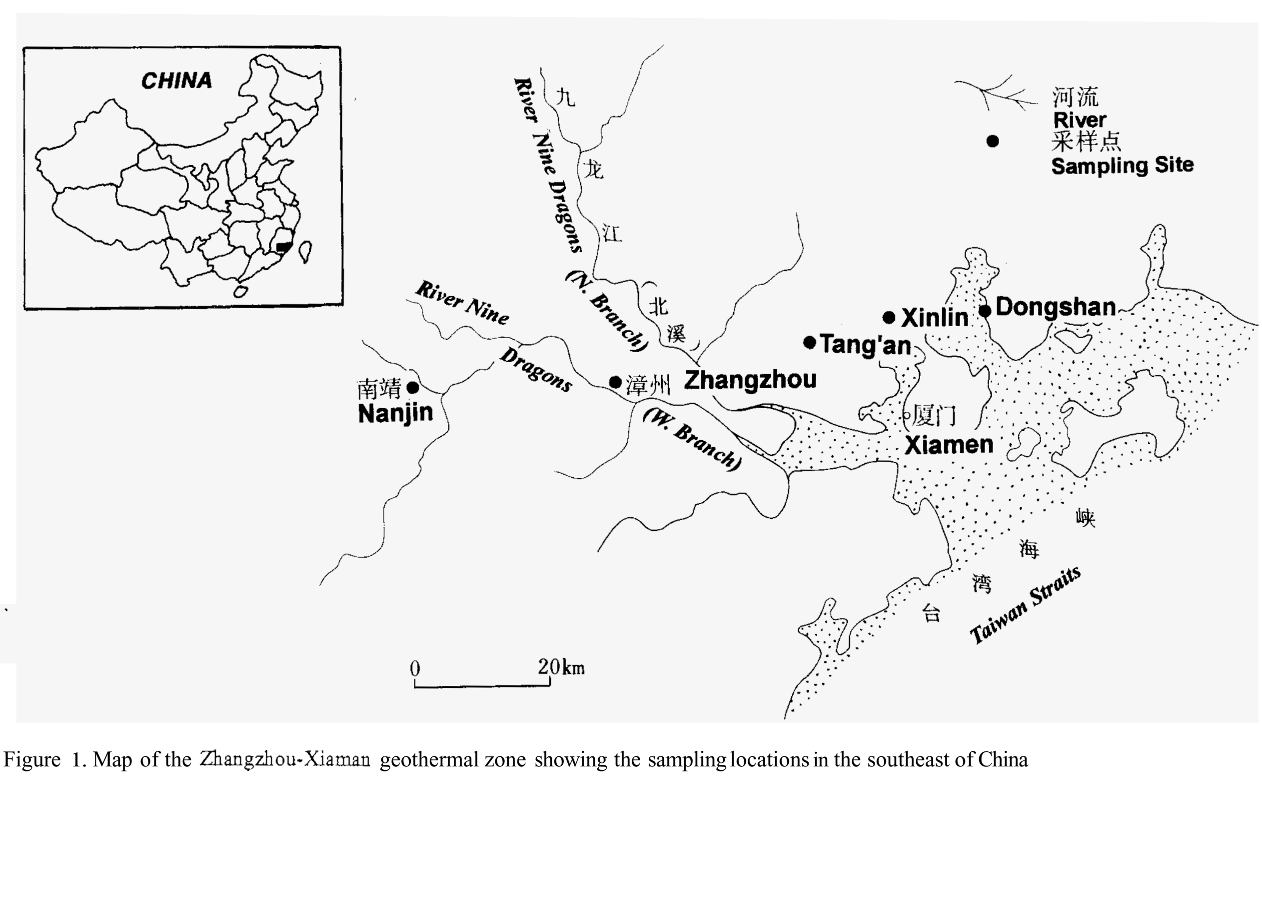

Figure 1. Map of the Zhangzhou-Xiaman geothermal zone showing the sampling locations in the southeast of China

of these geothermal systems and a discussion on the usefulness and effectiveness of the methods used as well as the problem encountered in the work. This work includes investigations on the chemical, gaseous contents and isotopic composition of the thermal water and of the dissolved species in it. A very short review paper was presented earlier by Pang and Wang (1991); but this paper includes progress made in the last a few years.

2. GEOLOGICAL BACKGROUND AND THE PROBLEMS

Zhangzhou geothermal field is located in the central part of the Zhangzhou basin, which is a fault basin formed in the late Quaternary by tectonic activity affecting the granite basement , which was formed in the Mesozoic era. The Quaternary cover, some 20 meters in thickness, is composed of inter-bedded continental and marine unconsolidated sediments, which contain a major aquifer and some small water-bearing lenses. Fractures are densely developed in the bedrock. Two groups of major faults have been identified, the NE, NW group and the NNE, WNW group, which form a fracture network that provides high permeability and porosity for water circulation and occurrence (Figure 2).

Attempts were made to investigate major problems such as, the origin and recharge of the thermal fluids and their salinity, the residence time of the thermal fluids, and the reservoir temperature , etc. Items covered in the investigation mainly include the major, trace and gaseous constituents in the water and isotope compositions of the water and of the dissolved carbon and sulfur. Computer modeling of fluid / mineral equilibrium was also camed out in combination with other techniques in the study and seems to have potential in improving conventional chemical geothermometers.

3. ANALYTICAL TECHNIQUES APPLIED

3.1 Chemical Analyses

Most of the thermal water samples were analyzed for their chemical compositions. Table 1 is a summary of selected chemical analytical results of the samples. The anions were analyzed on the Dionex 20201 Ion Chromatography; the cations by ICP spectrometer and other items by conventional chemical analytical methods. pH was measured both in the field and at the laboratory and results showed difference of approximately one unit (pH lab > pH field). Titration of

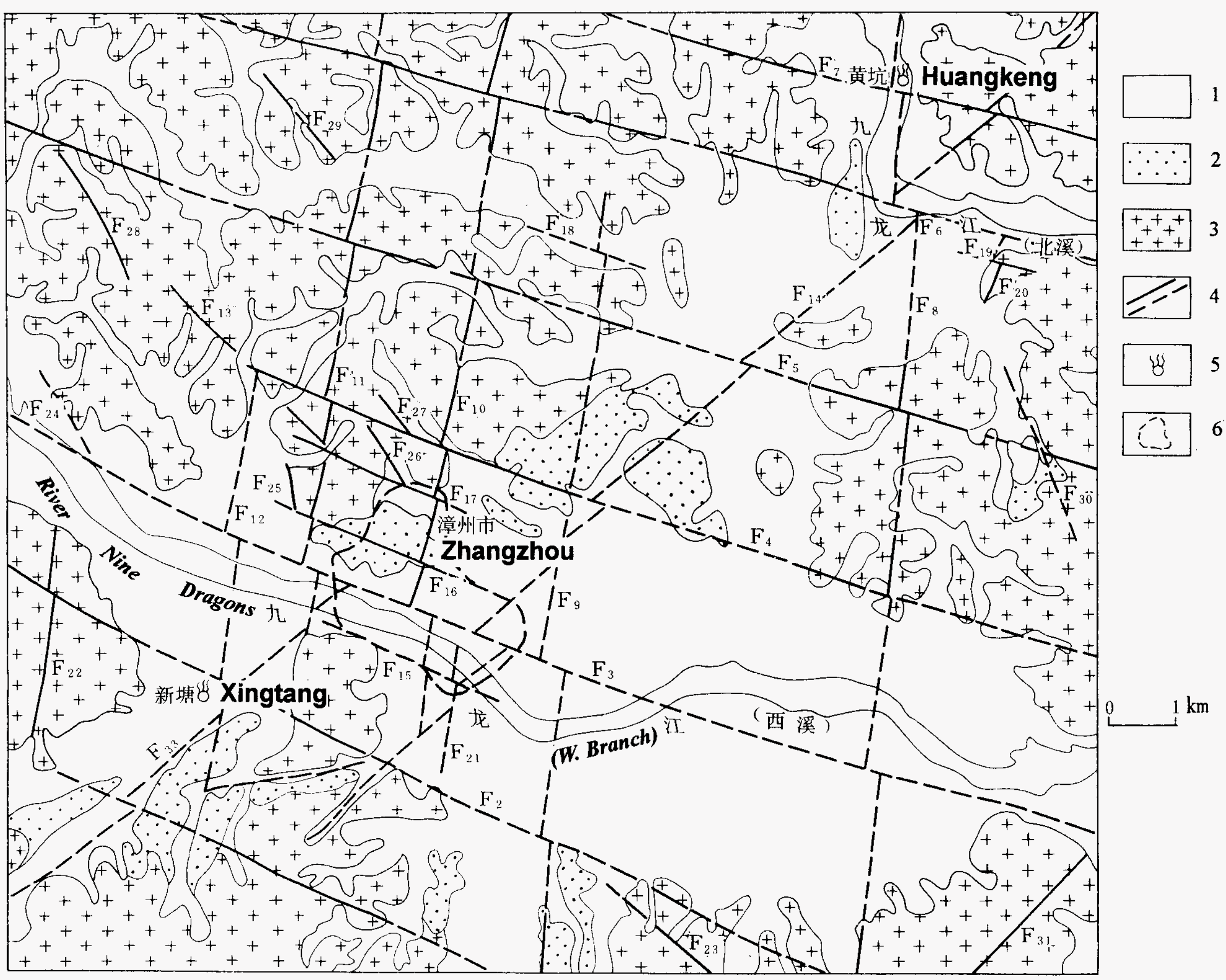

Figure 2. A geological map of the central part of Zhanghzou basin where Zhangzhou geothermal field is located
1) Q_4; 2) Q_3; 3) Granite bedrock; 4) Fractures; 5) Hot springs; 6) The geothermal field

Table 1. Selected chemical analyses of thermal and other natural. waters from Zhangzhou and surroundings

No	Location	Temp	pH	SiO_2	Na	K	Ca	Mg	SO_4	HCO_3	Cl	Al	Fe	^{18}O	^2H	^{14}C
1	Wuzhong, ZGF, W-B	98	7.59	136.4	1981.0	171.9	1382 1	123	2145	31 8	4895.1	0.015	0035	-550	-372	21 12
2	**Shuihua, ZGF**, W-B	97	6.52	114.4	2061.2	128.0	12520	220	1848	370	5420.0	0.242	0 154	-5 84	-41 1	
3	ZR18, ZGF, W-B	73	6.64	91.3	1500.0	85.0	14050	9 9	2370	390	52900	0.198	2 057	-5 58	-35 6	
4	ZR14, ZGF, W-B	105	8.43	140.0	2175.0	89.0	15182	173	2243	21 9	5973.7	**nd**	nd	-567	-379	
5	**Dongshan, W-Q**	52	6.92	93.9	4573.3	283.9	28564	450	3390	373	10573.5	<0.002	0 504	-3 85	-26 3	
6	Xiazhou, ZB,W-Q	20	7.46	22.5	54.2	15.6	593	7 5	815	110.0	90.6	<0.002	<0 002	-4 28	-30 1	
7	175**Yiyuan, ZB**, W-Q	20	6.55	33.6	37.3	13.8	10.4	2 7	104	389	55.3	<0.002	0 021	-5 57	-36 4	
8	**Nanjin, W-B**	73	7.58	74 0	111.1	5.4	1 9	0.1	1260	115.2	25 9	0.100	0 105	-769	-506	462
9	Xinlin, W-B	80	7.40	100.0	3837.6	97.8	13752	993	5780	71 7	7971.5	0.355	0 550	-4 65	-33 4	
10	Tang'an, Spring	81	6.82	82.2	892.8	41.0	5472	0 6	2334	31 0	2057.0	0.156	0 030	-6 60	-45 2	

Notes: ZGF: Zhangzhou geothermal field; W: well sample; Q: Quaternary aquifer; B: bedrock aquifer; The unit of ^{18}**O** and ^{2}**H** is ‰ vs SMOW, for ^{14}**C** is cpm/g. nd: not determined.

Table 2. Dissolved gases in thermal water and other natural waters in Zhangzhou basin

No	Type	Location	Temp	He	H_2	Ar	O_2	N_2	CH_4	CO_2	Total
1	Spring	Huangkeng	56 5	<0.01	<0.01	0.37(1 86)	0.99(5.03)	13.43(67.95)	<0.01	5 19(26 25)	1977(101)
2	Well	**ZR30**	41 5	<0.01	<0.01	0.40(2.02)	0.38(1 90)	18.36(91 80)	<0.01	0 85 (4 24)	20 00(100)
3	Well	**ZR26**	270	**<0.01**	<0.01	0.25(1 89)	0.21(1 61)	9.09(68.93)	3.44(26 11)	036 (275)	13 19(101)
4	River	Tianbao	21 0	<0.01	<0.01	0.43(2.08)	1 10(5 35)	17.82(86.72)	<0.01	122 (5 93)	20 55(100)

Notes: 1. Unit of gas contents is mL in per L of water.
2. Data in brackets are the percentage of each gas in the total gases dissolved in the water.
3. Samples were collected in **April,** 1987

HCO, at the laboratory does not differ very much fiom that in the field.

3.2 Gas Analyses

Thermal water and other natural water samples were collected for analysis of dissolved gases. Table 2 is a list of the results. Water samples were collected on glass bottles of 10 liters in volume, which were tightly sealed. The extraction of the gases and gas chromatographic analysis were done in the laboratory soon after collection.

3.3 Isotope Analyses

Many samples of both thermal and non-thermal natural waters have been collected and analyzed for **Oxygen - 18**, Deuterium and tritium contents (Pang and Wang, 1990) Sulfur and oxygen isotopes of aqueous sulfate were also studied (Pang, et al., 1995). Carbon - 14 is used as a dating tool. Both Carbonate and Sulfate were separated fiom the water through precipitation in the laboratory. See Table 2 for the data.

3.4. Alteration Mineral Study

Since tens of wells have been drilled in the geothermal field, their drill cores are used for the study on alteration minerals. Products of metasomatism were sampled from the cores and observations include mineralogy, fluid inclusions in alteration minerals were made in the laboratory.

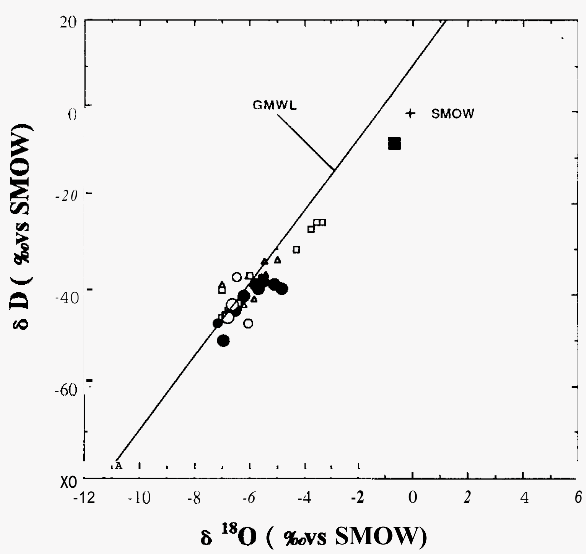

Figure 3. Comparison of isotope composition of the thermal water (circles) with that of the non-thermal meteoric waters (triangles and rectangles).

3.5 Fluid - mineral Equilibrium Modeling

The fluid / mineral equilibrium modeling approach first proposed by Reed and Spycher (1984) has been used. This was done on both the hot spring and well waters from the Zhangzhou - Xiamen zone (Pang and **Armmannson,** 1989). The WATCH program **(Amorsson** et at., 1982) was used for the calculations. The samples were collected and completely analyzed chemically for this purpose.

4 DISCUSSIONS

4.1 About the System

Origin of the thermal water and the recharge of the system

A local meteoric water line was determined based on compositions of different types of meteoric waters including rainwater, river water and shallow ground waters from the study area. The line is found to be identical to that of the global meteoric water line. The thermal waters plot very close to the meteoric water line, which indicates a meteoric origin (Figure 3). According to the "elevation effect" principle, the elevation of the recharge area for Zhangzhou geothermal system was found out to be 800 to 1000 meters higher that that of the discharge area. In most cases, recharge areas are the periphery of the basins. With reference to modeling of the mass and heat transport and conservation in the *systems* (Hochstein, et al., 1990; Hu, 1989), it is concluded that these hot spring systems are formed by the deep circulation of ground water within the basins by forced convection induced by the topography.

Origin of the High Salinitv in the Thermal Water

Most of the hot spring waters in the southeast of China are dilute. However, thermal waters from some geothermal systems close to the seashore are saline. The total dissolved solids in thermal waters in Zhangzhou geothermal field is as high as 10,000 to 12,000 mg / L. The mixing of meteoric water with sea water is evidenced by the close correlation of the chloride concentration with bromide contents (Figure 4). This is also supported by the close linear correlation between chloride concentrations and oxygen - 18 (Pang, et al., 1995).

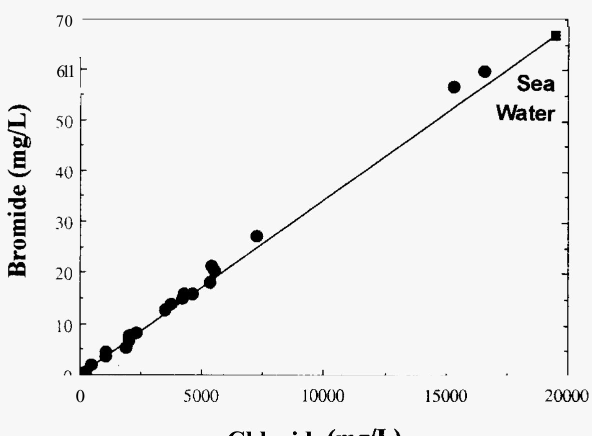

Figure 4. Linear relation between chloride and bromide in thermal waters from Zhangzhou and surroundings, which is an indication of mixing of meteoric water and sea water.

The Zhangzhou - Xiamen geothermal zone was selected as the sampling area for a detailed investigation on this sea water mixing processes. Samples at increasing distance from the sea and with different salinity were collected for chemical and isotopic analyses. The sea water in most of the geothermal systems seems to be connate water that entered the systems during a period of high sea level, which occurred, for the southeast of China, 6,000 - 7,000 years ago according to some geological evidences. The dilute waters from other systems have chemical features derived from the dissolution of the granite country rocks. Knowledge of the mixing processes has deepened the understanding of the genesis and origin of the systems. For instance, for Zhangzhou Geothermal Field, it is found out that two mixing phases took place: 1. Primary mixing at a depth of 3-4km; 2. Secondary mixing: the mixing between the ascending saline thermal water with the dilute ground water in the shallow Quaternary aquifer.

Reservoir Temperature and Thermal History of the System

An attempt was made by the authors to combine the conventional geothermometers with the chemical equilibrium modeling in order to verify the applicability of the conventional geothermonmeters in different conditions (Pang, 1991). After this consideration, the selected geothermometers may be applied better to other geothermal systems with similar geochemistry. By using a reference geothermal

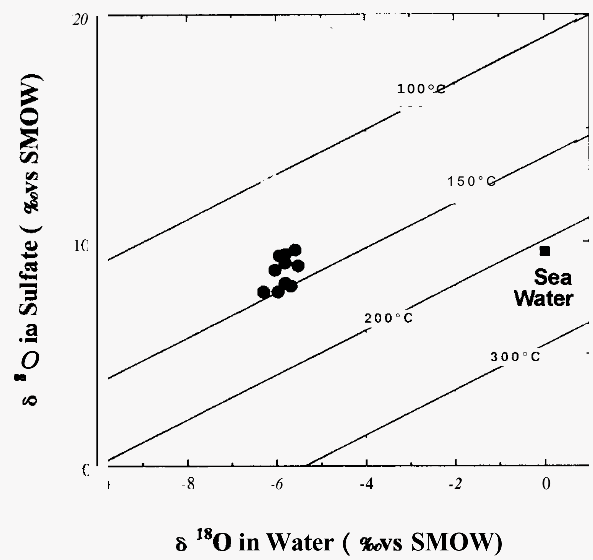

Figure 5. Reservoir temperature predicted by water-sulfate oxygen-18 geothermometer. The filled circles represent those samples from Zhangzhou geothermal filed.

system, this has been achieved for the Southeast China Geothermal Belt (Pang, 1992a), which includes the Zhangzhou - Xiamen geothermal zone.

An approximate range of reservoir temperatures could be obtained from the ^{18}O data of the thermal water, which implies limited water-rock exchange of isotopes due to the low-medium temperature environment of the systems. The water and dissolved sulfate show good equilibrium in ^{18}O, which serves as a very good indicator of the reservoir temperature (Pang et al., 1995).

The reservoir temperatures thus predicted for most of the geothermal systems in the SE China are between 100-- 120°C with the highest temperature (140-- 150°C) at Zhangzhou Geothermal Field (Pang, 1990c). Sulfate-water ^{18}O geothermometer yields very similar temperature (Pang, et al., 1995)(Figure 5).

Alteration minerals found frequently in the field are: epidote, quartz, calcite, laumontite, prehnite, pyrite, opal, fluorite, and chlorite, etc. The sequence of occurrence of these minerals represent a thermal evolution from high temperature (~300°C) to an inter-medium temperature (~150°C) of the present.

Residence Time of the Thermal Water

The residence time of the geothermal fluid is defined as the time since it was last isolated from atmosphere. Radioactive isotopes tritium

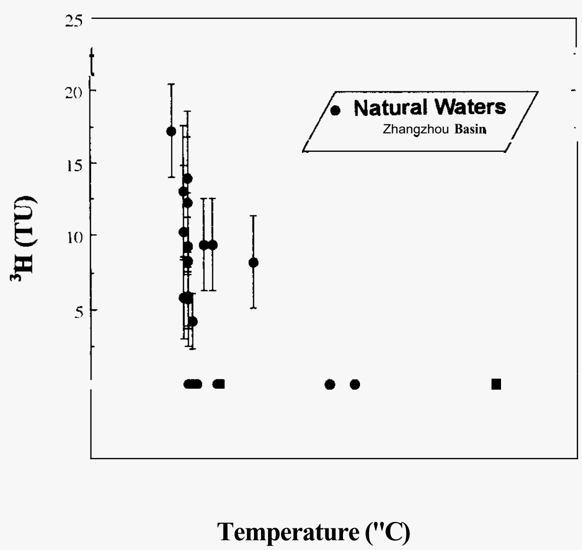

Figure 6. Tritium contents of the thermal water and other natural waters from Zhangzhou basin.

and carbon - 14 were use for dating of geothermal water and other natural waters in the study areas. (Figure 6).

Geothermal parent waters are tritium free. The presence of tritium in the thermal water is an indicator of dilution by the young shallow ground water. Tritium was found to be quite effective for the investigation on the relationship between different natural waters. However, it seems not to be a good dating method because the age of geothermal water is far beyond the limit (about 100 year) of the tritium method. Thermal water from Nanjin hot spring to the west of Zhangzhou Basin was dated using carbon - 14 method and the result turned out to be 1,755 ± 360 years old. However, carbon - 14 dating could not be applied to the saline thermal water because of its low carbon content.

4.2 About the Methodology

Modeling has proved useful in drawing conclusions about the fluid / mineral equilibrium state of the studied systems and improving the selection of conventional chemical geothermometers. However, the data for most of the low temperature minerals, especially the clay minerals, are not sufficient, which prevents the method from wider application in this type of systems.

Most of the gothermometers are empirical methods and involve may assumptions (Fournier, 1989, 1990). Different temperatures can be indicated using different geothennometers with the same set of geochemical data. A particular geothrmometer may be suitable to one place but not another. This deficiency prevents geothermometers from more effective application and causes considerable problems sometimes.

A theoretical calibration approach was proposed by Pang (1992a, b). The result was interesting for it shows reasonable mineral assemblage at equilibrium with the thermal water and reasonable agreement between temperatures fiom the equilibrium modeling and ftom some chemical geothermometers. In this way, conventional geothermometers can be selected and used later on for the investigation of other geothermal systems of the same type. However, attention must be paid to the salinity of the water. Geothennometers suitable to a dilute geothennal system must be used carefully for saline thermal waters. As mentioned above, the high salinity comes from the mixing with sea water. Applicability of conventional geothermometers to this type of systems is different from applicability to fresh water systems. For these systems, modeling of the fluid-mineral equilibrium shows that there is no overall equilibrium. Most cation geothermometers failed . However, the influence of the salinity on the silica geothennometers my be neglected, so they are still useful. In Zhangzhou geothermal field, with consideration of the mixing of deep saline thermal water with shallow cold ground water, the reservoir temperature obtained by using chalcedony geothermometer is 140°C (Pang, et al., 1990c)

Oxygen - 18 and deuterium are goodtracers for the origin of the water and for the salinity in the case of marine origin of the thermal water. Other natural waters as well as the thermal water must be studied in order to draw a completed picture of the water circulation system and to extract more comprehensive information on the hydrology of the system (Pang, et al., 1990a).

Tritium is more useful as a tracer rather than as a dating tool. The time range is limited to < 100 years, which is usually too short for most of the geothermal systems. But it is a quite good tool for distinguishing recent waters from old ones. It is also a good tracer of the flow path of the thermal water and of mixing with other waters (Pang et al., 1990b). Carbon - 14 is a good dating tool in many situations, especially in the granite terrain. But conventional methods require too large amount of carbon, which causes great **difficulty** for some saline thermal waters of low carbon contents. Accelerator mass spectrometers (AMS) should be used particularly in these cases. Sulfur - 34 in sulfate dissolved in thermal waters is a good indicator of the origin of the salinity of the water. This is particularly true in the case of marine sulfate, whose isotope ratio is very constant. Oxygen- 18 in sulfate is a good geothermometer even for low temperature geothermal system. Chemical methods should be combined with the isotope studies so as to reconstruct the evolution history of the sulfur species (Pang et al., 1995).

5. CONCLUSIONS

1) Geochemical and isotopic methods have been found to be very effective for the geothermal exploration and potential assessment of

Zhangzhou geothermal field and surrounding systems in the coastal area of southeast China, including the saline thermal waters close to the coast.

2) It can be concluded from the studies on the thermal water and gases dissolved in it that the geothermal systems under investigation are formed by the deep circulation of the meteoric water and that they all belong to the low-medium temperature category. The reservoir temperatures may not exceed 150 °C within the depth of interest.

3) Fluid / mineral equilibrium modeling helped the selection and improved the use of conventional chemical geothermometers.

4) Deuterium, oxygen - 18 and tritium contents of water are useful tracers for the meteoric origjn of the water and the marine **origjn** of the salinity in the saline thermal waters.

5) Carbon - 14 is a good dating tool for geothermal systems in the granite terrain. If sufficient dissolved carbon is available for analysis.

6) Sulfur and oxygen isotopes of dissolved sulfate are good tracers of the origjn of the salinity in the case of marine sulfate. The sulfate water ^{18}O geothermometer gives correct reservoir temperature prediction even for low temperature ***systems.***

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