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APPLICATION OF GEOCHEMISTRY IN GEOTHERMAL RESOURCE ASSESSMENTS

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ABSTRACT

The most important contribution of geochemistry to geothermal resource assessments is chemical geothermometery. Geothermometry is the application of geochemistry to infer reservoir temperatures from the composition of geothermal fluids. Geothermal fluids that can be found at the surface above geothermal systems include steam, boiled or cooled geothermal solutions, mixed waters, and steam heated surface waters. The concentration of many dissolved constituents of geothermal solutions is controlled by temperature sensitive equlibria and the chemical signature of the fluids can survive transport to the surface. Different kinds of chemical geothermometers have been developed for steam, geothermal solutions, and mixed waters but the steam heated water cannot provide any information on reservoir temperatures.

1. INTRODUCTION

Geothermal systems are like snowflakes in that sense that no two systems are exactly identical. As a result, geothermal utilization does always require a substantial amount of technical investigative work before it can be implemented. Furthermore, monitoring during the production phase is needed in order to observe potential changes in the system with the aim to prevent or at least minimize adverse effects, such as inflow of colder water, scaling, corrosion etc. Geochemistry is among the most important technical disciplines used for such investigations, both before utilization as well as during the production phase. In this publication we focus on the application of geochemical studies for geothermal resource assessments.

Geochemical observations are particularly important for geothermal resource assessment in the early stages of exploration. Prior to drilling, chemical geothermometers may provide the only information on potential reservoir temperatures. Similarly, geochemical studies may also be important to delineate the areal extent of the geothermal system prior to resistivity surveys. Even after resistivity surveys have been carried out geochemical data can still provide important supporting evidence to claims as to the extent of the reservoir made based on the results of the resistivity surveys.

Below we describe the different types of fluids that can be encountered in geothermal areas. Then we discuss how the chemical composition of the different fluids can be used to predict reservoir temperatures.

2. TYPES OF GEOTHERMAL FLUIDS

Geothermal systems consist of hot rocks and fluids that occupy the porosity of the rocks. The primary fluids in the undisturbed reservoirs can be liquid (liquid dominated systems), liquid with small amount of steam (boiling geothermal systems) and steam with a small amount of liquid (vapor dominated systems). The primary geothermal fluids of high temperature geothermal systems can generally not be obtained from natural geothermal manifestations at the surface (with the exception of submarine geothermal systems). The fluids available for surface geochemical investigations have all been affected by various processes such as boiling and phase separation, cooling, oxidation, and mixing and are referred to as secondary fluids (Arnórsson et al., 2007). Secondary geothermal fluids are the material that the geochemist has to work with during surface exploration. The main categories of secondary geothermal fluids that can be encountered at the surface of geothermal systems are:

1) geothermal steam
2) boiled (and in some cases cooled) geothermal solutions
3) mixed solutions involving shallow groundwaters and geothermal solutions (boiled or unboiled) or steam
4) steam heated surface waters

Of these fluid types the geothermal steam and the boiled geothermal fluids can give the most useful information on the reservoir temperature. Mixed solutions may under favorable conditions be used to determine the reservoir temperature. Steam heated surface waters; on the other hand, cannot be used for this purpose (D'Amore and Arnórsson, 2000a).

2.1 Geothermal steam

Geothermal steam vents (sometimes referred to as fumaroles) are among the most common surface manifestations of high enthalpy geothermal systems although some geothermal systems do not have any steam vent activity. If the steam vents are reasonably powerful they are easily identified from a distance by the rising steam and they are also easily identified by the characteristic (rotten egg) odor of H_2S, which is generally among the most abundant gases in geothermal steam. Steam vent activity is the characteristic feature where the water table of the geothermal water does not reach the surface.

2.2 Boiled or cooled geothermal solutions

Boiled or cooled geothermal solutions, on the other hand, are found where the hot water table does reach the surface. Hot springs are not as quite as common as steam vents in high temperature geothermal systems but they occur in many of the geothermal systems in Central-America that are associated with andesitic volcanoes, e.g. Amatitlán in Guatemala and Ahuachapan and Berlín in El Salvador (D'Amore and Arnórsson, 2000a). In these systems the hot springs occur at lower elevations in the flanks of the volcanoes, whereas the steam vent activity is more extensive at higher elevations. Boiled geothermal solutions do also reach the surface in many other systems, such as in Yellowstone in USA and in the Geysir area in Iceland. Hot springs with boiled geothermal solutions typically have a neutral to alkaline pH, and low dissolved gas content. On the other hand, hot springs that effuse geothermal solutions that have cooled by conduction on the way to the surface generally have a lower pH because they have not lost their dissolved CO_2 and H_2S. Hot springs in high temperature systems are commonly characterized by spectacular silica sinter deposits and carbonate deposits.

2.3 mixed solutions

Various different subcategories of mixed solutions can be found in and around geothermal areas. CO_2-rich waters can form where gas rich steam condenses in shallow aquifers. Similarly, CO_2-rich waters can form when unboiled (and undegassed) geothermal solutions mix with cold groundwater. Mixtures of boiled geothermal solutions and ground waters result in mixtures with a low gas content

but temperatures and concentrations of non-volatile components that are intermediate between those of the groundwater and the geothermal solutions. CO_2-rich waters are commonly found on the boundaries of active volcanic geothermal systems (see Arnórsson et al., 2007 and references therein) and around volcanoes (e.g. Aiuppa et al., 2003). Very high concentrations of CO_2 are sometimes observed the reservoir fluids in old and cooling geothermal systems (e.g., Haedarendi and Leirá, Iceland). Other types of "mixed solutions" are found in and around geothermal areas where the groundwater table is high. The mixed solutions tend to be most common on the peripheries of geothermal systems where there are steep temperature and chemical gradients between the geothermal system and the adjacent groundwater systems.

2.4 Steam heated surface waters

Steam heated surface waters are characterized by pH values as low as <1. This is because of oxidation of H_2S when steam reacts with oxygenated surface waters. This oxidation results in the formation sulfuric acid. Steam heated surface waters are typically found in mud pools and seeps around steam vent fields. These waters can contain a significant amount of dissolved solids but the solids are derived from dissolution of surface rock and therefore do not have any "memories" of the conditions in the geothermal system. The process of formation of sulfuric acid by oxidation of hydrogen sulfide in the surface environment of steam vent fields is responsible for the intense alteration commonly associated with steam vents and steaming ground in high temperature geothermal fields.

The four main categories of geothermal fluids that can be found in and around geothermal areas have different levels of utility for geothermal resource assessment studies. The geothermal steam and the geothermal solutions are most important for evaluating reservoir temperatures, whereas the mixed fluids can, under favorable conditions, provide important information on the temperature as well. The steam heated surface waters contain no information on the reservoir temperature but the intense alteration that is associated with these solutions provides an important, visible geothermal manifestation that can help delineate the structure of the geothermal system. Similarly, the presence of CO_2-rich springs may indicate the peripheries of the system and thus help constrain the areal extent of the system. Such information is particularly important in the initial phases of exploration before geothermal resistivity surveys have been carried out. However, as the most important contributions of geochemistry to geothermal resource assessment studies are constraints on the reservoir temperature, the remainder of this publication will focus on this aspect, i.e. the application of chemical geothermometers.

3. CHEMICAL GEOTHERMOMETRY

3.1 Assumptions

Chemical geothermometry, in the context of geothermal studies, refers to the use of chemistry to evaluate the temperature in geothermal reservoirs. The composition of geothermal solutions is commonly, to a large extent, controlled by local and partial chemical equilibria between the fluid and the host rock. These chemical equilibria are in many cases temperature-sensitive, i.e. the composition of the fluid is a function of the temperature in the system. Chemical geothermometry makes use of this by inferring subsurface temperatures from observed fluid compositions.

One of the fundamental assumptions in the use of chemical geothermometers is that a partial chemical equilibrium is attained in the geothermal reservoir. Dissolved chemical components in geothermal solutions are referred to as either *conservative components* or *rock-forming components*. The conservative components, such as Cl⁻, are generally not controlled by water-rock equilibria but their concentration is determined by their initial concentration in the source fluid (or fluids) or dissolution from the rock. The concentrations (or more correctly the activities) of the reactive components are, on the other hand, controlled by equilibria between the fluid and secondary minerals in the rock that are in contact with it. Most of the major and minor elements dissolved in geothermal solutions are

considered reactive components.   However, under some circumstances the assumption of partial equilibrium does not hold for some of the dissolved components.   Dissolved silica, for example, is almost universally controlled by equilibrium with quartz in most geothermal systems with the exception of young basalt hosted geothermal systems at temperatures below ~180 °C in which the silica is controlled by the solubility of chalcedony, a metastable silica polymorph (Arnórsson, 1975; Stefánsson and Arnórsson, 2000, Gíslason et al. 1997).   Similarly, dissolved CO_2 is generally considered a reactive component, but in some volcanic geothermal systems the rate of CO_2 influx from magma may, at least periodically, exceed the capacity of the secondary mineral assemblages to incorporate the CO_2.   During such periods of high magmatic gas influx, the concentration of CO_2 is controlled by the flux of gas from magma; not by chemical equilibria between the fluid and the rocks. Under such conditions CO_2 can not be considered a reactive component and the application of CO_2-geothermometers will give erroneous results. Considering that dissolved silica and CO_2 are involved in the most common chemical geothermometers is should be clear from these examples that caution must be exercised in the application of chemical geothermometers.

Another fundamental assumption is that the composition of the different geothermal fluids has not been affected by secondary processes, other than boiling, on the way to the surface.   While this assumption holds true in some cases it is by no means a law of nature.   Steam may be affected by condensation on the way to the surface, a process that increases the concentration of all the gases in the steam.   Similarly, geothermal solutions that boil and/or cool on the way to the surface may react to re-equilibrate with the rock under the changing temperature conditions.   There is, fortunately, a fair number of chemical geothermometers that are affected in different ways by such secondary changes. Consequently, it is very important to use as many geothermometers as possible for any given fluid sample, be it of steam or liquid, as the discrepancy between the results of the different geothermometers may be indicative of the secondary processes affecting the fluid (D'Amore and Arnórsson, 2000).

3.2 Chemical geothermometers

A brief discussion is given below on some of the most commonly used chemical geothermometers. This publication does not attempt to present an exhaustive literature review of this issue but rather present some examples that will be used in practical exercises during the short-course.   Isotope geothermometers will, for instance, not be discussed in this publication.   For thorough literature reviews of chemical geothermometry the readers are referred to Zhao-Ping and Ármannsson (1996), D'Amore and Arnórsson (2000b), and Zheng-Xilai et al. (2002).   The readers are also referred to Arnórsson (2000) for discussion of mixing models.

3.2.1 Univariant geothermometers

Chemical geothermometers can be univariant, i.e. based on the concentration of one reactive constituent (gas or aqueous species) or based on ratios of reactive components.   The most widely used univariant geothermometer is probably the silica geothermometer and univariant gas geothermometers (using the concentrations of CO_2, H_2, and H_2S) are also commonly used.   Several calibrations are available for these geothermometers.   The most widely used silica geothermometers are based on equilibrium between quartz and the geothermal solution but geothermometers for other silica polymorphs (most importantly for chalcedony) have also been published.   The quartz geothermometer of Fournier and Potter (1982) for boiled springs is given in Table 1 below.

TABLE 1: Selected geothermometers

Thermometer	
Quartz[a]	$T(°C) = -53.5 + 0.11236S - 0.5559*10^{-4}S^2 + 0.1772*10^{-7}S^3 + 88.39*\log S$
Na/K[b]	$T(°C) = \dfrac{1217}{1.438 + \log(Na/K)} - 273.15$
CO_2[c]	$T(°C) = \dfrac{\log(CO_2) + 3.28 + 1.5\log(a_{pre}) - \log(a_{czo})}{0.0097}$
H_2S[c]	$T(°C) = \dfrac{\log(H_2S) + 6.853 + \frac{2}{3}\log(a_{epi}) - \frac{2}{3}\log(a_{pre})}{0.01343}$
H_2[c]	$T(°C) = \dfrac{\log(H_2) + 4.686 + \frac{2}{3}\log(a_{epi}) - \frac{2}{3}\log(a_{pre})}{0.007962}$

a: Fournier and Potter (1982); S = concentration of SiO_2 in mg/kg; applies to solutions boiled to 100 °C; shown as reported by D'Amore and Arnórsson (2000).
b: Fournier (1979); Na and K refer to concentrations in mg/kg; shown as reported by D'Amore and Arnórsson (2000).
*c: Arnórsson et al. (2007); CO_2, H_2S, and H_2 refer to concentrations in steam in mmole/kg steam; a_{epi} and a_{czo} refer to the activities of the endmembers of the epidote solid solution ($Ca_2FeAl_2Si_3O_{10}(OH)$ and $Ca_2Al_3Si_3O_{10}(OH)$) and a_{pre} refers to the activity of prehnite.*

The univariant gas geothermometers are more complicated as several possible assemblages of secondary minerals can be identified at potential buffers of the gas concentrations. Arnórsson et al. (2007), for instance propose two possible mineral assemblages for controlling CO_2 concentrations in geothermal fluids and four different assemblages as buffers for the concentration of H_2 and H_2S in geothermal solutions. Predictions of reservoir temperature based on the different mineral assemblages do, fortunately, agree fairly well with each other so the choice of reaction does not greatly affect the predicted temperature. Three of the gas geothermometers reported by Arnórsson et al. (2007) for CO_2, H_2S, and H_2, based on the assumption of equilibrium with quartz, epidote, prehnite, and calcite in the case of CO_2 and pyrite and pyrrhotite in the case of H_2S and H_2 are listed in Table 1.

Simplicity is a benefit of the univariant geothermometers but they are also susceptible to secondary processes such as dilution and condensation. Errors due to condensation on univariant gas geothermometers can be prevented by using ratios of the reactive gases to conservative gas species such as Ar or N_2. In such cases the concentration of the conservative gas species is taken to be equal to that of air-saturated water.

3.2.2 Geothermometers based on ratios

The most commonly used geothermometer that utilizes cation ratios is the Na/K geothermometer. Several calibrations have been published, both empirical and theoretical. The Na/K geothermometer of Fournier (1979) is shown in Table 1. It is commonly assumed that the Na/K ratio in geothermal solutions is constrained by simultaneous equilibria between the geothermal solution and Na- and K-feldspar, described by the reaction:
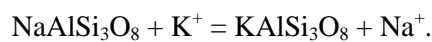
$NaAlSi_3O_8 + K^+ = KAlSi_3O_8 + Na^+$.
However, it has also been postulated that the Na/K ratio may in some geothermal systems just as well be controlled by ion-exchange equilibrium between Na- and K-clay minerals. Cation ratio geothermometers have been calibrated and published for other cation pairs such as K/Mg, Na/Ca, K/Ca, Na/Li and Li/Mg (see D'Amore and Arnórsson, 2000b, for discussion). A characteristic feature of the Na/K thermometer is that it seems to equilibrate slowly, which can be both an advantage and a disadvantage. For example, a discrepancy between the temperatures predicted by the Na/K

geothermometer and other, more rapidly equilibrated thermometers, such as the quartz thermometer, the discrepancy can be indicative of the cooling or heating history of the geothermal fluid.

The Na/K/Ca geothermometer proposed by Fournier and Truesdell (1973) uses both the Na/K and the Na/Ca$^{0.5}$ ratios to predict reservoir temperature. It has been used successfully on many occasions and it has been found to give reliable results at low temperatures, at which the Na/K geothermometers have a tendency to give erroneously high results (D'Amore and Arnórsson, 2000b). Giggenbach (1988) proposed a graphical method involving the simultaneous use of a Na/K and K/Mg$^{0.5}$ ratio geothermometers. The advantage of this method is that it gives both an estimate of the reservoir temperature and indicates the "maturity" of the geothermal solution by combining the results of the fast equilibrating K/Mg$^{0.5}$ geothermometer and the slow Na/K geothermometer. An example of a Na-K-Mg ternary diagram is shown on Figure 1.
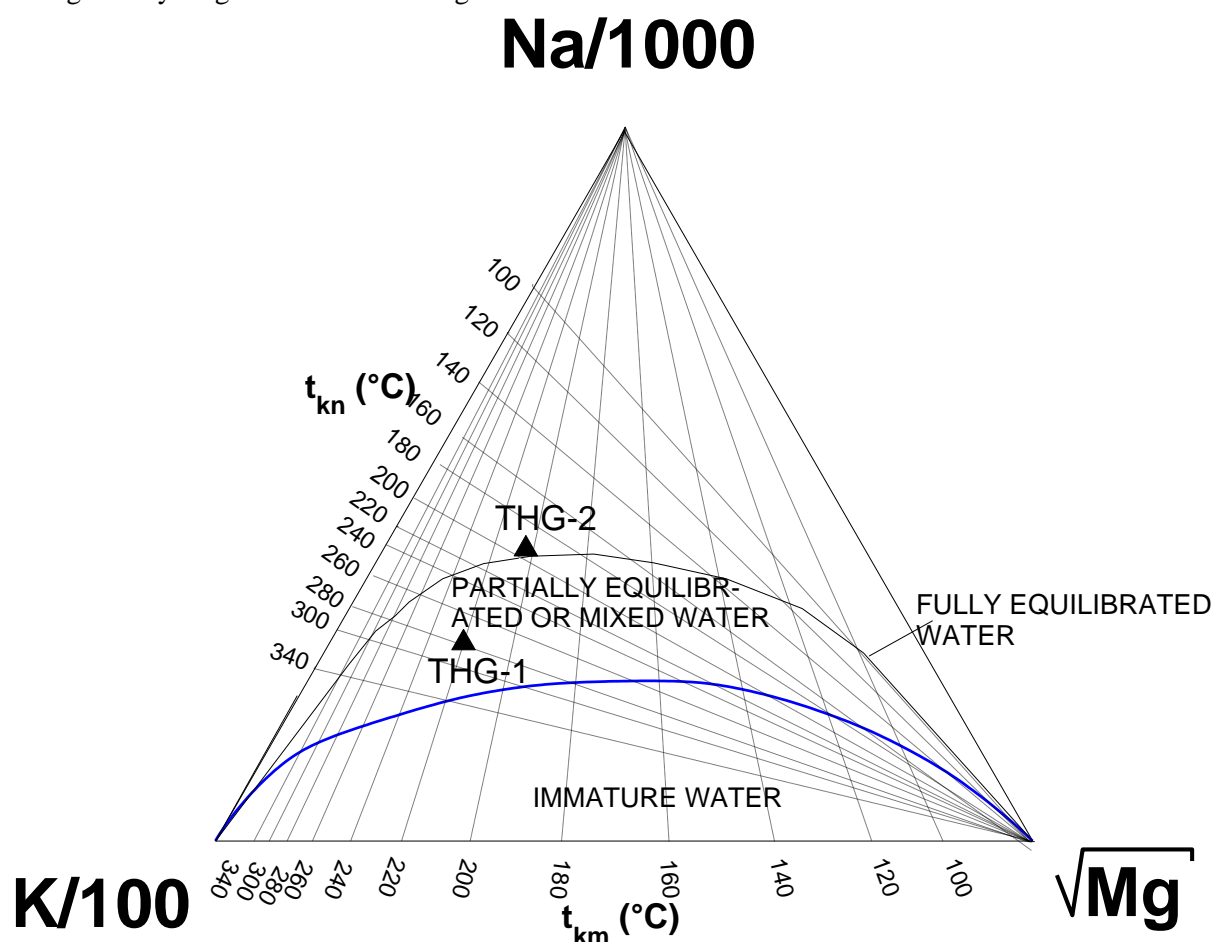

FIGURE 1: Na-K-Mg ternary diagram showing the temperature and "maturity" of two geothermal solutions from Theistareykir, NE-Iceland. The sample labeled ThG-1 is only partially equilibrated, the Na/K geothermometer predicts 220 °C for this sample but the K/Mg$^{0.5}$ indicates that the reservoir temperature is 280 °C. The sample labeled ThG-2 is fully equilibrated according to this analysis and the resulting reservoir temperature is around 200 °C.

3.2.3 Multiple mineral equilibria approach

Reed and Spycher (1984) proposed this method for evaluating reservoir temperatures. It is based on computation of the saturation state of typical secondary minerals in geothermal systems over a range of temperatures. The results are presented on a graph showing the saturation state (presented as log(Q/K)) for the different minerals as a function of temperature. If the fluid has been in equilibrium with a certain assemblage of secondary minerals the log(Q/K) curves for these minerals will intersect

at zero (indicating equilibrium). The temperature at which the curves intersect zero is then the reservoir temperature. This method has the advantage of discriminating between equilibrated and non-equilibrated solutions. However, this method is sensitive to the choices of secondary minerals considered, the quality of thermodynamic data for the minerals, and to the quality of analysis of elements such as Mg, Al, and Fe that occur in the geothermal solutions in very low concentrations. An example of a multiple mineral equilibria analysis is shown on Figure 2.
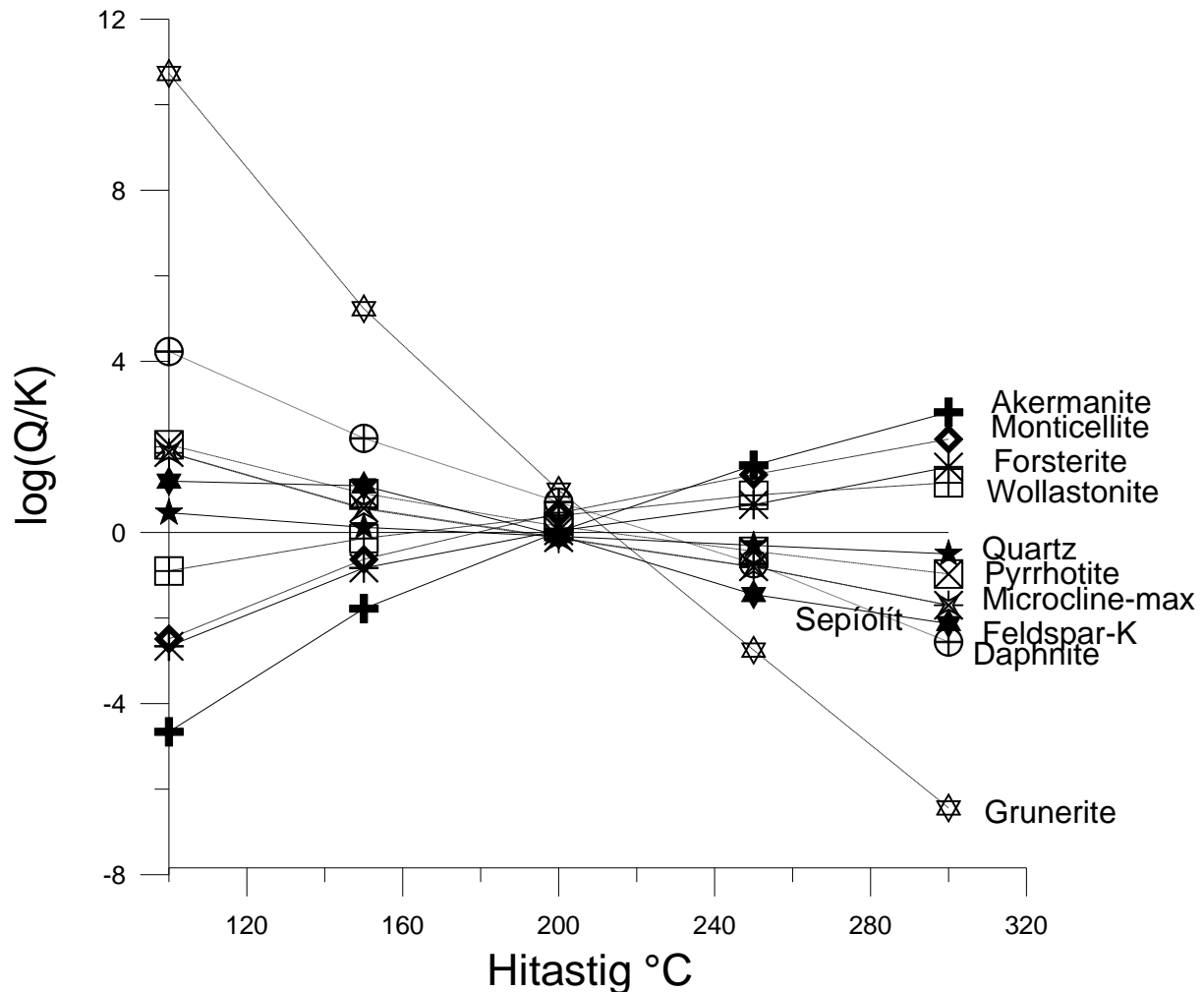

FIGURE 2: Multiple mineral equlibria analysis of sample ThG-2 shown in Figure 1. This analysis indicates that the reservoir temperature is around 200 °C, in good agreement with the Na-K-Mg analysis shown in Figure 1.

4. CONCLUDING REMARKS

- Geochemical studies provide important input for geothermal resource assessments, particularly, at the early stages of exploration.
- The most important contribution is an estimate of reservoir temperature *via* chemical geothermometers.
- Careful geochemical studies can also help delineate the boundaries of geothermal systems.
- The application of chemical geothermometers is founded on a number of assumptions.
- Discrepancy between the results of different geothermometers can be indicative of the processes affecting the fluids in the subsurface.
- For best results it is important to apply as many chemical geothermometers as possible.

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