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Analysis of Experimental Variables during Water-Rock Interaction Experiments for Solute Geothermometer Calibration

Daniel Pérez-Zárate, Ignacio S. Torres-Alvarado, Edgar Santoyo, Lorena Díaz-González

Departamento de Sistemas Energéticos, Centro de Investigación en Energía, Universidad Nacional Autónoma de México (UNAM),
Privada Xochicalco s/n, Centro, Temixco, 62584 Morelos, Mexico

dapez@cie.unam.mx, ita@cie.unam.mx, esg@cie.unam.mx, ldg@cie.unam.mx

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ABSTRACT

An extensive world-wide compilation of geothermal fluid compositions demonstrated an important lack of hydrogeochemical data below 200ºC. These data revealed to be essential for a correct statistical evaluation of the linear regression between temperature and elemental concentrations when proposing new solute geothermometers. In order to shed some light on the fluid composition in this temperature range, water-rock interaction studies are being performed using batch reactors at 25, 90, and 150ºC. However, we have considered necessary to analyze with detail the variables involved in water-rock interaction in different experimental system conditions in order to obtain the best control in the experiment. In this work we present an analysis of the most important experimental variables to take into account during water-rock interaction experiments. These variables are: (1) temperature, (2) experimental system; (3) water/rock ratio, (4) rock grain size, (5) fluid and rock initial compositions, (6) sampling techniques and (7) reaction time. Among these, temperature and reaction time seem to be the most important ones. Reaction times longer than 4000 hours are needed to perform water/rock interaction experiments at temperatures < 200°C.

1. INTRODUCTION

The temperature measurement in deep geothermal reservoirs is a relevant problem in the geothermal industry. Solute geothermometers use the chemical composition of fluids coming from thermal springs and geothermal wells for estimating the reservoir temperature during geothermal exploration and exploitation. The most commonly used solute geothermometers are silica, Na/K, and Na-K-Ca (Mimi et al., 1998; Verma, 2002; Xilai et al., 2002; Porowski and Dowgiallo, 2008; Verma et al., 2008; Mutlu and Kilic, 2009). While silica geothermometer employs mineral concentration, cation exchange equilibrium between feldspars provides the basis for the Na-K and Na-K-Ca geothermometers (Fournier and Potter, 1982; Giampaolo et al., 1992; Arnórsson, 2000; Verma, 2000). Solute geothermometers applied to a same geothermal system should give similar temperature estimations. However, some authors have reported inconsistent temperatures from different geothermometers in the same geothermal system (Verma et al., 2008 and references in it).

The Na/K geothermometer has shown the most consistent results when predicting reservoir temperatures (Verma et al., 2008). This geothermometer employs the Na/K ratio of a geothermal fluid, considering that three conditions are met (Alekseyev, 1997): (1) the main changes in the Na and K contents in the solution are controlled by the transformation of albite to sanidine, (2) the solution in the deep geothermal reservoir is in equilibrium with alkali feldspars, and (3) as the solution filters towards the surface, its composition remains the same. The Na/K geothermometer has been studied, criticized, and improved since the first work from White (1957) (e.g., Ellis and Mahon, 1967; Fournier and Truesdell, 1973; Truesdell, 1976; Fournier, 1979; Tonani, 1980; Arnórsson et al., 1983; Nieva and Nieva; 1987; Giggenbach, 1988; Verma and Santoyo, 1997; Arnórsson, 2000; Bayram, 2001; Verma, 2002; and Can, 2002). Recently, Díaz-González et al. (2008) improved the Na/K geothermometer with an extensive world-wide compilation of geothermal fluid compositions. They noted that the Na/K geothermometer overestimated the geothermal temperatures in systems of low and medium enthalpy (T <160ºC). This problem was attributed to the lack of reliable data between 100 and 160°C used for the derivation of their geothermometer.

Trying to understand the processes occurring in natural hydrothermal systems, numerous experimental water-rock interaction studies have been carried out for about 50 years. Those studies have used different experimental equipment and conditions showing the complexity of the system and the importance of some parameters during water-rock interaction studies (e.g., fluid temperature and pH, water/rock ratio, rock grain size, reaction time). These experimental investigations have also shown that our knowledge is still very limited concerning the physico-chemical processes occurring during water-rock interactions in natural hydrothermal systems.

We have recently initiated a series of water-rock interaction experiments at the Centro de Investigación en Energía (UNAM), trying to understand some of the processes involved in the Na/K geothermometer for low and medium enthalpy systems. Before starting our experimental work, we found necessary to exhaustively review the literature to analyze the variables involved in water-rock interaction experiments, as well as to set up an extensive compilation of the results already published from previous water-rock interactions studies. These two compilations build the core of the present paper.

The objectives of this work are: (1) to present the main conclusions aroused during the analysis of previously published water-rock interaction experiments; (2) to list the main variables affecting water-rock interaction experiments; (3) to study the suitability of applying the chemical composition of fluids produced during water-rock interaction experiments for Na/K geothermometry.

2. BRIEF DESCRIPTION OF PREVIOUS WORK

The first systematic fluid-rock interaction experiments were reported by Hawkins and Roy (1963), as well as by Ellis and Mahon (1964, 1967). Ellis and Mahon (1964) reacted basalt, andesite, and dacite with pure water at different temperatures between 150 to 350°C and a maximum reaction time of about 12 days. They observed that the Na and K concentrations in the solution were a function of temperature and rock type. Furthermore, they noted that with longer reaction times, alkali concentrations increased and the ratio of Na/K decreased indicating that potassium was liberated more rapidly than sodium. Ellis (1968) studied the liberation of trace elements from rocks reacting andesite with NaCl-rich solutions at 400°C and noted that high sodium chloride concentrations greatly enhanced the dissolution of some metal ions (e.g., B, Mg, Al, Mn, Fe, Cu, and Pb). Seyfried and Bischoff (1979) reacted basaltic glass with seawater at 70°C at 1 bar, and at 150°C at 500 bars. They reported that changes in seawater composition were a function of temperature and basalt crystallinity. The experiment at 70°C produced a minor but continuous loss of Mg, Na, and K, as well as an enrichment of Ca and SiO_2 in the reacted seawater. At 150°C, in contrast, Mg and SO_4 were quickly removed, while Ca, SiO_2, Na, K, Fe, Mn, and Ba were added to the seawater. Several experimental studies continued these efforts (e.g., Hajash and Archer, 1980; Savage and Chapman, 1982; Dickson and Potter, 1982; Gislason and Eugster, 1987; Kancandes and Grandstaff, 1989; Shiraki and Iiyama, 1990; Stoffregen and Cygan, 1990; Savage et al., 1992; Gislason et al., 1993; Robert and Goffé, 1993; Liu et al., 2003; Heimann et al., 2008). Some important conclusions of these later works will be presented in the following sections.

Water-rock experiments have also been performed to study solute geothermometers, quantifying the dissolution rate of some minerals and studying the chemical evolution of the reacted fluid under controlled conditions (principally temperature, pressure, and initial reactants composition). However, the amount of the experiments with these objectives is still limited. Potter et al. (1982) studied the Na/K geothermometer reacting oligoclase and microcline with a fluid containing 100 ppm NaCl. They observed that the Na/K ratio increased with increasing time and approached a nearly constant value for feldspar exchange. These experiments showed that long reaction times are needed to ensure formation of the expected feldspars. Later, Benjamin et al. (1983) took the data compiled by Fournier and Truesdell (1973) and joined them with their own data obtained with a flow-through experimental system. Using a least-squares method they proposed new constants for the Na-K-Ca geothermometer. This comparison and their own experimental observations let them conclude that feldspar and quartz are not the mineral assemblage controlling solution compositions. Instead, they proposed that the composition of the thermal waters was controlled by many different alteration reactions involving clays and zeolites. Savage (1986) reacted granite with water at 100°C and 500 bars for 203 days. The author reported that Na and K reached an apparent steady-state concentration in the fluid phase after 10 days. However, the Na/K ratio was smaller than in natural water. Application of Na/K geothermometer to his data indicated an equilibrium temperature between 500 and 600°C. The applications of the Na-K-Ca geothermometer (Fournier and Truesdell, 1973) yield a temperature of 190°C. On the other hand, Pope et al. (1987) studied the effect of the solution composition in solute geothermometers reacting rhyolite with two different experimental solutions, one rich in NaCl and other with $NaHCO_3$. They noted that silica concentration was constant in both fluids, while the highest Na, K, and Ca concentrations were present in the NaCl solution. Finally, Savage et al. (1992) conducted a set of experiments reacting granite with fluids similar to those circulating in a geothermal system at 60, 80, and 100°C. They took solutions with two different pH values (pH=7.0 and 8.0) observing that chemical changes were dominated by the dissolution of plagioclase, biotite, quartz, and calcite. Chemical components were removed from the rock depending on the chemical composition of input fluids. Mg was removed from the fluid with pH=7.0, whereas Mg, Ca, Sr, Fe, Mn, and F were removed from the fluid with pH=8.0. Potassium was co-precipitated with Mg from fluid with pH=8.0 with elevated K concentrations.

3. PRINCIPAL VARIABLES AFFECTING WATER-ROCK INTERACTION EXPERIMENTS

Studies of rock dissolution and chemical evolution of fluids during water-rock interaction experiments have been carried out using different methodologies and contrasting types of experimental apparatus (Hajash and Archer, 1980; Brantley and Chen, 1995). These studies have shown that the most important variables affecting water-rock experiments are: (1) temperature, (2) experimental system; (3) water/rock ratio, (4) rock grain size, (5) fluid and rock initial compositions, (6) sampling techniques and (7) reaction time.

3.1 Temperature

The temperature effect in natural or experimental systems is perhaps the most important variable for water-rock interaction (Ellis and Mahon, 1964, 1967; Ellis, 1968; Seyfried and Bischoff, 1979; Hajash and Archer, 1980; Azaroual and Fouillac, 1997). Temperature is the main factor for dissolution of chemical species and formation of secondary phases in the rock (Ellis and Mahon, 1964; Seyfried and Bischoff, 1979; Dickson and Potter, 1982; Moore et al. 1985; Savage, 1986; Savage et al., 1992; Robert and Goffé, 1993).While in most natural systems at temperatures close to 280°C the main secondary mineral phases are albite, K-feldspar, illite, clorite, epidote, calcite, quartz, and smectite, in experimental systems normally only zeolites are produced (e.g., analcime, mordenite, wairakite, clinoptilolite, and smectite; Dickson and Potter, 1982; Kancandes and Grandstaff, 1989).

3.2 Experimental System

The experimental water-rock interaction studies have been performed in four different reactors (Brantley and Chen, 1995): batch reactors, flow-mixed reactors, plug reactors, and Dickson type reactors. The main advantages of batch reactors are that they allow a relaxed approach to equilibrium and the reaction rates can be determined by mathematical functions when the chemical compositions of reacting fluid and rock are known (Missen et al., 1999). While batch reactors control the fluid movement only with stirrers, a flow-mixed reactor causes suspension of rock particles due to strong agitation of fluid (White and Brantley, 1995). Due to the same agitation, flow-mixed reactors have been also criticized to cause continuous abrasion in the mineral surface area (White and Brantley, 1995). On the other hand, plug reactors are fast to reach a steady state in the solution's chemical composition compared to batch reactors. However, in plug reactors the solution can react with the vessel, there is no control of the water/rock ratio, the reaction time for all fluid components is not the same, and the installation of the equipment is rather complex (Dickson and Potter, 1982). Finally, Dickson et al. (1963) designed an experimental apparatus to study water/rock interaction under hydrothermal conditions. This device is known as Dickson experimental system and it has been broadly used (e.g., Seyfried and Bischoff, 1979;

Hajash and Archer, 1980; Dickson and Potter, 1982). This type of equipment present some disadvantages, for example, it does not allow studying the solid phase during an experiment; the same quantity of sampled liquid should be re-injected into the system generating uncertainty in the water/rock ratio in the system; and finally, it is relatively more expensive (Hajash and Archer, 1980).

3.3 Water/Rock Ratio

The Water/Rock ratio (W/R) is the total mass of water divided by the total mass of rock in the system (Hajash and Chandler, 1981). Some authors have reported that high W/R-ratio experiments are generally more efficient in leaching elements from the rock than lower ratio experiments (Hajash and Chandler, 1981; Dickson and Potter, 1982). Using experimental results reported in the literature, we compared the chemical composition (ratio Na/K) of reacted fluids produced in experiments with W/R=3 and W/R=10 (Figure 1). When W/R=3 the Na/K ratio decrease in the first reaction hours and reach a relative steady state during the first 1000 hours of reaction. On the other hand, fluids produced in experiments with W/R=10 present variable Na/K ratios and do not appear to reach a relative steady state during the experimental time.

3.4 Grain Size

This variable is highly dependent on the experimental apparatus used. While in the experiments with batch reactors different grain sizes are possible, plug reactors demand rock cores to be used.

Hoareau et al. (2003), Liu et al. (2003), Crovisier et al. (1987) and Crovisier et al. (1983) worked with rock blocks in form of rectangular prisms. Chandrasekharam and Antu (1995), Hajash and Chandler (1981) and Hajash and Archer (1980) worked with disks of different diameter. However, most studies have used rock fragments of different grain sizes after crushing and sieving (e.g., Ellis and Mahon, 1964; Ellis, 1968; Hajash and Chandler, 1981; Savage and Chapman, 1982; Potter et al., 1982; Pope et al., 1987; Gislason and Eugster, 1987; Savage et al., 1992; Ghiara and Petti, 1996; Strömberg and Banwart, 1999; Möller, 2002; Yinian et al., 2003; Hara and Tsuchya, 2005; Seyfried et al., 2007). As expected, grain size affects the dissolution rates of a rock, as fine grain sizes increase the reacting surface area. However, the dissolution rate can be limited by diffusion of some chemical elements when using very fine materials (Yinian et al., 2003; Ghiara and Petti, 1996; Strömberg and Banwart, 1999).

3.5 Initial Compositions of Reactants

3.5.1 Rock Type

Several water/rock interaction experiments have been designed to study the effect of rock type in the hydrothermal system. Ellis (1968) studied the fluid composition generated by the reaction of andesite and limestone with NaCl-solutions. Hajash and Chandler (1981) reacted different igneous rocks (rhyolite, andesite, basalt, and peridotite) with sea water at temperatures > 200°C. Ghiara and Petti (1996) studied the reaction of leucite, obsidian, and pumice with deionized water to investigate the crystallization of secondary phases in volcanic rocks. Möller (2002) used basalt, andesite, and amphibole reacted with distilled water to systematically study the dissolution of rare earth elements. Takaya et al. (2006) experimented with sedimentary rocks (limestone, chert, sandstone), plutonic rocks (dune, gabbro, diorite, granodiorite, granite), volcanic rocks (basalt, andesite, dacite, rhyolite, tuff) and metamorphic rocks (serpentine, hornfels) reacted with distilled water. They found that electric conductivity of the reacted fluid increased with increasing temperature in almost all rock types (except sandstone). Kancanes and Grandstaff (1989) reported that the rock type factor is temperature dependent. They established that < 250°C the chemical composition of the reacted fluid is independent of the rock type if this is volcanic. Very important are the rock porosity and permeability, which control the fluid quantity that can be in contact with the rock (Zeng et al., 2006).

3.5.2 Fluid Type

The most common fluid composition present in high-temperature geothermal systems is of near-neutral pH, with chloride as the dominant anion (Arnórsson et al., 1983, 2006). Several water-rock interaction experiments have been performed trying to reproduce the chemical composition of natural thermal fluids and to understand the physico-chemical processes present in geothermal reservoirs. Figure 1 exemplifies the fluid type effect in Na/K ratio using reported water-basalt experiments using the Dickson experimental apparatus. NaCl-solutions with a pH value (first three studies in legend of Figure. 1) show a tendency of increasing Na/K ratios with higher NaCl concentration of the initial fluid. These Na/K ratios seem to reach a steady state after the first 700 hours of reaction. On the other hand, the ratios obtained with solutions with pH values between 8 and 9 (studies done by Moore et al., 1985, and Kancandes and Grandstaff, 1989) do not show a tendency to steady-state during the first 2000 hours of reaction, but the higher pH value seems to produce higher Na/K ratios. Finally, the experiment carried out with distilled water generated the smallest Na/K ratios, indicating the importance of the initial fluid chemical composition for the mobilization of ions from the rock.

3.6 Sampling Techniques

The sampling technique is among the most complex variables for water/rock interaction experiments. In general, it depends on the type reactor used. For instance, in batch reactors it is obligatory to carry out a quick cooling (quench) to take the final samples (fluid and rock). In mixed-flow and plug flow reactors, having a solution in constant circulation, they allow to take the fluid sample in certain time intervals. The fact of removing samples during the development of an experiment forces the investigators to add an equal fluid volume to the system, with the disadvantage of the need of mass balance adjustments (Ellis and Mahon, 1964; Seyfried and Bischoff, 1979; Seyfried and Bischoff, 1981; Seyfried and Mottl, 1982; Potter et al., 1982; Moore and Grandstaff, 1985; Yinian et al., 2003). Some authors have neglected the mass loss during sampling introducing large water/rock ratios (Benjamin et al., 1983; Dove and Crerar, 1990; Berger et al., 1994; Metz and Ganor, 2001).

3.7 Reaction Time

Figure 1 shows that long reaction times (> 1000 hours) are needed for reaching a relative steady state in the system, although this variable is highly dependent on other experimental conditions (Yadav and Chakrapani, 2006).

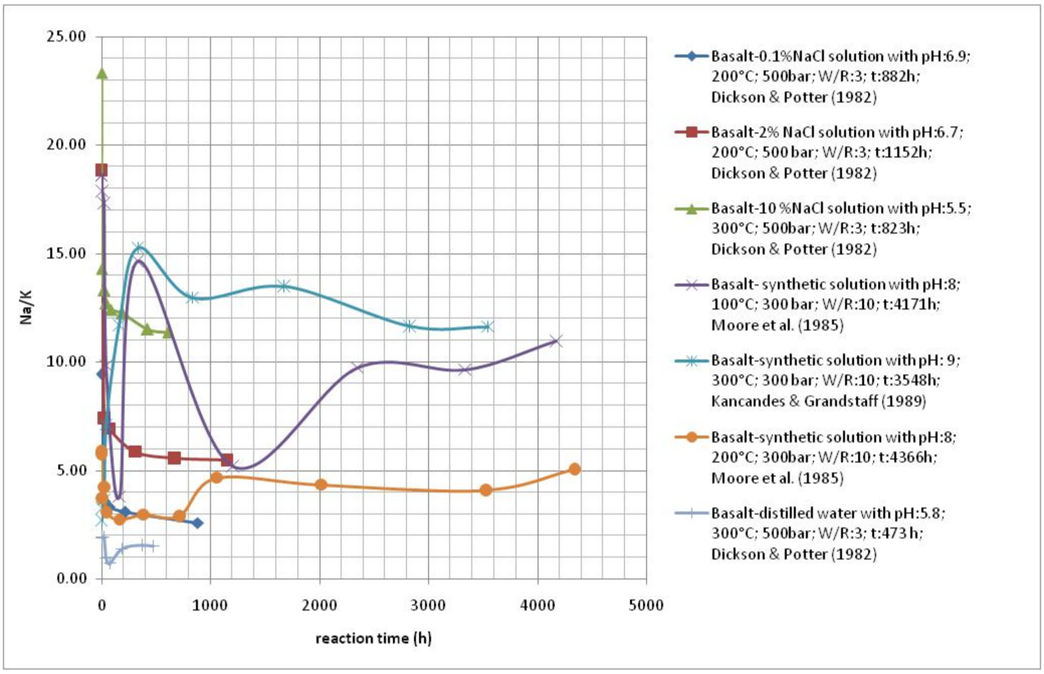

Figure 1: Comparison of Na/K ratio from different water-basalt experiments; W/R indicates the water/rock ratio used and t indicates the amount of hours of reaction. All experiments were performed in Dickson experimental systems.

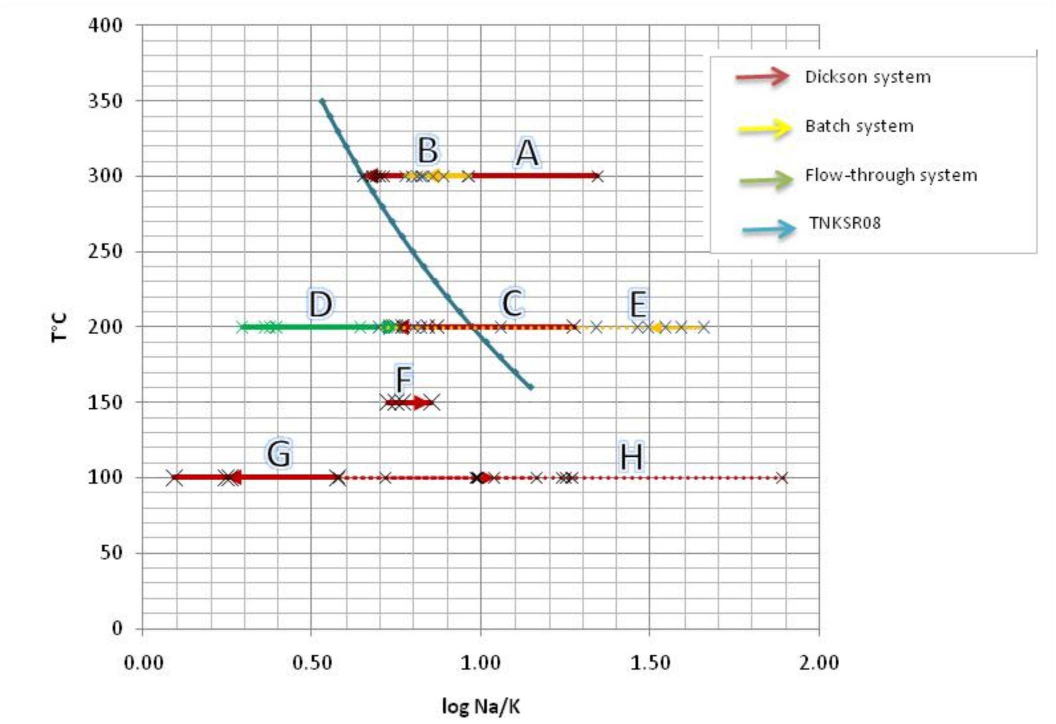

Figure 2: Comparison of the Na/K geothermometer to the Na and K concentrations (log Na/K) obtained from different water-rock interaction experiments. The experimental equipment used is indicated by colors in inset. TNKSR08 (blue continuous line) represent the geotermometer regression between 150 and 350°C as proposed by Díaz-González et al. (2008). (A) reaction of andesite and 0.1%NaCl solution at 300°C and 500 bar, with 2032 h reaction time; Dickson and Potter (1982); (B) rhyolite and 0.1M NaCl solution at 300°C and 1000 bar, with 3120 h reaction time; Pope et al. (1987); (C) basalt and 2% NaCl solution at 200°C and 500 bar, with 1152 h reaction time; Dickson and Potter (1982); (D) granodiorite and deionized water at 200°C and 333 bar, with 6570 h reaction time; Benjamin et al. (1983); (E) basalt and deionized water at 200 °C and 1 bar, with 2184 h reaction time; Ghiara et al. (1993); (F) oligoclase-microcline and 100 ppm NaCl solution at 150°C and 200 bar, with 2276 h reaction time; Potter et al. (1982); (G) granite and deionized water at 100°C and 500 bar, with 4872 h reaction time; Savage (1986); (H) basalt- pH 9 solution experiment at 100°C and 300 bar, with 4172 h reaction time; Moore et al. (1985).

Table 1: Calculated temperature at the final reaction time from water-rock interaction experiments.

Experiments	Reactants	Experimental apparatus	Reaction time(h)	Experimental presure (bar)	Experimental temperature (°C)	TNKSR 08* (°C)	Difference %**
A	0.1%NaCl solution-andesite	Dickson	2032	500	300	301	0.3
B	0.1M NaCl solution-rhyolite	Batch	3120	1000	300	240	-20.0
C	2% NaCl solution-basalt	Dickson	1152	500	200	269	34.5
D	Deionized water-granodiorite	Flow-through	6570	333	200	264	32.0
E	Deionized water-Basalt	Batch	2184	1	200	97	-51.5
F	100 ppm NaCl solution- oligoclase-microcline	Dickson	2276	200	150	234	56.0
G	Deionized water-granite	Dickson	4872	500	100	508	408.0
H	Synthetic solution (pH:9)- basalt	Dickson	4172	300	100	184	84.0

*TNKSR08 represents the calculated temperature using the geothermometer proposed by Díaz-González et al. (2008).
**Difference between the calculated and the experimental measured temperature in %.

4. RESULTS OF WATER-ROCK INTERACTION EXPERIMENTS APPLIED TO NA/K GEOTHERMOMETRY

Natural hydrothermal fluids present different degrees of equilibrium with host rocks, depending principally (but not only) on the reservoir temperature and reaction time in the system. Often these fluids have been interpreted (sometimes with no evidence) to be in equilibrium with feldspars and thus allowing the application of solute (Na/K) geothermometers (e.g., Arnórsson et al., 1983; Arnórsson, 2000).

Figure 2 and Table 1 show the results of water-rock interaction experiments carried out at different temperatures and reaction times. These results are compared with the improved Na/K geothermometer, recently proposed by Díaz-González et al. (2008). The experiments accomplished at 200 and 300ºC show a tendency to reach or even to cross the Na/K geothermometer curve (experiments A to E in Figure. 2). These experiments present differences between the measured experimental temperature and the calculated temperature normally below 35% (Table 1). Reaction times were relatively long, varying from 1152 to 3120 hours. Noteworthy, the longest reaction time registered in the analyzed works (6570 hours for experiment D in Figure. 2) falls away from the geothermometer curve. This may reflect the influence of the flow-through experimental apparatus selected for this experiment, which did not allow a better ion removal from the rock. Initial fluid composition or the rock type appears to have a smaller influence, as experimental results between basalt and fluids of different concentrations at 200°C overlap (experiments C and E in Figure 2).

On the other hand, the experimental results obtained during the water-rock interaction reactions carried out at 150 and 100°C fall away from the geothermometer curve. Experiments F and H (Figure 2) present differences between measured and calculated temperature of 56 and 84%, although they observed reaction times of 2276 and 4172 hours (Table 1), respectively. Experiment G (carried out at 100°C) shows the biggest difference between measured and calculated temperature (408%, Table 1).

The experimental studies analyzed for this work remark the conclusion that temperature is the main variable in the water-rock interaction processes. Furthermore, reaction time is a very important variable as well, because longer reaction times increase chemical concentration in the fluids. Based on this analysis, reaction times longer than 4000 hours are necessary to perform water/rock interaction experiments, especially for temperatures < 200°C.

5. CONCLUSIONS

The temperature and reaction time seem to be the most important variables in water-rock interaction experiments. The type of fluid is a complex variable, which importantly affect the velocity of the ion exchange between water and rocks. Dissolved ions enhance mineral dissolution, while the use of distilled or deionized water requires longer reaction times. Reaction times longer than 4000 hours are needed to perform water/rock interaction experiments at temperatures < 200°C.

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