

# Isotope and chemical geothermometry and its applications

PANG Zhonghe (庞忠和)

Isotope Hydrology Section, International Atomic Energy Agency, Vienna, Austria

Corresponding address: z.pang@ieae.org

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**Abstract** The Na-K-Mg Geoinicator created by Giggenbach (1988) is convenient to use but it is still based on the empirical geothermometry equations and discrepancy for different cation geothermometers is observed. In fact, the location of the curve of "full equilibrium" is different if a different Na-K geothermometry equation is used. The difference is pronounced for temperatures lower than about 220°C. A case study on the Zhangzhou geothermal field of SE China resulted in a reliable estimate of reservoir temperature of 150°C by the SO<sub>4</sub>-H<sub>2</sub>O pair Oxygen-18 isotope geothermometer. This has provided an example of attained equilibrium of the marine sulphate in the geothermal system in the low-medium temperature range (<150°C). A recent refinement of the theoretical geothermometry was achieved by the FixAl method, which provides the possibility to identify and solve problems such as an erroneous analytical value of Aluminium, and influence of processes such as mixing and degassing, and therefore makes it possible to reconstruct most of the "lost equilibrium" in geothermal systems.

**Keywords:** isotope, geothermometry, geothermal resources, Zhangzhou, China.

## 1 Introduction

Chemical and isotopic geothermometers are equations or models based on temperature-dependent chemical reactions or isotope equilibrium fractionation relations from which equilibrium temperatures of these reactions can be calculated.

Conventional chemical geothermometers based on solutes (Silica Geothermometers, Cation Geothermometers) and gases (Gas Geothermometers) as well as on the atoms in water molecules and dissolved substances (Isotope Geothermometers) in geothermal discharges have been used in the last three decades to predict the temperature at depth of geothermal systems (reservoir temperature), which is a key parameter in geothermal resources assessment. The major drawback of all the conventional geothermometry methods lies in their incapability in making a judgement on the equilibrium status of the studied systems. In this review emphasis is laid on two recent approaches in this field. The use of isotope geothermometers in the low-medium temperature range (<150°C) is discussed, with the oxygen geothermometer based or the sulphate-water pair as an example.

Zhangzhou geothermal field is located in a Quaternary fault basin with a Mesozoic granite basement<sup>[1]</sup>. The deeply circulating thermal water has a temperature of 114°C at the wellhead and 122°C at a depth of 90 m. The water is highly saline: 12g/L of total dissolved solids and 6g/L of

$\text{Cl}^-$ .  $\text{SO}_4$  is mainly of marine origin. The reservoir temperature of this system has been estimated using the different methodologies including the  $\text{SO}_4\text{H}_2\text{O}$  pair, the geoinicator as well as the FixAl method<sup>[2]</sup>. It has been used as an example to demonstrate the techniques.

## 2 Na-K-Mg Geoinicator

The combination of Na-K and Mg-K geothermometer equations allows the construction of Na-K-Mg ternary diagram or the so-called Na-K-Mg Geoinicator created by Giggenbach<sup>[3]</sup>, which provides the possibility in distinguishing equilibrium status in the geothermal systems by the Na-K-Mg inter-relations. The advantage of this diagram is remarkable. It allows the effect of Mg on the Na-K geothermometers to be assessed more easily and the unique graphical presentation of geothermometry results makes it convenient to compare different samples and to identify possible mixing relations among them. However, the method is still based on the empirical geothermometry equations and discrepancy for different cation geothermometers still exists. In fact, the location of the curve of equilibrium” is different if a different Na-K geothermometry equation is used. The difference is pronounced for temperatures lower than about 220°C (Fig. 1).

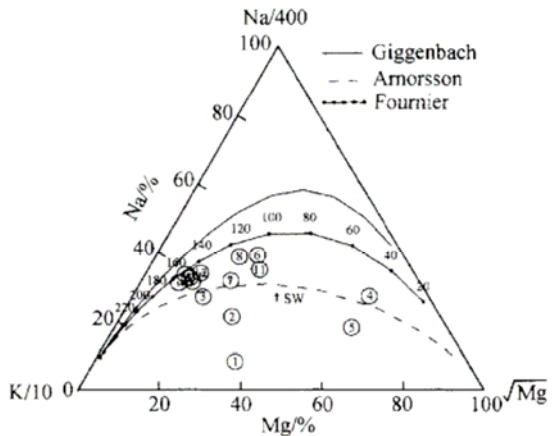


Fig. 1. Na-K-Mg Geoinicator with samples from Zhangzhou geothermal field plotted. The three different curves for equilibrium” are based on Na-K geothermometry equations by the indicated respective authors<sup>[4]</sup>.

Equilibrium situation is indicated and maximum reservoir temperature of about 150°C is obtained based on the geothermometry equation by Fournier<sup>[5]</sup>, partial equilibrium by Giggenbach<sup>[3]</sup>, and super-saturation by Arnorsson<sup>[6]</sup>.

## 3 Sulphate-water oxygen isotope geothermometer in low to medium temperature environment

The usefulness of this isotope geothermometer for water-dominated geothermal fields is well proven. Two equations by Lloyd<sup>[7]</sup> and Mizutani et al.<sup>[8]</sup> are valid for the temperature range of 0 to 300. The results differ by about 10. The corresponding isotopic-exchange reaction rate is inversely proportional to the pH. Under neutral conditions the time required to reach 90% isotopic equilibrium is 500 and 2 years at 100 and 300, respectively. Residence times of water in most geothermal reservoirs are larger.

The drawback of this geothermometer is that mixing with sulphate bearing, shallow groundwater oxidation of  $\text{H}_2\text{S}$  by atmospheric  $\text{O}_2$  and evaporation may modify the isotopic composition of the dissolved sulphate. In these cases the isotopic signature does no longer reflect that of the

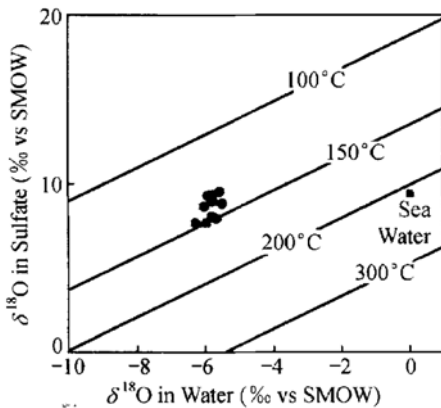


Fig. 2. Oxygen isotope geothermometer based on the  $\text{SO}_4\text{-H}_2\text{O}$  pair. Filled circles are samples of geothermal water from Zhangzhou geothermal field, China. The iso-temperature lines are based in refs. [7, 11].

deep geothermal sulphate.

The usefulness of the geothermometer in low-medium temperature environment (<200, for example) has not been thoroughly tested and verified as shown in the literature<sup>[9]</sup>.

In the case of Zhangzhou geothermal field, the reservoir temperature of 150°C was confirmed by the  $\text{SO}_4\text{-H}_2\text{O}$  pair oxygen-18 geothermometer (Fig. 2), which provides an example of attained equilibrium between marine sulphate and the granitic reservoir rock in the low-medium temperature range.

#### 4 Whole-system chemical geothermometry

The geothermometry method first proposed by Reed et al.<sup>[10]</sup> is referred to as theoretical chemical geothermometry or whole system chemical geothermometry. The theoretical basis of this geothermometry method is chemical thermodynamic calculations of multi-component equilibria involving mineral, water and gas phases. The result of the thermodynamic calculations allows:

- To evaluate the equilibrium status of the system;
- To obtain equilibrium temperature if an equilibrium for a mineral assemblage does exist;
- To acquire information as to whether a dilution or degassing process has taken place.

Aside from the conventional geothermometers, this method for the first time provided the possibility to judge the equilibrium status of the studied systems before making a temperature estimate.

However, this geothermometry method with sound theoretical basis did not receive immediate wide application due to the fact that in reality there exist many factors that would blanket the equilibrium fingerprint.

A recent refinement of the theoretical geothermometry was achieved by the FixAl method<sup>[2]</sup>, which provides the possibility to identify and solve problems such as an erroneous analytical value of Aluminium, and influence of processes such as dilution and degassing, and therefore makes it possible to reconstruct most of the system equilibrium.

Errors in Al analyses impose strong effect on theoretical chemical geothermometry based on multi-component chemical equilibrium calculations of mineral equilibria. The FixAl method employs a modified  $Q/K$  graph to eliminate problems with water analyses lacking Al or with erroneous analyses of Al. This is made possible by forcing the water to be at equilibrium with a selected Al-bearing mineral, such as microcline. In a FixAl graph, a modified  $Q/K$  value is plotted against temperature for Al-bearing minerals. Saturation indices of non-aluminous minerals are plotted in the same way as in an ordinary  $Q/K$  graph (Fig. 3).

In addition to Al concentration errors, degassing of  $\text{CO}_2$ , and dilution of reservoir water interfere with computed equilibrium geothermometry. These effects can be distinguished in a  $Q/K$  graph by comparing curves for non-aluminous minerals to those of aluminous minerals then correcting for  $\text{CO}_2$ , loss and dilution by a trial and error method.

Geothermal waters from China, Iceland, and the USA that are used to demonstrate the methods show that errors in Al concentrations are common, and some are severe. The FixAl approach has proved useful for chemical geothermometry for geothermal waters lacking Al analysis and for waters with an incorrect Al analysis. The equilibrium temperatures estimated by the FixAl approach agree well with

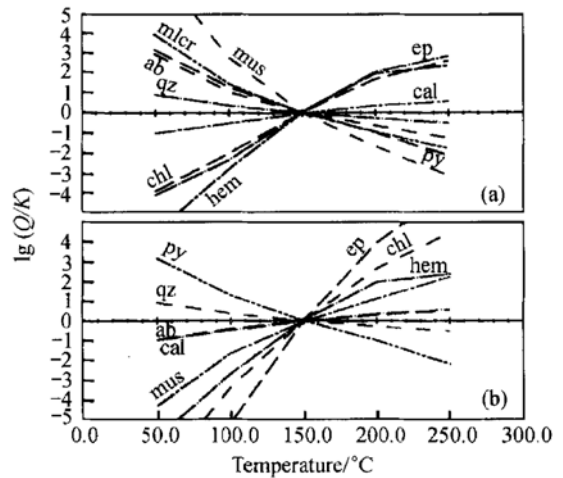


Fig. 3. A comparison of a normal  $\lg(Q/K)$  graph (a) with a FixAl graph (b), where the Aluminium-bearing minerals show different curves while non-Aluminium minerals remain unchanged. The equilibrium temperature indicated by the convergence of curves is the same<sup>[2]</sup>.

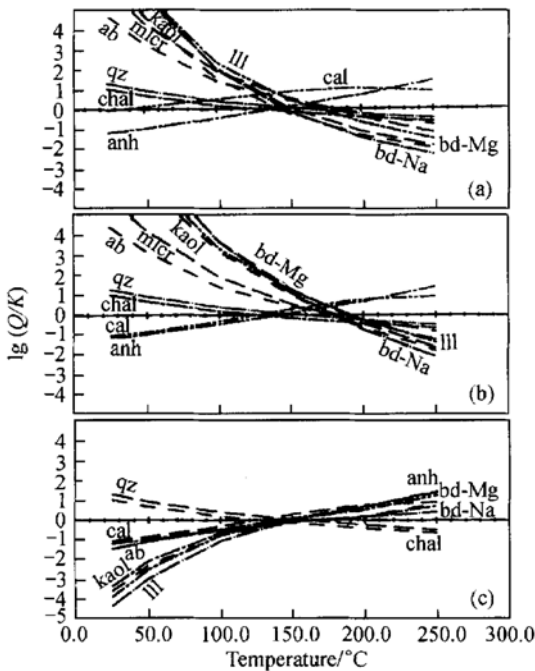


Fig. 4. FixAl result of a geothermal water sample from Zhangzhou geothermal field, China showing (a) original  $\lg(Q/K)$  graph; (b) the same graph but with 100%  $\text{CO}_2$  added back; (c) FixAl graph showing the reconstructed equilibrium at  $150^\circ\text{C}$ <sup>[2]</sup>.

quartz, or chalcedony, and isotopic geothermometers. Fig. 4 is the example of Zhangzhou geothermal system, which shows the reconstructed equilibrium after both effects of Al and  $\text{CO}_2$  are removed.

The best choice of mineral for forced equilibrium depends on pH. For most neutral pH waters, microcline and albite work well; for more acidic waters, kaolinite or illite are good choices. Measured pH plays a critical role in computed equilibria, and we find that the best pH to use is the one to which the reported carbonate also applies. Commonly this is the laboratory pH instead of field pH, but the field pH is still necessary to constrain  $\text{CO}_2$  degassing.

## 5 Future perspective

The use of chemical or isotopic composition of geothermal fluids (water & gas) to estimate subsurface temperature (reservoir temperature) is a routine practice in any geothermal

project. The development and application of chemical and isotopic geothermometers have evolved from empirically calibrated equations based on individual components or minerals (gases) to the modelling of the equilibrium scenario of the whole water-gas-mineral geochemical interaction system in the geothermal environment as briefly discussed in this review. Furthermore, as isotopes are being incorporated into the chemical reaction models<sup>[12]</sup>, it can be expected that isotopic geothermometry methods based on an integrated whole system isotope equilibrium approach will be available in the future for geothermal investigations, which will not rely merely on individual isotope exchange relations.

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