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# ISOTOPE GEOCHEMISTRY OF GEOTHERMAL WATERS IN NORTHERN NORTH CHINA BASIN: IMPLICATIONS ON DEEP FLUID MIGRATION

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## ABSTRACT

An isotope geochemical investigation was carried out on geothermal formation waters of the Jidong (Eastern Hebei) area in northern North China Basin. 11 water samples were collected from geothermal and non-thermal water wells located mainly in the Liuzhan region where the highest thermal gradient (7.5 °C/100m) was found in North China Basin.

Results confirmed that the extra-ordinary high thermal gradient is formed by upward migration of deeper, more saline and hotter geothermal fluid into the shallower aquifers. Interpretation of results supports a conceptual model to classify the system as a new type of geothermal systems in the sedimentary basins in China that is formed by migration of fluid from deeper aquifers into shallower ones. Furthermore, vertical fluid migration is probably also the reason for secondary oil reservoir being found in Ng formation.

With rather low salinity (1-3 g/l), and relatively higher temperatures of 100-120 °C at rather shallow depth (1000-1500m), the thermal water in the Liuzhan system is the most favourable for exploitation in North China Basin.

## 1. INTRODUCTION

North China Basin is a Mesozoic-Cenozoic basin rich in geothermal resources. More than 50 % of basin type geothermal energy in China is stored in this basin (Chen et al., 1988; 1994; Wang et al., 1996). Geothermal waters are usually found in oil exploration wells. However, in big cities located in the basin, like Beijing and Tianjin, many wells have been drilled solely for geothermal development. The importance of the basin to geothermal development is obvious.

The genetic mechanism of the geothermal systems in North China Basin has been studied (Chen, 1988). Most geothermal anomalies have been found to be related to the relief of the pre-Cenozoic basement, positive anomalies (higher thermal gradient) correspond to basement uplift. These geothermal systems belong to low-medium temperature conductive geothermal systems, in which the key point is that the heat transfer mechanism is conduction rather than convection.

However, extra-ordinarily high thermal gradient was found in some of the drill holes in the Liuzhan region, which is as high as 7.5 °C/100m in the Cenozoic sedimentary cover at less than 1500 meter depth, as compared to the regional background of 2.5-3.0 °C/100m. A geo-temperature field modelling has showed that the conductive heat contribution is about 50%. The other half has to be from convective heat. Migration of hotter waters from deeper formations to shallower aquifers must have taken place. Obviously, no better techniques than isotope and geochemical methods can trace this process.

Origin of fluid and its salinity is closely related to geothermal resources exploration and development. Investigations in SE China (Pang et al., 1995) have proved very useful. Geothermal fluid in sedimentary basins has been studied by many authors (e.g. Hitchon and Friedman, 1969; Marty et al., 1988; Fouillac, 1990; Connolly et al., 1990; Pauwels et al., 1993). In China, systematic isotope geochemical investigations for geothermal purposes have been very few. In order to optimise the geothermal development, it is necessary to get better understanding of the fluid.

Fluid migration and water-rock interactions are relevant to the genesis analysis of geothermal systems but are important issues in oil exploration as well.

The aim of this paper is to assemble all of the available geochemical data from oil exploration and incorporate them with our new data from this study for a discussion on the origin of the thermal waters and their chemical compositions; the possible processes controlling the genesis of geothermal anomalies like that in Liuzhan region. We have also tried to understand the controversies over the applicability of isotope and chemical geothermometers in the sedimentary basin.

## 2. GEOLOGICAL SETTING AND GEOTHERMAL BACKGROUND

North China Sedimentary Basin is a re-activated Mesozoic-Cenozoic basin that attracts great attention of tectono-geologists and economic geologists because of its diverse geological structures and rich resources. The dominant tectonics is fault-block structure in the basin. There are too many fractures in the basin, therefore it has got a well-known name: a broken plate.

Geothermal background and geothermal resources in the basin have been studied in detail by the geothermal research group of the Institute of Geology and Geophysics, Chinese Academy of Sciences in Beijing (Chen et al., 1988). The average heat flow for the whole basin is $62mW/m^2$. Geothermal resources are mainly stored in the Upper Tertiary sandstone formations and the limestone of lower Palaeozoic in the northern part of the basin.

## 3. SAMPLING AND ANALYSES

11 water samples, thermal and non-thermal, were collected from wells (Figure 1) producing from different formations for analysing isotopic composition, sulphur and oxygen isotopes in the dissolved sulphate as well as complete chemical composition. The sample sites include shallower wells for domestic drinking water supply, oil production wells and two oil exploration wells now used for supplying geothermal water. These samples have enabled us to establish a reference

column for the chemistry of different formations in an age and depth sequence.

All the samples were analysed for deuterium ($\delta^2H$) (‰ V SMOW) and oxygen-18 ($\delta^{18}O$) (‰ VSMOW) of the water, sulfur-34 ($\delta^{34}S$) (‰ CDT) and oxygen-18 ($\delta^{18}O$) (‰ VSMOW) of the dissolved sulphate ($SO_4$). A few of them failed to give a result on $\delta^{34}S$ of aqueous sulphate due to their very low $SO_4$ concentrations. Trace element contents of the waters were also analysed using ICP-MS. Analyses of chemical and isotope compositions of the waters were carried out in the Institute of Geology and Geophysics, Chinese academy of Sciences in Beijing. The cations were analysed using ICP-MS. Ion chromatography and titration methods were used for the analysis of anions. Samples from oil production wells went through a filtration process to extract water from the mixture for analysis.

Aqueous sulphate was collected by precipitating from the water after acidification as $BaSO_4$. The precipitate was then reacted with carbon powder to produce $CO_2$ and CO, the later is then converted to $CO_2$ in catalytic process of hypothermal nickel metal, as described in Zhao, et al., 1995).

Water chemistry data from oil exploration wells were used as background data to work out the general trend in chemical variations of the thermal waters. Most of the chemical analyses include only major ions and salinity, few include complete chemistry.

## 4. RESULTS AND DISCUSSION

### 4.1 Chemical Characteristics of the Thermal Water in Different Formations

Except the wells producing from upper part of Nm for drinking water supply, thermal waters from Upper and Lower Tertiary are similar to oil filed waters, which have low sulphate concentration. It is also the case for waters from the Lower Palaeozoic aquifer if they are associated with an oil reservoir (Table 1).

As shown in the Piper diagram in Figure 2, Sodium is dominant as cation for all of the waters except for that in Palaeozoic (Ordovician), where it is Calcium. As for the anions, $HCO_3$ or $HCO_3$-$SO_4$ and $HCO_3$-Cl for the Upper Tertiary aquifers (Nm+Ng); for the lower Tertiary aquifers (Ed+Es), it is $HCO_3$, $HCO_3$-Cl and Cl-$HCO_3$. For Lower Palaeozoic (Ordovician) aquifer, it is $SO_4$.

Based on our data and referring to the exiting data from oil exploration, the chemical type of thermal waters from the Upper Tertiary aquifers changes with the rise of salinity and the increase of depth, from $HCO_3$-Na to $HCO_3$-Cl-Na, and further to Cl-Na, which is an evolution path towards maturation.

The Lower Palaeozoic (Om) limestone has a water type of Ca-$SO_4$.

Salinity of waters from the study area is relatively low as compared to that of waters from other areas of North China Basin. This is favourable for geothermal exploitation. The mean salinity of thermal water from the Lower Tertiary is around 3.5 g/l based on data of 128 wells in the area; the mean salinity of Upper Tertiary is 1.20 g/l based on data of 106 wells, which is agreeable to the sedimentological conclusion that these sediments were formed in fresh water lake environment.

Trace elements, such as Li, Sr and B are found higher in deeper formations on the average.

A comparison of temperatures calculated from chemical geothermometers with the measured formation temperature shows that the thermal waters are approaching Chalcedony equilibrium (Figure 3).

### 4.2 Stable Isotope Composition of the Thermal Waters

Local meteoric water line was established using GNIP (Global Network for Isotopes in Precipitation) station at Tianjin (IAEA, 1998), which has a record of five years. The annual mean values are -7.67 for $\delta^{18}O$, and -51.0 for $\delta$ D. The correlation between $\delta^{18}O$ and $\delta$ D is $\delta D=7.45\ (\pm 0.26)\ \delta^{18}O\ +6.60\ ((\pm 2.08)$, which is slightly different from the Global Meteoric Water Line (GMWL). For simplicity, in our discussion, the GMWL is used in the plot (Figure 4). In fact, the mean value of Tianjin is plotted on the GMWL.

The $\delta^{18}O$ versus $\delta$ D plot is also typical of formation waters in sedimentary basins (Table 2 and Figure 4) as has been discussed by Kharaka et al. (1983). The thermal waters are of meteoric origin, but they are enriched both in O-18 and Deuterium isotopes. Furthermore, the linear relationship between $\delta D$ and $\delta^{18}O$ tends to support a mixing relationship of E waters and N waters to produce the isotope composition of the Ng water such as the one for well L25x13. If all samples except those for Ed and the one for HC-1, the strata of which are not present in the Liuzhan area, the correlation between O-18 and Deuterium gives a possible mixing line of $\delta D = 0.5\ \delta^{18}O + 67.44$, in which n = 8, $r^2$ = 0.66 (Figure 4). The slop of this line is 0.5, which is too small for a reasonable evaporation line (usually between 3 and 7)

Interaction of the thermal waters with the surrounding rocks is evidenced in the depth profiles of isotopes. In the Tertiary aquifers, deuterium has very slight variation with depth, while oxygen-18 is enriched with the increase of depth (Figures 5 and 6), where depth can be considered an alternate for temperature. This implies that the interaction between water and rock is affected by temperature and that this has produced strong O-18 shift in the Tertiary aquifers. Due to low salinity, thermal water is leaching the rock matrix. This is one of the cases where Deuterium is least affected during this process.

Among the most direct evidences for the migration of formation waters from probably E aquifers to N aquifers to form the geothermal resources with very much pronounced thermal gradients. Other hints can be noticed from salinity of thermal waters, where it was found that thermal waters close to the fractures have higher salinity values, possibly due to the involvement of more saline waters from deeper aquifers.

The Tertiary water line intersects the GMWL at a point that is very different from the point for long-term annual mean of isotope composition in the precipitation of Tianjin station. This implies paleo recharge to the system. Another explanation is the recharge from a much higher altitude, which requires more investigations. Lower Paleo water sample has a much depleted deuterium concentration, implying recharge from higher altitude as compared to the Upper Tertiary aquifers. The relatively lower salinity also indicates a better hydraulic circulation condition than the sandstone aquifers that are rather stagnant.

### 4.3 Isotopes of Aqueous Sulphate in the Thermal Waters

Due to the low sulphate concentration of the thermal waters only 5 out of the 11 samples could be used for determining Oxygen-18 in aqueous sulphate (Table 2). It is though confirmed that the thermal waters from different aquifers are of non-marine origin (Figure 7). Isotope geothermometers based on Oxygen-18 in aqueous sulphate don't give acceptable temperature estimates comparable to the measured ones.

## 5. CONCLUDING REMARKS

A preliminary interpretation of results shows that the salinity of the thermal waters from Upper Tertiary and Lower Palaeozoic aquifers in the study area is low. The thermal waters have a meteoric origin and most probably have been recharged long time ago (without participation in modern hydrological cycle). The current isotope geochemistry investigation supports a conceptual genetic model for the Liuzhan geothermal system to be called "Low-Medium Temperature Convective Geothermal System" in sedimentary basins.

The characterics of the system can be summarised as follows (Figure 8):

(1) The heat source of the system is the terrestrial heat flow which is around 60 $mW/m^2$ (Chen, 1988);

(2) Thermal anomaly is partly caused by the re-distribution of heat due to the differences in thermal conductivity of the rocks from the Cenozoic sediments;

(3) Vertical thermal waters migration/exchange between hotter deeper formations, such as the Es aquifers (3500-4000m), with the shallower colder aquifers enhances the thermal anomaly and creates a geothermal gradient much higher than that of a normal geothermal system in the basin.

(4) The intersection of two major fractures provides high permeable conduit for the migration to take place. With low salinity and high thermal gradient (up to 7.5 °C/100m), thermal waters with temperatures of 100-120 °C at a depth between 1000 and 1500m, are the most favourable for exploitation in the North China Basin.

## ACKNOWLEDGEMENTS

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## REFERENCES

Chen M. (ed.), 1988, Geothermics of North China, Science Press, Beijing, 218 (In Chinese with an English abstract)

Chen, M., Wang J., Deng, X., 1994, Geothermal resources in China: genetic characteristics and potential assessment, Science Press, Beijing

Connolly, C., Walter, L., Baadsgaard, H.. and Longstaff, F., 1990, Origin evolution of formation waters, Alberta Basin, Western Canada Sedimentary Basin, II. Isotope systematics and water mixing, Applied Geochemistry, Vol. 5, 397-413.

Fouillac, C., Fouillac, A. And Criaud, A., 1990, Sulfur and oxygen isotopes of dissolved sulfur species in formation waters from the Dogger aquifer, Paris Basin, France, Applied Geochemistry, Vol. 5, 415-427.

Hitchon, B. and Friedman, I., 1969, Geochemistry and origin of formation waters in the western Canada sedimentary basin. I. Stable isotopes of oxygen and hydrogen, Geochimica et Cosmochimica Acta, 33, 1321-1349.

IAEA, 1998, GNIP (Global Network for Isotopes in Precipitation) data online release 2, at http://www.iaea.org/programs/ri/gnip/gnipmain.htm

Marty, B., Criaud, A., and Fouillac, C., 1988, Low enthalpy geothermal fluids from the Paris sedimentary basin, 1-Chanrateristic and origin of gasses, Geothermics, Vol. 17, 619-633.

Pang, Z. H., Wang, J. Y., Zhao, P. and Jin, J., 1995, Saline thermal waters from geothermal systems in the granite terrain (Zhangzhou geothermal system and surroundings, southeast of china), 1. Origin and recharge traced by oxygen and hydrogen isotopes, Geothm. Sci. & tech., 4(4), 273-286.

Pauwels H., Fouillac C. and Fouillac A. -M., 1993, Chemistry and isotopes of deep geothermal saline fluids in Upper Rhine Graben: Origin of compounds and water-rock interactions. Geochimica et Cosmochimica Acta 57, 2737-2749.

Wang J. (ed), 1996, Geothermics in China, Seismological Press, Beijing, 304.

Zhao R., Shen Y., Xie Y., Huo W., and Yao Y., 1995, An analytical method of oxygen and sulfur isotope composition of $BaSO_4$ and their practical application to geology research, Acta Petrologica Sinica, Vol. 11, no. 3, pp 320-324.

**Table 1 Chemical composition of thermal and non-thermal waters in Jidong area**

| Code | Name | Form. | $PH_L$ | $SiO_2$ | Na | K | Ca | Mg | $HCO_3$ | $CO_3$ | $SO_4$ | Cl | B | Li | Sr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Qy-1 | $Nm^u$ | 7.85 | 16.92 | 237.59 | 0.42 | 7.12 | 1.24 | 364.17 | 11.23 | 120.05 | 81.54 | 2.5020 | 0.0149 | 0.0857 |
| 2 | Tn-2 | $Nm^u$ | 7.82 | 17.46 | 144.90 | 0.25 | 6.10 | 0.62 | 239.12 | 8.98 | 85.44 | 28.83 | 0.0000 | 0.0074 | 0.0973 |
| 3 | Xg-3 | $Nm^u$ | 7.27 | 15.21 | 109.42 | 0.25 | 5.70 | 0.25 | 204.96 | 0.00 | 66.90 | 19.60 | 0.0966 | 0.0054 | 0.0817 |
| 4 | L21x10 | $Nm^l$ | 8.30 | 54.01 | 338.28 | 3.98 | 3.05 | 1.61 | 510.57 | 45.00 | 6.69 | 196.01 | 0.3789 | 0.0425 | 0.0240 |
| 5 | L25x13 | Ng | 8.27 | 51.70 | 366.47 | 4.73 | 3.05 | 0.99 | 630.13 | 56.16 | 4.83 | 163.73 | 1.8880 | 0.0784 | 0.1064 |
| 6 | N34x1 | Ng | 7.44 | 29.49 | 252.22 | 3.74 | 20.95 | 2.10 | 183.00 | 0.00 | 336.23 | 92.24 | 0.2662 | 0.0603 | 0.5754 |
| 7 | M2-3 | Ed | 8.22 | 50.92 | 441.60 | 7.97 | 8.14 | 1.85 | 593.84 | 55.55 | 0.00 | 325.15 | 6.5820 | 0.6185 | 1.3530 |
| 8 | M16x1 | Ed | 8.36 | 71.37 | 1288.96 | 17.93 | 11.80 | 2.72 | 2771.23 | 67.40 | 0.00 | 345.90 | 6.5820 | 0.6185 | 1.3530 |
| 9 | L20x2 | Es | 7.27 | 113.81 | 515.59 | 17.93 | 71.19 | 20.02 | 548.16 | 0.00 | 171.38 | 547.68 | 12.2400 | 1.1700 | 2.1990 |
| 10 | L90x2 | Es | 8.23 | 78.32 | 382.05 | 7.72 | 7.12 | 3.09 | 628.10 | 33.70 | 114.84 | 149.89 | 4.9380 | 0.2818 | 0.3642 |
| 11 | Hc-1 | O | 7.08 | 83.05 | 245.55 | 112.07 | 220.69 | 19.16 | 296.92 | 0.00 | 809.73 | 140.67 | 2.9010 | 3.8270 | 8.0520 |

**Table 2 Isotope composition of thermal and Non-thermal waters**

| Code | Name | Form. | Depth (m) | $\delta^{18}O$ (‰VSMOW) | $\delta^2H$ (‰ V SMOW) | $\delta^{18}O(SO_4)$ (‰ VSMOW) | $\delta^{34}S(SO_4)$ (‰ CDT) |
|---|---|---|---|---|---|---|---|
| 1 | Qy-1 | $Nm^u$ | 350 | -9.63 | -71.30 | 10.8 | 27.38 |
| 2 | Tn-2 | $Nm^u$ | 383 | -9.56 | -73.60 | | |
| 3 | Xg-3 | $Nm^u$ | 500 | -9.57 | -71.10 | | |
| 4 | L21x10 | $Nm^l$ | 1816 | -8.29 | -71.40 | | |
| 5 | L25x13 | Ng | 1994 | -8.01 | -72.20 | | |
| 6 | N34x1 | Ng | 1128 | -9.37 | -74.60 | 10.6 | 19.92 |
| 7 | M2-3 | Ed | 2700 | -8.21 | -76.60 | | |
| 8 | M16x1 | Ed | 2872 | -5.44 | -66.60 | | |
| 9 | L20x3 | Es | 3400 | -4.60 | -69.90 | 7.3 | 11.1 |
| 10 | L90x2 | Es | 3057 | -6.04 | -70.80 | 10.2 | 14.59 |
| 11 | Hc-1 | O | 3075 | -9.28 | -82.30 | 9.3 | 24.79 |

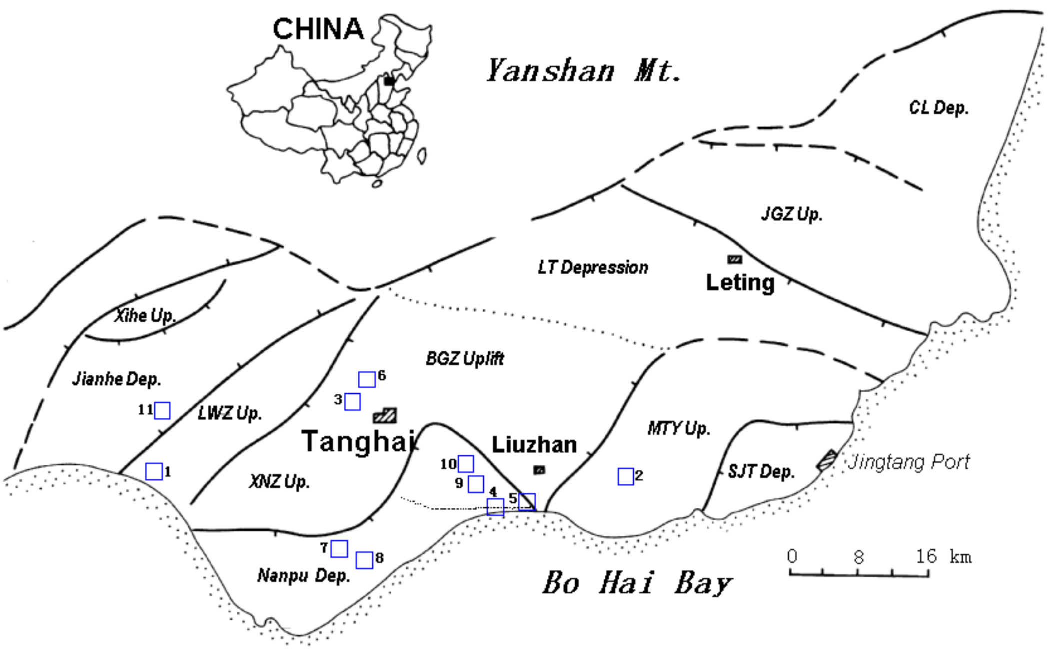


Figure 1. Location of the study area and sampling sites.

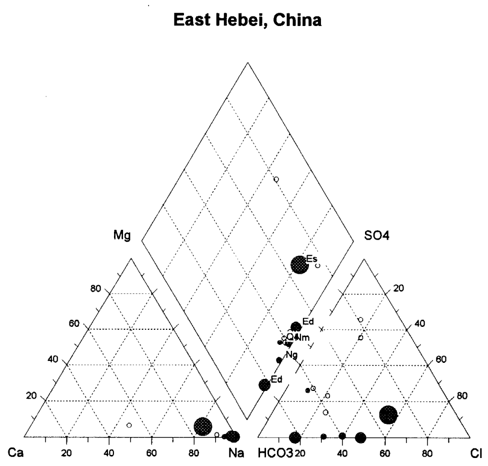


Figure 2. Piper diagram of 11 samples showing the chemical type of the thermal and non-thermal waters.

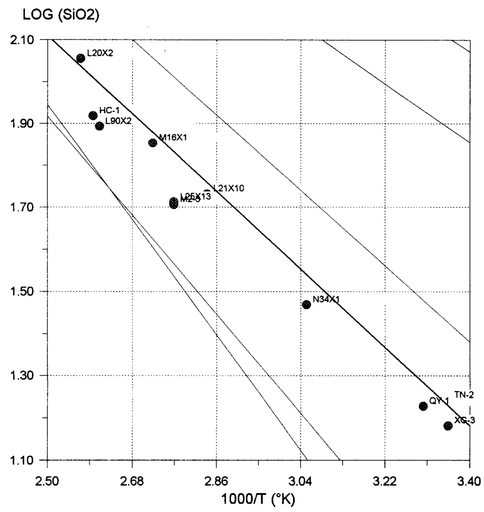


Figure 3. Comparison of silica geothermometer temperatures with measured values

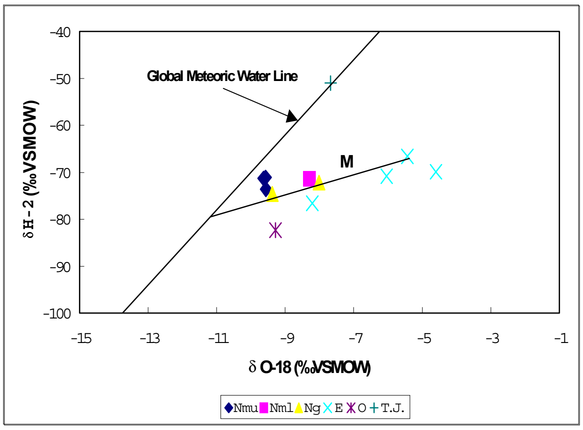


Figure 4. Isotope composition of thermal and non-thermal waters

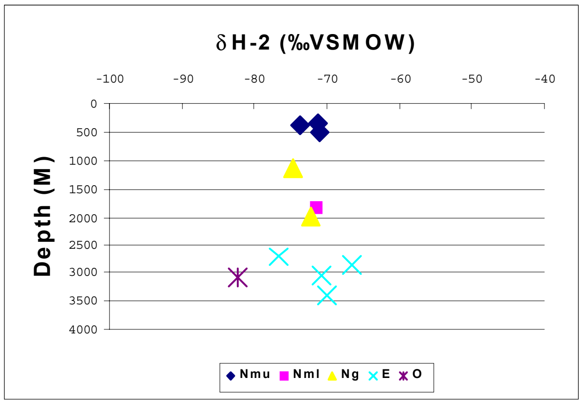


Figure 5 Depth profile of Deuterium

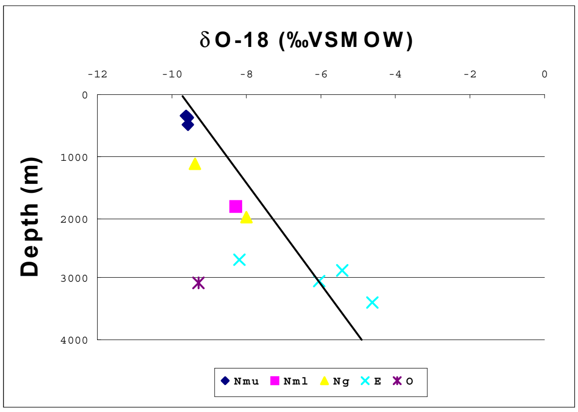


Figure 6 Depth profile of Oxygen-18

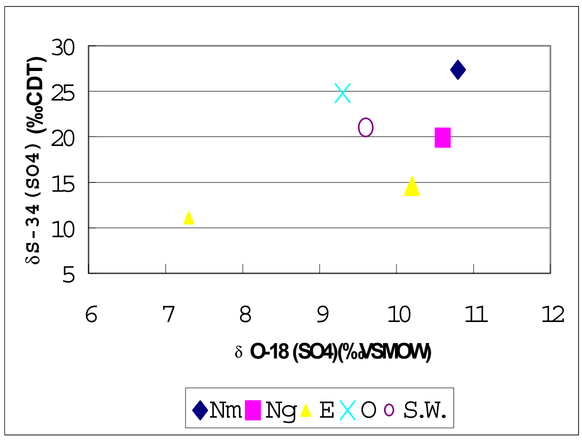


Figure 7 Isotopes in aqueous sulphate of thermal and non-thermal waters

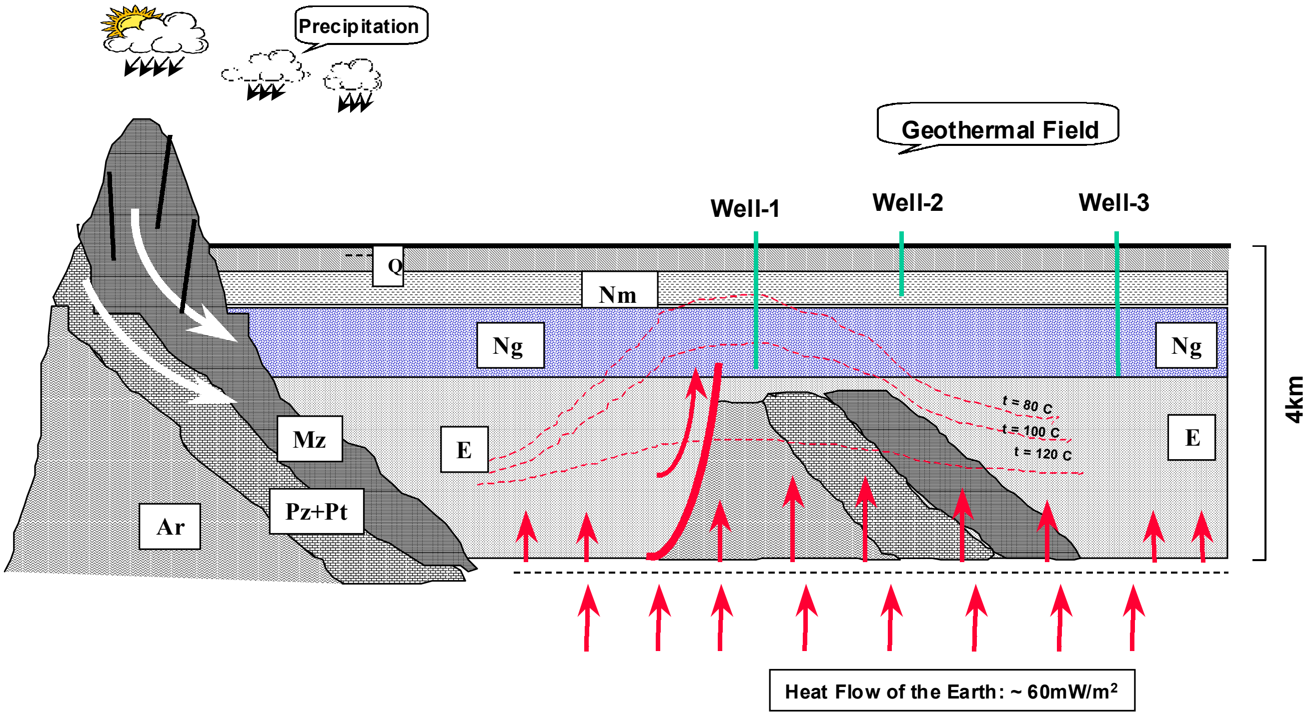


Figure 8 A conceptual model for the genesis of Low-Medium Temperature Convective Geothermal System in sedimentary basins