http://www.geojournals.cn/dzxbcn/ch/index.aspx

## Theoretical Calculation Model of Heat Transfer for Deep-derived Supercritical Fluids with a Case Study

HU Wenxuan<sup>1</sup>, JIN Zhijun<sup>2</sup>, SONG Yucai<sup>1</sup>, SUN Rui<sup>3</sup> and DUAN Zhenhao<sup>3</sup>
1 State Key Laboratory of Mineral Deposits Research, Department of Earth Sciences,
Nanjing University, Nanjing, Jiangsu 21009; E-mail: huwx@nju.edu.cn
2 Basin and Reservoir Research Center, Petroleum University, Changping, Beijing 102200
3 Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029

**Abstract** Based on a set of equations established by Duan et al. (1992, 1996) for a geofluid system  $H_2O-CO_2-CH_4(-N_2)$ , a formula is obtained to calculate the heat changes. Combining the geological T-P conditions (geothermal gradients and lithostatic and hydrostatic pressures), the enthalpy of some typical geofluids is figured out. Then the principles of heat transfer of deep-derived supercritical fluids are discussed. The result shows that deep-derived geofluids can bring a large amount of thermal heat and release most heat to the shallow surroundings as they move up, because the molar enthalpies vary very greatly from the deep to shallow, increasing with the increases of T and P. Generally, more than tens of kilojoules heat per molar can be released. Furthermore, the molar enthalpy is affected by the compositions of the geofluids, and the molar enthalpy of  $CO_2$ ,  $CH_4$ , or  $N_2$  is greater than that of  $H_2O$ , being twice, more than twice, and about 140% of  $H_2O$ , respectively. Finally, a case study is conducted by investigating a source rock sequence affected hydrothermally by magmatic fluids in the Huimin depression of Shengli Oilfield. The thermal heat calculated theoretically of the fluids related to a diabase intrusion is quite large, which can increase the temperature near the diabase to about 300°C, and that can, to some extent, account for the abnormal rise of the vitrinite reflectance, with the highest of about 3.8%  $(R_0)$ .

Key words: heat transfer, enthalpy, theoretical calculation, deep-derived fluids, a case study

#### 1 Introduction

As magmas or geofluids move upward from the deep to shallow of the earth, the energy carried by them can be transferred from the inner of the earth into the outer, which, meanwhile, can trigger various geological processes in the crust. More and more observations show that except for the magma, geofluids in the deep play a very important role in the process of heat transfer. It can be confirmed that there is a great amount of geofluids activating inside the earth (Xia et al., 1999; Zhang et al., 1999). For example, about 800 million tons of CO<sub>2</sub> are erupted throughout terrestrial volcanoes in one year alone (Gerlach, 1991; Zhang and Zindler, 1993). And most of hydrothermal fluids in the crust have intimate relationship with "the deep process" (Du, 1996). On the other hand, "the energy effect" related to fluid migration is quite obvious and it leaves its geochemical fingerprints in many geothermal systems, hydrothermal ores, and some petroleum reservoirs (Xu et al., 1996; Mao et al., 1999; Hu et al., 2001; Zhang et al., 2001; Jin et al., 2002). Even the El Nino phenomena are possibly related to heat discharged from deep fluids below the sea floor (Du, 1996). Therefore, the energy from deep fluids has an important effect on various geological processes that have taken place or are still going on in the outer spheres.

It is necessary to determine the quantity of heat before "the energy effect" is discussed. For example, how much heat will be released when supercritical fluids are discharged from the deep to the shallow? Is there any difference in the amount of heat for compositionally different geofluids? These problems have not been solved yet due to the difficulty of experiments and the lack of thermodynamic data. Fortunately, a series of equations of state (EOS) for fluids have been established recently, which makes it possible to calculate heat transfer quantitatively. Duan (1996) found his EOS for the H<sub>2</sub>O-CO<sub>2</sub>-N<sub>2</sub>-CH<sub>4</sub> system for the most representative of the deep geofluid compositions. The results calculated by the EOS agree well with experimental data (Duan, 1996) and they can predict various thermodynamic properties under supercritical conditions, including the change of enthalpy. In this paper, we will deduce the equation to calculate heat changes based on this EOS firstly. Then the general principles of heat transfer of deep-derived supercritical fluids can be summarized according to the results calculated by the equation. It is believed that this work provide valuable information for discussing profoundly the mechanism of geological processes related.

### 2 Basis and Method

## 2.1 The system selection and the *T-P* condition determination

Geofluids are generally composed of three parts: water (H<sub>2</sub>O), salts (NaCl, CaCl<sub>2</sub> etc.), and gases (CO<sub>2</sub>, CH<sub>4</sub> etc.). Deep fluids are under supercritical conditions and contain little salts. Fluid inclusions derived from the deep indicate that CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> are the predominant components of deep geofluids, so we take the quaternary H<sub>2</sub>O-CO<sub>2</sub>-N<sub>2</sub>-CH<sub>4</sub> system as representative of deep geofluids.

Deep fluids are of high temperature and high pressure, which vary with different geological settings. We apply Pollack and Chapman's (1977) geothermal model to give temperature variation ranges (shown in Fig. 1), and hydrostatic pressures ( $P_{\text{hydro}}$ ) and lithostatic pressures ( $P_{\text{litho}}$ ) as pressure variation ranges (shown in Fig. 2).

## 2.2 The EOS used and the equation deduced to calculate enthalpy changes

Enthalpy changes ( $\Delta H$ ) is used to estimate the heat absorbed or released for a fluid system. To get the  $\Delta H$ , it is necessary to adopt a suitable EOS to deduce the expression of enthalpy changes. For a supercritical fluid system, many EOS have been published, but few can predict the various thermodynamic properties (especially the enthalpy) accurately in a wide range of temperature and pressure. Duan (1996) established a new EOS for the  $H_2O-CO_2-N_2-CH_4$  system, which can predict the *PVT* properties of supercritical fluids in a wide *T-P* range. Later on, the EOS was improved by us and Duan (Sun et al., 2000). All experimental data of various thermodynamic

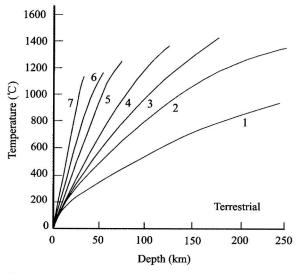


Fig. 1. Terrestrial geothermal temperature curves corresponding to depth.

1-7 denote heat flow values, which are 30, 40, 50, 60, 90, 120 and 150 mW/m<sup>2</sup> respectively, representing different geothermal gradients.

properties (including the PVT data, fugacity, enthalpy and phase equilibrium) in the range from  $T_{\rm c}$  (H<sub>2</sub>O critical temperature) up to 1700°C and from 0 to 10 GPa can be well duplicated (Sun et al., 2000). It provides a valid approach for a systematical study of the thermodynamic properties of deep geofluids. The expression of this EOS is:

$$Z = \frac{P_r V_r}{RT_r} = 1 + \frac{a_1 + a_2 / T_r^2 + a_3 / T_r^3}{V_r} + \frac{a_4 + a_5 / T_r^2 + a_6 / T_r^3}{V_r^2} + \frac{a_7 + a_8 / T_r^2 + a_9 / T_r^3}{V_r^4} + \frac{a_{10} + a_{11} / T_r^2 + a_{12} / T_r^3}{V_r^5} + \frac{a_{13}}{T_r^3 V_r^2} (1 + \frac{a_{14}}{V_r^2}) \exp(-\frac{a_{14}}{V_r^2})$$

$$P_r = \frac{3.0626\sigma^3 P}{\varepsilon} \quad T_r = \frac{154}{\varepsilon} \quad V = 1000 V_r \left[ \frac{\sigma}{3.691} \right]^3$$
 (1)

where  $P_r$  denotes pressure (10<sup>5</sup> Pa);  $T_r$  is temperature (K); and  $V_r$  means volume (dm³); R is the gas constant (=0.08314467); the subscript r denotes the reference fluids system (where CH<sub>4</sub> is the reference system). Parameters  $a_1$  to  $a_{14}$  and  $\varepsilon$  and  $\sigma$  as L-J parameters for pure fluids are shown in Duan's paper (1996). Parameters  $\varepsilon$  and  $\sigma$  for mixed fluids system, will be given as follows:

$$\varepsilon = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j k_{1,ij} \sqrt{\varepsilon_i \varepsilon_j} \qquad \sigma = \sum_{i=1}^{n} \sum_{j=1}^{n} x_i x_j k_{2,ij} (\sigma_i + \sigma_i) / 2$$

where  $x_i$  and  $y_{es}$  denote the molar fractions of component i; k is the interaction parameter between particle i and j. The value of  $k_{1,ij}$  and  $k_{2,ij}$  are listed in Duan's paper (1996).

Based on the above EOS and the definition of enthalpy, and with reference to the previous work by Duan et al.

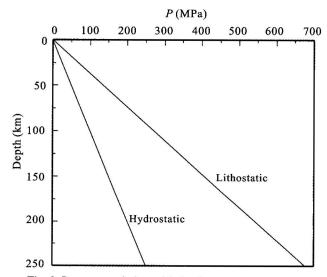


Fig. 2. Pressure variation with depth.

(1992a, b, c; 1995), the equation to calculate H can be deduced:

$$H(T,P) = \frac{\varepsilon}{154} RT(Z-1) + \frac{\varepsilon}{154} RT^{2}$$

$$\left[ \frac{2a_{2}/T_{r}^{3} + 3a_{3}/T_{r}^{4}}{V_{r}} + \frac{2a_{5}/T_{r}^{3} + 3a_{6}/T_{r}^{4}}{2V_{r}^{2}} + \frac{2a_{8}/T_{r}^{3} + 3a_{9}/T_{r}^{4}}{4V_{r}^{4}} + \frac{2a_{11}/T_{r}^{3} + 3a_{12}/T_{r}^{4}}{5V_{r}^{5}} + \frac{3a_{13}}{2a_{14}T_{r}^{4}} [2 - (2 + \frac{a_{14}}{V_{r}^{2}}) \exp(-\frac{a_{14}}{V_{r}^{2}})] \right]$$
(2)

The symbol  $\Delta H'\Delta H = H(T, P) - H^{id}(T, 0 \text{ Pa})$ ) represents the enthalpy change of the real fluid at T and P of interest from that of an ideal gas at 0 Pa. The ideal gas enthalpy,  $H^{id}(T, 0 \text{ Pa})$ , can be derived from the canonical partition function (Mcquarrie, 1976). The ideal gas  $N_2$ ,  $H_2O$ ,  $CO_2$ ,  $CH_4$  enthalpy can be calculated from the following formula:

$$H^{id}(T, 0 \text{ Pa}) = RT[3.5 + 0.5hv + \frac{hv}{e^{hv/k_BT} - 1}]$$
 N

where h is Planck's constant,  $k_{\rm B}$  is Boltzmann's constant, and u denotes the vibrational frequency calculated from the microwave spectra (see Fig. 6-1 in Mcquarrie's paper, 1976).

$$H^{id}(T, 0 \text{ Pa}) = RT[3.5 + \sum_{i=1}^{3n-5} (\frac{\Theta_{vj}}{2T} + \frac{\Theta_{vj}/T}{e^{\Theta_{vj}/T} - 1})]$$
 CO<sub>2</sub>

where  $\Theta_{vj}$  is the vibrational characteristic temperature (see Fig. 8-1 in Mcquarrie's paper (1976)).

$$H^{id}(T, 0 \text{ Pa}) = RT[4 + \sum_{i=1}^{3n-6} (\frac{\Theta_{vj}}{2T} + \frac{\Theta_{vj}/T}{e^{\Theta_{vj}/T} - 1})] \quad \text{H}_2\text{O} \text{ and CH}_4$$

#### 2.3 Comparison with Experimental Data

The enthalpies of  $H_2O$  and  $N_2$  calculated from Eq. (2) are listed in Table 1 and Table 2 respectively. The former are compared with the experimental data of Harr et al. (1984), and the later compared with the data of Angus et al. (1979) (here,  $\Delta H$  is the value relative to  $10^5$  Pa and 298 K). It is shown that the enthalpy values calculated from Eq. (2) agree well with the experimental data; therefore, it is believed that the equation can calculate enthalpy changes for various fluid systems.

### 3 Results

The enthalpy changes for a system are usually expressed in terms of the molar enthalpy changes. Based

Table 1 The H<sub>2</sub>O enthalpy changes derived from theoretical calculation compared with the values from experimental measurement (J/mol)

<i>T</i> (K)	1×10 <sup>5</sup> Pa		1×10 <sup>7</sup> Pa		1×10 <sup>8</sup> Pa		1×10 <sup>9</sup> Pa		3×10 <sup>9</sup> Pa	
	Eq. (2)	Haar								
800	74.9	74.9	74.2	74.1	68.3	66.7	69.2	65.8	93.3	89.6
1000	83.5	83.6	83.0	83.1	78.9	78.6	79.9	78.2	105.2	101.4
1500	106.9	107.3	106.7	107.1	104.9	105.4	107.5	107.9	132.9	130.1
2000	132.1	132.9	132.0	132.8	131.4	132.5	135.9	137.4	160.9	158.6

Note: Experimental data quoted from Haar et al., 1984.

Table 2 The  $N_2$  enthalpy changes derived from theoretical calculation compared with the values from experimental measurement (J/mol)

T (K)	P (10 <sup>5</sup> Pa)	ΔH (Eq. 2)	ΔΗ (Angus et al., 1979)
300	1	713	716
500	1	6626	6626
800	1	15768	15786
300	50	456	468
500	50	6599	6588
800	50	15837	15841
300	500	-409	-345
500	500	6763	6762
800	500	16660	16648
300	5000	10684	10584
500	5000	17670	17450
800	5000	27872	

on the above EOS and the conditions of temperature and pressure which vary with depth, the molar enthalpies of  $H_2O$ ,  $CO_2$ ,  $CH_4$  and  $N_2$  in the supercritical region are calculated and shown in Figs. 3, 4, 5 and 6. The (a), (b), (c), (d) of each figure describe the  $\Delta H$  profile on depth response respectively to the different geothermal values of 120, 90, 60 and 30 mw/m<sup>2</sup>. Two curves are plotted in each picture, indicating that the molar enthalpies are under the hydrostatic pressure ( $H_{\text{T-Phydro}}$ ) or the lithostatic pressure ( $H_{\text{T-Phydro}}$ ). The molar enthalpy DH is located in the X-coordinate (kJ/mol), and the Y-coordinate represents the depth (km). From these figures, we can draw the following conclusions:

(1) In any case, ranging from the earth's surface down to several kilometers, the molar enthalpy for any fluid system is quite low, only 0.n to 1.n kJ. However, it can amount to tens or hundreds of kilojules (kJ) in the deep, increasing by two or three orders. This indicates that when fluids move upward from the deep and reaches the

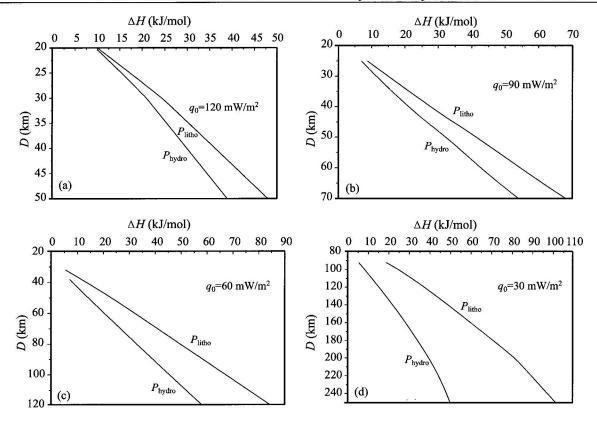


Fig. 3. The H<sub>2</sub>O enthalpy changes vs. depth for different geothermal gradients.

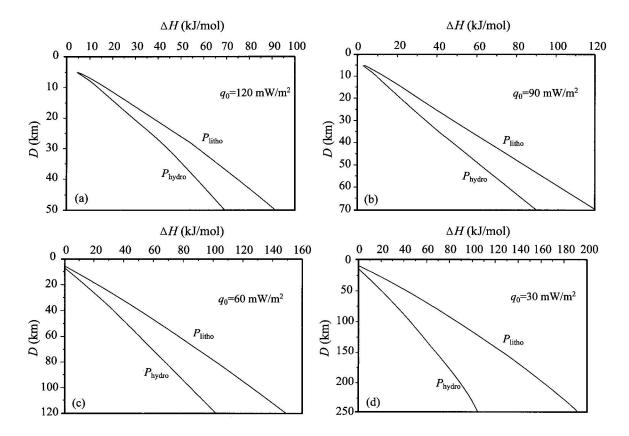


Fig. 4. The CO<sub>2</sub> enthalpy changes vs. depth for different geothermal gradients.

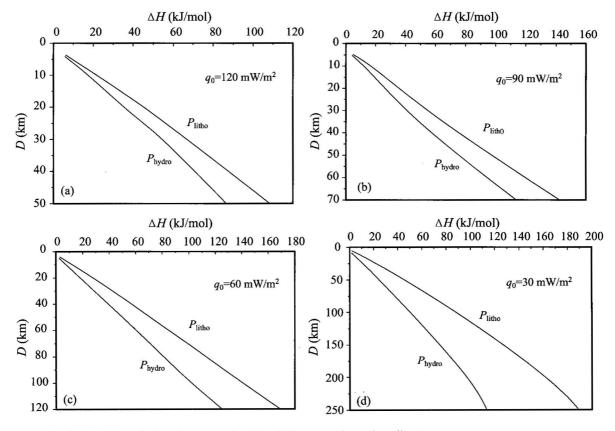


Fig. 5. The  $\text{CH}_4$  enthalpy changes vs. depth for different geothermal gradients.

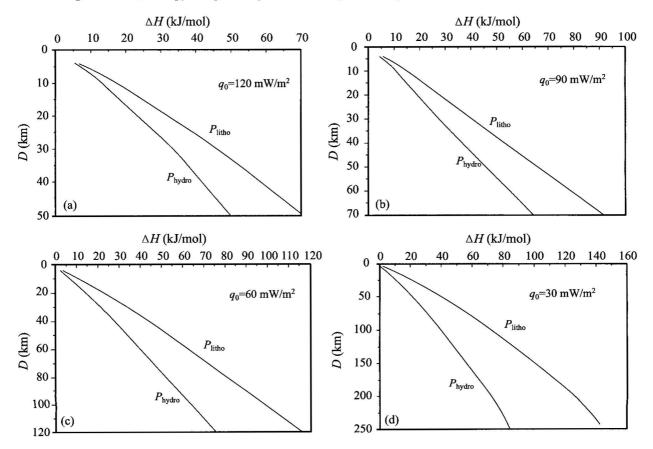


Fig. 6. The N<sub>2</sub> enthalpy changes vs. depth for different geothermal gradients.

shallower, most of heat taken from the deep will be released.

- (2) The molar enthalpy of  $H_2O$ ,  $CO_2$ ,  $CH_4$  and  $N_2$  will increase with the increase of depth. For example, under  $q_0$ =60 mw/m² and lithostatic pressure, the molar enthalpy of water is 84.7 kJ/mol at 120 km, while it is 13.7 kJ/mol at 40 km (see Fig. 3c). This means that if  $H_2O$  goes up from 120 km to 40 km, 71 kJ of heat per molar will be released. If this fluid reaches a sedimentary basin only several kilometers deep, the enthalpy left will be less than 1 kJ, while more than 80 kJ of heat per molar can be released.
- (3) At a constant geothermal gradient and depth, the enthalpy under  $P_{\rm litho}$  is higher than that under  $P_{\rm hydro}$ , and the gap becomes wider and wider with the depth increasing, presenting a reversal 'V' shape. In Fig. 3c, the enthalpy is 33 kJ/mol under  $P_{\rm hydro}$  at 80 km and it is 52 kJ/mol under  $P_{\rm litho}$ , indicating that pressure has a positive effect on the enthalpy. At depths less than 10 km, the difference between  $P_{\rm hydro}$  and  $P_{\rm litho}$  becomes smaller with decreasing depth .
- (4) At a constant temperature and pressure, the molar enthalpy of  $CO_2$ ,  $CH_4$  or  $N_2$  is greater than that of  $H_2O$ , being twice, more than twice, and about 140% of  $H_2O$ , respectively. For example, under the conditions of  $q_0$ =60

mw/m<sup>2</sup> and  $P_{\text{litho}}$ , the molar enthalpies of H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> are 41.1 kJ/mol, 84.0 kJ/mol, 97.3 kJ/mol and 65.8 kJ/mol respectively, which indicate that these species are good carriers of heat discharging from the inner of the earth to the outer.

For a mixed system, such as a binary H<sub>2</sub>O-CO<sub>2</sub> system or H<sub>2</sub>O-CH<sub>4</sub> system, or a ternary H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> system, the first step to calculate enthalpy is to determine the mixing parameters according to a certain mixing law. Then the enthalpy will be calculated by the equation with these parameters. A typical binary H<sub>2</sub>O-CO<sub>2</sub> system enthalpy and ternary H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> system enthalpy are given in Fig. 7 and Fig. 8 respectively. The above principles are generally duplicated.

## 4 Application and Discussion

When deep fluids move upward to the shallower parts, the heat energy carried by them will be transported to the surroundings. As a result, it will increase the temperature of a shallow geologic system to create a high geothermal field and accelerates various geochemical reactions and geological processes (such as hydrocarbon generation). It is interesting to know how high temperature will rise on the earth. According to the above results, a quantitative

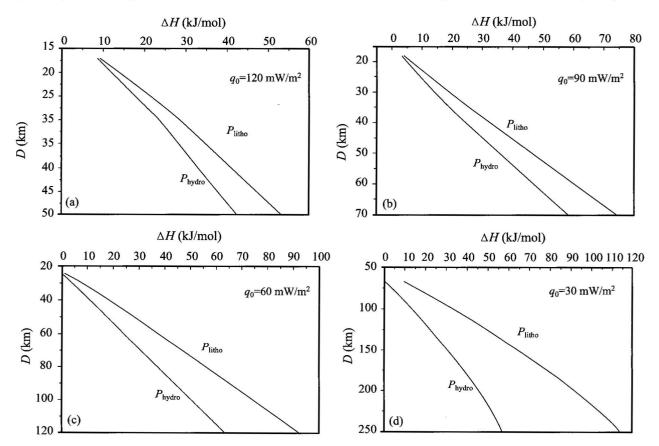


Fig. 7. The H<sub>2</sub>O-CO<sub>2</sub> enthalpy changes vs. depth for different geothermal gradients (0.9 H<sub>2</sub>O+0.1 CO<sub>2</sub>).

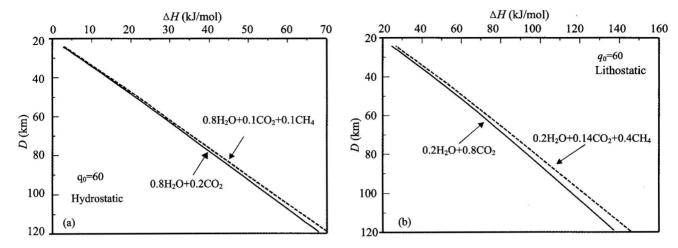


Fig. 8. The H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub> system enthalpy changes compared with the H<sub>2</sub>O-CO<sub>2</sub> system enthalpy changes.

calculation can be theoretically carried out using Eq. (2). However, since it is difficult to determine the initial conditions for a specific geological process, a semi-quantitative calculation is carried out here. We shall hereinafter discuss the thermal effect by magmatic fluids on the thermal evolution of hydrocarbon source rocks, based on a case study of the Well Xia-38 district in the Huimin depression of the Shengli Oilfield.

#### 4.1 The thermal records on hydrocarbon source rocks

A diabase bed is found at 3727-3777 m depth in the Well Xia-38 Area in the Huimin depression, with the thickness ranging from 40 m to 70 m, and extending about 20 km<sup>2</sup> with a total volume of some 1.2 km<sup>3</sup>. As shown in Fig. 9, the hydrocarbon source rocks near the bedrock are hydrothermally altered and even metamorphosed to different degrees. The effect is more serious on the rocks below the bedrock than those above the diabase, where the vitrinite reflectance (R<sub>o</sub>) of keoregen ranges from 1.0% to 3.8% within a thickness of about 10 m. However, the effect is slight on the rocks above the bedrock where only the mudstone near the diabase appears to be baked and the  $R_0$  is lower than 1.0%. This fact indicates that the thermal effect triggered by magmatic water fluids cannot be neglected. On the other hand, it also implies that heat release relies mainly on fluid convection, because the fluids above the bedrock are in a relatively open condition. As a result, heat is dispersed quickly and the temperature of the rocks above the bedrock will rise greatly. On the contrary, the fluids below the bedrock are under a relatively closed environment, where their convection and dispersion are restricted, and heat can accumulate in a limited space to result in the remarkable thermal alteration of hydrocarbon source rocks.

	Depth (m)	Lithologic succession	Lithologic description	Vitrinite reflectance (Ro%)
rd sequence)	3630 <b>-</b> 3680 <b>-</b> 3727		Gray or purplish gray bedded silty mudstone, with little thermal metamorphism	1.0 2.0 3.0 4.0 Ro
Shahejie Group (Es3-third sequence)	3730 <b>–</b> 3755 3777	* * * * * * * * * * * * * * * * * * *	texture, hydro- thermally altered. Fractured, with	
Shahejie	3780-		(Main altered horizons)  Blackish gray	ports
	3830 -		mudstone, having suffered thermal metamorphism and some become hornfels.	1
	3880 -			l l

Fig. 9. The source rock sequence showing increase of vitrinite reflectance near the diabase bedrock.

# 4.2 The composition of the thermal fluids and the T-P conditions (TPX)

To quantitatively calculate the thermal effect, the first step is to determine its composition and the temperature and pressure. Compositionally, the whole Jiyang depression is dominated by basic rocks (diabase and basalt), and the fluids carried by them are characterized by a mantle origin. Although the compositions vary in different samples, CO<sub>2</sub> is generally the main component. In

a summary of the compositions of fluid inclusions in the mantle source rocks, Rosenbaum et al. (1996) pointed out that CO2 is dominant in fluid inclusions in most rock samples, the next is CO, and there are also minor He,  $N_2$ , Ar, H<sub>2</sub>S, SO<sub>2</sub> and H<sub>2</sub>O. Zhang et al. (1999) studied the components of the fluids in xenoliths in several Cenozoic alkali basalts of eastern China, and gave the average contents of various volatile species as follows: CO2 54.98%, SO<sub>2</sub> 30.00%, H<sub>2</sub> 6.11%, CO 6.22%, CH<sub>4</sub> 0.65%, H<sub>2</sub>S 0.10% and N<sub>2</sub> 1.68%. Yang et al. (2001) carried out a research on Cenozoic inclusions in the peridotite xenoliths in basalts and in the ultra-high pressure eclogites in eastern China, and reached at a similar conclusion that CO2 is the dominant component in most fluid inclusions, and its average content may reach 70 mol% in the volatiles. He et al. (1996) analyzed the inclusions in volcanic rocks of the Shengli Oilfield with the Laser Raman Probe. The result shows that CO<sub>2</sub>, the dominant component in the inclusions, varies from 50% to 80%, and there are some other components such as H<sub>2</sub>O, N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>S. Putting the typical data mentioned above into a triangle composition diagram of H<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> (Fig. 10), it is seen that the compositions of the deep-derived geofluids tend to be near the CO<sub>2</sub> end number. The determination of the compositions of the inclusions in pyroxene phenocrysts of the diabase from Well Xia-38 reveals that CO<sub>2</sub> ranges from 52% to 92% and CH<sub>4</sub> from 10% to 25%, with varying H<sub>2</sub>O and N<sub>2</sub>. Based on the data above, a typical composition of the deep-derived fluids is decided as follows: 80% CO<sub>2</sub>, 15% CH<sub>4</sub> and 5% H<sub>2</sub>O. Temperature and pressure are also determined by a study of the inclusions in the phenocryst, which gives the following results: T=720-1160°C; P=120-200 MPa. In such a way, the PTX conditions for

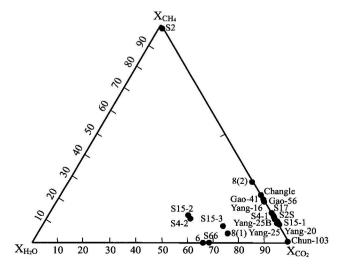


Fig. 10. Triangle diagram of H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub>, showing the basic characters of the compositions of the deep-derived fluids.

the calculation of enthalpy of a typical deep fluid are determined. Using the equation (2) in this paper, the enthalpy range of the deep fluids is obtained as  $\Delta H$ =45-65 (kJ/mol), with an average of 55 kJ/mol, which is the basic parameter for prediction of the heat amount that was ever brought by the hydrothermal fluids from the deep.

#### 4.3 Estimation of the thermal effect

The total amount of the deep fluids should first be determined in order to calculate the bulk thermal effect. According to the data in literature, the basaltic magma contains averagely 2.5 wt% of fluids (CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O etc.), it can be calculated that the fluid amount related to the diabase bedrock in the Xia-38 district is about 1×10<sup>8</sup> t for its 1.2 km³ volume (about 4×10<sup>9</sup> t in weight at the given density of 3.3 g/cm³). Suggesting that the deep fluids are of the typical composition mentioned above, the amount of the fluids is about 2.6×10<sup>12</sup> moles. Such fluids contain averagely 55 kJ/mol of heat as calculated above, therefore, the total enthalpy amounts to about 1.4×10<sup>14</sup> kJ, i.e. 3.3×10 lis kcal. That means the hydrothermal fluid related to diabase intrusion released some 3.3×10<sup>13</sup> kcal of heat into the surroundings.

According to Fig. 9, the hydrothermally affected range by the bedrock is mainly within 10 to 15 m. The 15-m rocks above and below the intrusives are ascertained here, so the total affected volume of the source rock is  $20 \, (\text{km}^2) \times 15 \, (\text{m})$  $\times 2 = 0.6$  km<sup>3</sup>. As the average porosity of the source rocks is considered to be 15%, the water content will be 0.09 km<sup>3</sup>  $(0.6 \text{ km}^3 \times 15\%)$ , about  $9 \times 10^7$  t. The specific heat of water is about 1 cal/°C·g in general conditions, meaning that if 1 g of water is increased by 1°C, 1 cal of heat will be needed. Therefore, 3.3×10<sup>13</sup> kcal of heat from the deep-derived fluids brought by the bedrock can raise the temperature of  $9\times10^7$  t of water by 367°C. Obviously, the thermal effect of fluids is quite remarkable. Considering that fluids are flowing, the thermal fluids near the bedrock will continually disperse by convection. Therefore, the temperature is not likely to rise to the theoretically calculated value. It is suitable to introduce the temperature gradients, as recorded in the profile in Fig. 9. The temperature of the rocks near the bedrock is higher than that of those away from the bedrock. However, above the bedrock, the better convection results in a lower increase in temperature, while below the bedrock, the limited convection leads to a much higher increase in temperature. In the latter case,  $R_0$  reaches 3.8%, which implies that the temperature should be higher than 300°C.

A semi-quantitative calculation has thus been made, but the geological system is much more complex. For example, the velocity of the fluid movement cannot be ascertained, the chemical reactions and/or the water-rock interactions during the processes of the heat fluids will have some effects, and even the heat transfer of the solid bedrock should be considered. To investigate the "thermal effect" of a geological system, all these factors should be taken into consideration.

### Acknowledgements

This research was financially supported by the Major State Basic Research Development Program of China (G1999043309) and the National Natural Science Foundation of China grant 49973001. We thank Dr. Liu Huawen for his helping improve our manuscript.

Manuscript received May 27, 2003 accepted Dec. 23, 2003 edited by Zhu Xiling

#### References

- Angus, S., DeReuck, K.M., and Armstrong, B.N., 1979.
  International Thermodynamics. Tables of Fluid State 6-Nitrogen. Oxford: Pergamen, 244.
- Duan Z.H., Moller, N. and Weare, J.H., 1992a. An equation of state for the CH<sub>4</sub>-CO<sub>2</sub>-H<sub>2</sub>O system: Mixtures from 50 to 1000°C and 0 to 1000 bar. *Geochim. Cosmochim. Acta*, 56: 2619–2631.
- Duan Z.H., Moller, N. and Weare, J.H., 1992b. Molecular dynamics simulation of PVT properties of geological fluids and a general equation of state of nonpolar and weakly polar gases up to 2000K and 20,000 bar. Geochim. Cosmochim. Acta, 56: 3839-3845.
- Duan Z.H., Moller, N. and Weare J.H., 1992c. The prediction of methane solubility in natural waters to high ionic strength from 0 to 250°C and from 0 to 1600 bar. *Geochim. Cosmochim. Acta*, 56: 1451–1460.
- Duan Z.H., Moller, N. and Weare, J.H., 1995. Equation of state for the NaCl-H<sub>2</sub>O-CO<sub>2</sub> system: Prediction of phase equilibria and volumetric properties. *Geochim. Cosmochim. Acta*, 59: 2869–2882.
- Duan Z.H., Moller, N. and Weare, J.H., 1996. A general equation of state for supercritical fluid mixtures and molecular dynamics simulation of mixture PvTx properties. *Geochim. Cosmochim. Acta*, 60(7): 1209–1216 (in Chinese with English abstract).
- Du Letian, 1996. The relationship between crust fluids and mantle fluids. *Earth Science Frontiers*, 3: 172–180 (in Chinese with English abstract).
- Gerlach, T.M., 1991. Present-day CO<sub>2</sub> emissions from volcanoes. Eos., 72(23): 249–255.
- Haar, L., Gallagher, J.S. and Kell, G.S. 1984. NBS/NRC Steam Tables, Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI Units. Washington D.C.: Hemisphere Publishing Co., 320.
- He Ying, Wang Dingyi, Feng Youliang, Liu Hongying and Song

- Lailiang, 1996. Compositions of fluid inclusions and implications in volcanic rocks, Shengli Oil-field. *Geochimica*, 25(5): 468–474 (in Chinese with English abstract).
- Hu Wenxuan, Sun Rui, Zhang WenLan and Sun Guoxi, 2001. Characteristics of gold ore-forming fluids and metallogenic process by mutual mixing and acting of deep-derived fluids and shallow-seeped ones. *Earth Science Frontiers*, 8: 281–288 (in Chinese with English abstract).
- Rosenbaum, J.M., Zindler, A., and Rubenstone, J.L., 1996.

  Mantle Fluids: Evidence from inclusions. *Geochim. Cosmochim. Acta*, 60(17): 3229–3252.
- Jin Zhijun, Zhang Liuping, Yang Lei and HU Wenxuan, 2002. Primary study of geochemical features of deep fluids and their effectiveness on oil/gas reservoir formation in sedimental basins. Earth Science Journal of China University of Geosciences. 27: 659-665 (in Chinese with English abstract).
- Mao Jingwen, Zhang Zhaochong, Ren Fengshou, Zuo Guochao, Zhang Zuoheng, Yang Jianmin and Wang Zhihiang, 1999. Temporo-spatial distribution and evolution of ore deposits in the west sector of the Northern Qilian Mountains, *Acta Geologica Sinica* (English edition), 73(2): 230–241.
- McQuarrie, D.A., 1976. Statistical Mechanics. New York: Harper & Row Pub., 641.
- Pollack H.N., and Chapman, D.S., 1977. On the regional variation of heat flow, geotherms, and lithosphere thickness. *Tectonophysics*, 38: 279–296.
- Sun Rui, Hu Wenxuan and Duan Zhenhao, 2000. Theoretical calculation of thermodynamic functions of supercritical fluids. *Geological Review*, 46(2): 167–177 (in Chinese with English abstract).
- Xia Linqi, Xia Zuchun and Xu Xueyi, 1999. Fluids and Melts in the Upper Mantle. *Acta Geologica Sinica* (English edition), 73 (3): 330–340.
- Xu Yongchang, 1996. The mantle noble gas of natural gases. *Earth Science Frontiers*, 3: 63–71 (in Chinese with English abstract).
- Yang, X.-Y., Zheng, Y.-F., Liu, D., and Dai, J., 2001. Chemical and carbon isotope compositions of fluid inclusions in peridotite xenoliths and eclogites from eastern China: geodynamic implications. *Physics and Chemistry of the Earth, Part A: Solid Earth and Geodesy*, 26(9–10): 705–718.
- Zhang Jinlian, Jin Zhijun, Yang Lei and Rui Handong, 2001. Relationship between oil-gas reservoirs and deep-derived geofluids of Tarim Basin. *Xinjiang Petroleum Geology*, 22(5): 371–375 (in Chinese).
- Zhang Mingjie, Wang Xianbin, Liu Gang and Li Liwu, 1999. The composition of the fluids in alkali basalts and mantle-derived Xenoliths in eastern China. *Acta Geologica Sinica* (Chinese edition), 73(2): 162–166 (in Chinese with English abstract).
- Zhang Ronghua and Hu Shumin, 1999. Experimental observation of the ore-forming fluid NaCl-H<sub>2</sub>O system in the Earth interior. *Acta Geologica Sinica* (English edition), 73(1): 47–64.
- Zhang Y., and Zindler A., 1993. Distribution and evolution of carbon and nitrogen in earth. Earth Planet. Sci. Lett., 117: 331-345.