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Kinetic Study of Alkali-Feldspars Dissolution Reactions by Using Controlled Water-Rock Interaction Experiments at Low-to-Medium Geothermal Temperature Conditions

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ABSTRACT

Water-rock interaction (WRI) experiments were conducted for the kinetic study of the alkali-feldspars dissolution reactions under low-to-medium geothermal conditions. Ionic exchange reactions between Na-K and alkaline-feldspar minerals were analyzed for a reaction time of nearly 24 months. A geochemometric (geochemical and statistics) modeling was used together with the WRI experimental results for predicting the kinetic behavior of the reaction at quasi-steady state conditions. Rock powder samples were reacted with deionized water in batch reactors (with a W/R mass ratio of 5:1) at 90°C and 150 °C. The kinetic evolution of the fluid composition was studied by predicting both the concentration of reaction products [through the $log(Na/K)$] and the reaction time parameters, which may represent the most probable quasi-steady state conditions of the experiments (i.e., as a hypothetical quasi-steady state when $t\rightarrow\infty$). With the aid of rational polynomial regression models, $log(Na/K)_{RPR}$ and reaction time (t_∞) estimates for all the WRI experiments were predicted and compared with theoretical data inferred from Na-K geothermometers [$log(Na/K)_{GEO}$] (assuming a theoretical equilibrium condition). Details of the numerical and experimental studies are briefly described in the present work.

1. INTRODUCTION

The reliable estimation of deep reservoir temperatures in convective geothermal systems (CGS) is a fundamental task required for geothermal industry (e.g., Verma, 2002; Pandarinath, 2011; Peiffer et al., 2014). Deep equilibrium temperatures of CGS are usually estimated by solute geothermometers, which are based on the temperature-dependent equilibrium reactions that occur under water-rock (mineral) interaction processes (Verma and Santoyo, 1997; Arnórsson, 2000; Díaz-González et al., 2008). The most frequently used geothermometry tools include cationic (e.g., Na-K) and silica geothermometers (Nicholson, 1993; Verma, 2002).

The Na-K geothermometer is based on the temperature-dependent variation of Na-K compositions of geothermal waters due to ion exchange processes between the fluid and coexisting alkali feldspar minerals (Fournier, 1979). Up to date, several empirical calibrations of the Na-K geothermometers have been proposed from world geochemical databases and geochemometric techniques (Verma and Santoyo, 1997; Can, 2002; Diaz-Gonzalez et al., 2008; Serpen et al., 2009; Santoyo and Diaz-Gonzalez, 2010), as well as from a few thermodynamic databases (Giggenbach, 1988; Arnórsson, 2000). Some authors have pointed out that Na-K geothermometers usually tend to overestimate underground temperatures of low-enthalpy geothermal systems (T<200 °C) probably due to the lack of reliable fluid chemistry data collected under full equilibrium conditions (Giggenbach, 1988; Santoyo and Díaz-González, 2010). The systematic overestimation problem observed, in mostly applications of the Na-K geothermometers to low-enthalpy systems, demand the generation of new reliable data for correcting the performance of such geothermometric tools at these temperatures (Porowski and Dowgiallo, 2008). Experimental calibrations of Na-K geothermometers are therefore needed for the improvement of their prediction performance (Potter et al., 1982; Benjamin et al., 1983; Arnórsson 2000; Marini, 2013).

Laboratory experiments emulating geothermal reservoir conditions are considered as useful tools for understanding mineral-water interactions, the evaluation of the reaction kinetics (through the equilibrium constants and reaction rates), and the chemical weathering of volcanic rocks (Alekseyev and Mendvedeva, 2006; Arvidson and Luttge, 2010; Chardon et al., 2006). Such experiments are generally controlled by dissolution reactions of primary minerals, and the precipitation of secondary minerals (Zuddas, 2010). These experiments are hypothetically designed to reach quasi-steady state conditions. However, due to the slow dissolution of minerals at low temperatures, such equilibrium conditions are hardly achieved because long reaction times are required. WRI experimental investigations with implications on geothermometry are rarely reported in the literature (Potter et al., 1982; Benjamin et al., 1983; Pope et al., 1987; Alekseyev; 1997). The present contribution is therefore justified for gaining knowledge about the WRI processes involved in geothermometry applications.

Based on a novel geochemometric methodology (through rational polynomial regressions), the present study was focused to analyze WRI experimental data for the prediction of the reaction times required to achieve quasi-steady state conditions. This methodology was validated against some WRI experimental data (previously reported in the literature), where the quasi-steady state conditions are known with accuracy. The results of these experimental works were used to describe the kinetic behavior of such reactions. The concentration of the reaction products ($log\ Na/K$) and the reaction times needed to reach the quasi-steady state conditions were estimated by applying the geochemometric method. Finally, the novel methodology was successfully applied to analyze new WRI experimental data with the same objectives. Details of the numerical and experimental studies are briefly described in the present work.

2. METHODOLOGY

The objective of the methodology developed in this work was to demonstrate the application of a geochemometric approach for fitting the kinetic evolution data of WRI experiments, and to predict the reaction times under hypothetical quasi-steady state conditions (t_∞). The methodology consisted of four major tasks: (1) To create a working database with geochemical data logged from alkali-feldspars dissolution experiments under geothermal conditions; (2) To analyze and to validate the kinetic behaviour of WRI experiments (previously reported in literature) using rational polynomial regression models; (3) To design new WRI experiments of alkali-feldespar dissolution reactions by using batch reactors at low-to-medium temperatures; and (4) To apply the geochemometric methodology to the new WRI experiments for estimating the *log(Na/K)* values under quasi-steady state conditions, and their corresponding reaction times.

2.1 Geochemical Database

WRI experiments based on the dissolution reactions of alkali-feldspars under geothermal conditions were compiled in a geochemical database. Fluid chemistry compositions and reaction times (*t*) were collected from previous WRI experiments reported in the literature. The logarithmic value of the Na/K ratio was used as a monitoring key parameter for studying the reaction kinetics of these experiments through the analysis of ion exchange reactions among alkali-feldspar minerals and fluids. With these purposes, four experimental studies of water-rock interaction were compiled in the geochemical database. The experimental conditions of the compiled experiments are summarized in Table 1.

Table 1. Experimental conditions of some WRI experiments reported in the literature

Exp. ID	Rock	Solution	Temp (°C)	Pressure (bars)	W/R ratio	Time (h)	Reference
A	Granite	Deionized water	100	500	10	4872	Savage (1986)
B	Granite	Stream water	200	500	2	1459	Savage et al. (1993)
C	Andesite	Brine: 0.1% (v/v) NaCl	200	500	10	740	Dickson and Potter (1982)
D	Andesite	Brine: 0.1M NaCl+0.02M KCl	350	500	1	380	Zhou and Zhang (2005)

For the WRI experiments reported by Savage (1986) [A], five measurements of Na and K concentrations in the fluid were collected at different reaction times, where the interacted fluid apparently reached quasi-steady state concentrations after 10 days. For the experiments reported by Savage et al. (1993) [B], eight measurements of the Na and K composition were logged at different reaction times. The concentration change of Na in the fluid revealed a plagioclase feldspar dissolution characterized by a rapid release of Na into the aqueous phase with a curvilinear approach in both experiments. For the experiment [C] reported by Dickson and Potter (1982), five measurements of Na and K were recorded at different reaction times. In all these experiments, the fluid quickly reacted with the rock samples, and it was assumed that quasi-steady state concentrations were nearly attained in a few days. Finally, thirteen logged data were collected from the experiment reported by Zhou and Zhang (2005) [D]. In this experiment the content of Na increased continuously, whereas the concentration of K reached a peak in the first 10 days. Additional operating conditions of all selected water-rock experiments are found in detail in the original literature source.

2.2 Geochemometric modeling

A novel geochemical and statistical (geochemometric) method was developed for the prediction of the *log(Na/K)* and reaction time data (*t*) needed to reach quasi-steady state conditions in all the WRI experiments compiled. A schematic diagram showing the numerical methodology is presented in Figure 1. The geochemometric methodology was based on the application of rational polynomial regression (RPR) models and well-known Na-K geothermometer equations. Seven computing tasks were required both for reproducing the kinetic behaviour, and for the estimation of the reaction time at theoretical equilibrium conditions (t_∞): (1) The calculation of the *log(Na/K)* experimental values; (2) The analysis of the kinetic behaviour between *log(Na/K)* and reaction time data; (3) The assessment of the RPR model for the statistical fit between *log(Na/K)* and *t* measurements; (4) The selection and validation of the best RPR models to reproduce the experimental WRI data with accuracy; (5) The calculation of the corresponding $log(Na/K)_{RPR}$ under quasi-steady state conditions; (6) The statistical comparison between the theoretical prediction of $log(Na/K)_{GEO}$ values inferred from well-known Na-K geothermometers (assuming a full equilibrium condition) and those estimated from the RPR; and (7) the estimation of the reaction times at equilibrium conditions (t_∞).

2.2.1 Analysis of the kinetics of the dissolution reactions of alkali-feldespar minerals

A typical asymptotic behavior was observed in most of WRI experiments, which seems to show a tendency to quasi-steady state conditions. The asymptotic tendency given by either an increase or decrease of the *log(Na/K)* with time was studied, depending on the initial ionic concentration of the interacting working solutions.

2.2.2 Fundaments of the Rational Polynomial Regression (RPR) model

The kinetic evolution observed between the *log(Na/K)* and the reaction time data of WRI experiments was fitted by RPR model. The RPR is based on the well-known mathematical Padé approximation, which is actually a rational polynomial function that could be used as a generalization of the Taylor polynomial model, where the mathematical function is given by the ratio of two polynomials (Wong-Loya et al., 2012). RPR enables a dependent variable (*y*) to be extrapolated when the value of the independent variable (*x*) tends to infinity, which fulfils the mathematical analysis required by the WRI experiments for predicting their kinetic history at quasi-steady state conditions.

Such a mathematical approach can be defined by the following generalized equation:

$$y(x) = \frac{p_0 + p_1 x + p_2 x^2 + ... + p_n x^n}{1 + q_0 x + q_1 x^2 + ... + q_m x^m} \quad (1)$$

where the coefficients p_i and q_j, {from $i=0, 1, 2, \ldots, n$, and $j=1, 2, \ldots, m$, respectively} in equation 1 may have distinct specifications, leading to different approaches, and may be integer coefficients or fractions. A fundamental condition to extrapolate the y variable when x tends to infinity is actually given by the n and m exponents, which must be equal ($n=m$). According to this condition, equation 1 may be reduced to:

$$\lim_{x\to\infty} y(x) = \frac{p_n}{q_m} \qquad (2)$$

For predicting the y values from x data, it was necessary to compute numerically the coefficients p_i and q_j. Details of the RPR algorithm are described in Wong-Loya et al., 2012.

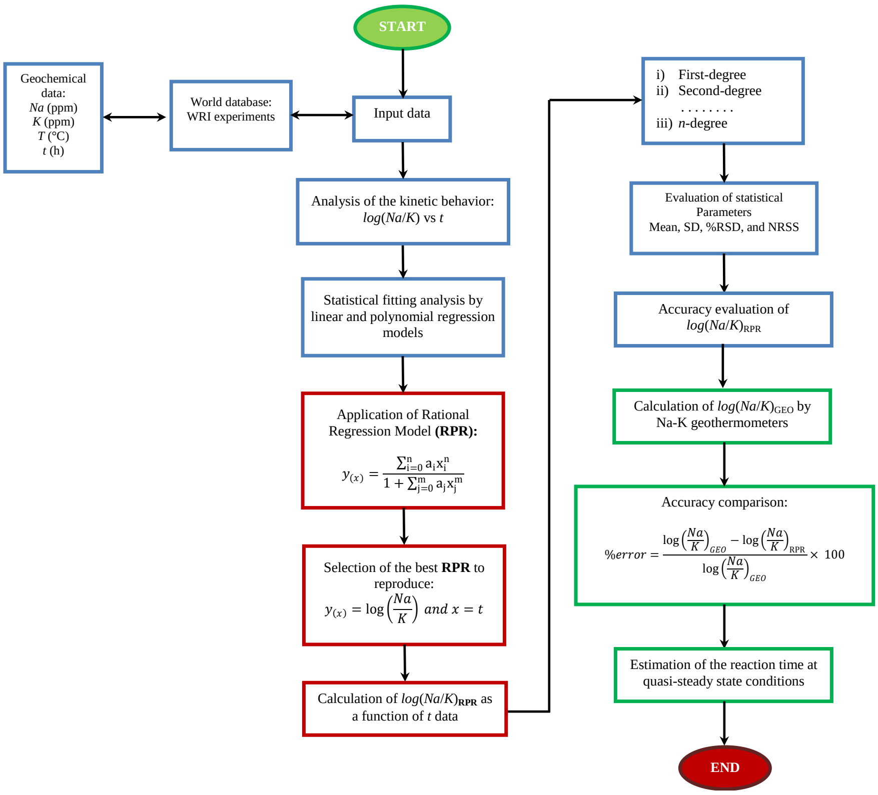

Figure 1: Flow diagram used for the estimation of the reaction time and the log(Na/K) at quasi-steady state conditions in water-rock interaction experiments.

2.2.3 Selection and validation of the best RPR model

An evaluation of the RPR models was performed by applying the statistical methodology proposed by Wong-Loya et al. (2012). In a summarized form, such an assessment considers the following five numerical steps: (i) the creation of i-combinations with smaller data subsets from the original data sets; (ii) the determination of the RPR coefficients; (iii) the preliminary estimation of $log(Na/K)_{RPR}$ for each data subset by using eq. 2; (iv) the calculation of statistical parameters (mean, standard deviation, and coefficient of variation) for all $log(Na/K)_{RPR}$ estimations; and (v) the selection of the best RPR model in conjunction with the data subset through a statistical evaluation of normal residual sum of squares (*NRSS*), where the best RPR model will enable the full kinetic behavior of $log(Na/K)$ with reaction time (t) data to be accurately described. The NRSS was calculated by means of the following equation:

$$NRSS = \sum_{i=1} \frac{y_i - \hat{y}}{y_i} \qquad (3)$$

where $\hat{y}_i$ represents the dependent variable predicted by means of the best rational polynomial regression equation [$log(Na/K)_{RPR}$], and y_i the $log(Na/K)$ values measured in the WRI experiments. The regression equation corresponding with the best RPR was finally applied for estimating the reaction time under quasi-steady state conditions following the numerical procedure described in the next sections.

The last data pair of each experimental dataset (i.e., the longer reaction time of the WRI experiment) was not considered for the regression procedure because such data pair was used as an accuracy reference to validate the prediction performance of each RPR model. A goodness of fit evaluation was calculated through the statistical parameter *%DEV* by means of the following equation:

$$\%DEV = \frac{y_m - y_p}{y_m} \times 100 \qquad (4)$$

where y_m represents the last measured data from WRI experiments and y_p is the value predicted from RPR model. Based upon the best fitting results and the lowest statistical residuals, the RPR model was finally selected to describe the full kinetic evolution of the WRI experiments.

2.2.4 Comparison between $\log(Na/K)_{RPR}$ and the theoretical $\log(Na/K)_{GEO}$

As the full equilibrium conditions are very difficult to achieve from short time experiments, the $\log(Na/K)_{RPR}$ predictions inferred from the RPR model were compared to the theoretical *log(Na/K)* values inferred from Na-K geothermometer calculations. The Na/K geothermometers proposed by Fournier and Truesdell (1973) [*FT73*] and Verma and Santoyo (1997) [VS97] were used and defined as $\log(Na/K)_{GEO}$ for determining the most probable theoretical *log(Na/K)* values at hypothetical full equilibrium conditions. These Na/K geothermometers are based on the well-known reaction among alkali feldspar, and these are given by following equations:

$$TFT73 = \frac{777}{\log\left(\frac{Na}{K}\right) + 0.7} - 273.15 \tag{5}$$

$$TVS97 = \frac{1289(\pm 76)}{\log\left(\frac{Na}{K}\right) + 1.615(\pm 0.179)} - 273.15 \tag{6}$$

where TFT73 and TVS97 are the temperature in °C for the Na/K geothermometers proposed by Fournier and Truesdell (1973), and Verma and Santoyo (1997) respectively. The Na and K concentrations are in ppm.

A statistical comparison between the $\log(Na/K)_{\mathrm{RPR}}$ (inferred from RPR model) and the mean $\log(Na/K)_{GEO}$ (inferred from the Na/K geothermometer) values was made to evaluate the prediction performance of the regression model by using the following equation:

$$\%error = \frac{\log\left(\frac{Na}{K}\right)_{GEO} - \log\left(\frac{Na}{K}\right)_{RPR}}{\log\left(\frac{Na}{K}\right)_{GEO}} \times 100 \tag{7}$$

The lowest % error values calculated enabled the best regression model to be used for predicting the reaction time at theoretical full equilibrium or quasi-steady state conditions (i.e., at t_∞).

2.3 New WRI experiments

For studying the kinetics of the mineral dissolution reactions, new WRI experiments were carried out in sealed Teflon autoclaves placed within an oven of controlled temperature at 90°C, and in a batch reactor at 150 °C. Such WRI experiments consisted of three principal stages: (i) Collection and preparation of rock samples; (ii) Design and performing of well-controlled WRI experiments; and (3) Sampling and analysis of the water-rock reaction products. The study of these new experiments was focused on the chemical monitoring of the Na/K ratio changes (before and after the WRI reactions).

2.3.1 Description of rock samples

Non-altered rock samples collected in the Xitle volcanic zone were used for the dissolution experiments for a reaction time of nearly 24 months. Xitle volcanic zone is located in the central part of the Mexican Volcanic Belt (MVB). Crystalline basalt, unaltered dacite, and deionized water were used as starting materials for the WRI experiments. The basalt rock shows a texture porphyritic with phenocrystals of labradorite and some phenocrysts of olivine, whereas the dacite sample shows a holocrystalline porphyritic texture with largest phenocrysts of biotite. These rock samples were previously analyzed for their use as internal geochemical reference standards (Pérez et al., 1979). The rock samples were crushed and sieved to obtain a homogeneous 0.5-1 mm size fraction. Powder samples were washed in an ultrasonic bath using pure water for 30 min, followed by a drying at 105 °C. The specific surface areas of the rock samples were 2.07 m^2/g and 17.95 m^2/g for the basalt and dacite samples respectively. The deionized water was obtained from a distillation-deionization Millipore® system with an electrical conductivity of 0.05 μS/cm.

2.3.2 WRI equipment and methods

Batch autoclave systems and *W/R* ratios of 5:1 were used in the mineral dissolution experiments. Such WRI experiments were performed in two series: (i) experiments at 90 °C for 24 months; and (ii) experiments at 150 °C for nearly 3 months. The first series of experiments were allowed to interact in weighted Teflon autoclaves Savillex® with a volume capacity of 180 ml and 1000 ml, and kept at isothermal conditions using a thermostat controlled oven at 90.0±0.2°C. After each experimental test was completed, the autoclave was quickly quenched in cool water. The *pH* and bicarbonate (HCO_3^-) content were measured immediately after opening the autoclave.

The fluid was filtered through 0.2 µm Millipore® filters, and two fractions of it were collected: (1) an acidified fluid sample with ultrapure nitric acid to stabilize the dissolved cations, and (2) a non-acidified fluid sample for the determination of the anion composition. For the assessment of the rock mass balance, the samples were weighted prior to, and after drying. Replicates of all the experimental data were collected for a better control of the precision errors, and statistically optimized by using thirteen discordant tests to have measurements with a normal distribution (following the methodology proposed by Verma and Díaz-González, 2012).

On the other hand, the mineral dissolution experiments were performed in a Parr® reactor at 150 °C. A photograph of the experimental system is shown in Figure 2. Rock powder samples and deionized water were placed in a weighted PTFE cylinder with capacity of 2000 ml, and then it was put in a steel-alloy vessel. Before starting the experiment, the air was removed from the vessel with helium gas to avoid sample oxidation. Afterwards the vessel was heated with a flexible heating mantle by increasing the temperature at the rate of 10 °C per 15 min. The temperature of the WRI experiment was fixed at 150.0± 2 °C together with 57.1± 4.4 bars of pressure for a time period of 3 months. The fluid samples resulted from the WRI experiments were sampled through a spiral coil of cooling, which was connected to the vessel. The experiments were stopped after the fluid sample collection; the vessel was then quenched by a closed-loop cooling system. For the WRI experiments carried out in an oven of controlled temperature at 90 °C, the same procedure was used for handling the resulting fluid samples.

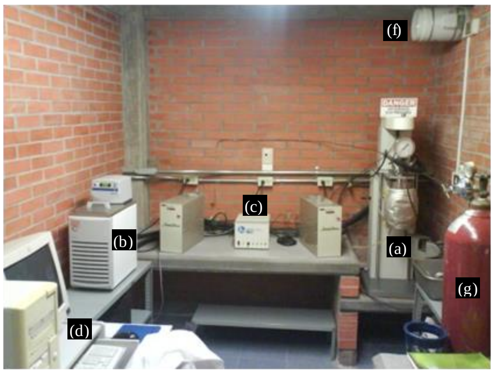

Figure 2: Experimental system used in the WRI experiments: (a) Parr® reactor; (b) Cooling bath and pumping module; (c) Analytical interface controller; (d) Data acquisition system; (e) Helium gas reservoir; and (f) Hot air extractor.

2.3.3 Analytical techniques

Sampled fluids were analyzed for Si, Na^+, K^+, Ca^{2+}, and Mg^{2+} with inductively couple-plasma emission spectrometry (ICP-OES). Ion chromatography was used for measuring the anion composition of fluids (F^-, Cl^-, and SO_4^{2-}) whereas the content of bicarbonate was determined by a titration volumetric method.

2.4 Results and Discussion

2.4.1 Analysis of the kinetic evolution of WRI experiments (data previously reported in the literature)

Plots with curves showing the kinetic behavior of some previous experimental studies (reported in Table 1) are shown in Figure 3. As it can be observed in the experimental works performed with distilled and streamwater as aqueous interacting solutions, the kinetic behavior observed between the *log(Na/K)* and time data suggests a typical asymptotic increase with a tendency to achieve a quasi-steady state condition at long reaction times, except for the the WRI experiments carried out with brines, which showed a reverse process of dissolution. Reaction times up to 400 h were observed in nearly all the experimental works, except for the measurements reported by Savage (1986) which were obtained for ~200 h. After plotting the kinetic behavior of the four WRI experiments, the geochemometric procedure was applied for fitting the *log(Na/K)* and time data.

2.4.2 Regression results and estimation of reaction times under quasi-steady state conditions

After applying the RPR model to the previous WRI experiments, it was observed that first- and second- degree approaches generally provided the best regression models for fitting the experimental data. Mean values of $log(Na/K)_{RPR}$ together with their standard deviations were estimated. All these regression results are graphically shown as solid lines in the plots of Figure 4. The predicted performance and the goodness of the regressions were subsequently validated by using the statistical parameters NRSS and %DEV (eqs. 3 and 4, respectively). The NRSS and %DEV estimates ranged from 0.0004 to 0.034, and from 0.2 to 4.7, respectively for the WRI experiments previously reported in literature; which enable the quality of the fitting procedures to be verified. The mathematical regression results obtained after applying the RPR model are summarized in Table 2.

The Na/K geothermometers reported by Fournier and Truesdell (1973); and Verma and Santoyo (1997) were used for calculating the $log(Na/K)_{GEO}$ values using the experimental temperatures as main input data. The prediction performance of each regression model was evaluated through the relative standard error (%error). This statistical analysis found an acceptable agreement between the RPR estimates and mean values inferred from the Na/K geothermometers (Figure 4) in nearly all the WRI experiments, except for the experimental work reported by Savage (1986) in which the statistical test was rejected (Table 2).

2.4.3 New WRI Experiments

In order to evaluate the chemical composition of the fluids produced from new WRI experiments, the results of the first and the last sample were plotted on a distribution diagram (Figure 5). According to this diagram, all final sampled fluids were enriched with Na^+, F^-, Cl^-, SO_4^{2-}, and HCO_3^-. High concentrations of sodium and bicarbonate were observed in all final sampled solutions at the end of the experiments. These results indicate that the volcanic rocks interacting with water at 90 and 150 °C produce bicarbonate-sodium fluid type. For the basalt and dacite rock interactions at 90 ˚C, it was found that the pH of the resulting fluids ranged from 6.00 to 8.78 and from 5.87 to 8.74 respectively, whereas for the basalt rock interactions carried out at 150 ˚C the pH of the resulting fluids ranged from 5.58 to 7.84.

The kinetic behavior observed between the *log(Na/K)* and reaction times is described by an asymptotic increase with a tendency to reach a quasi-steady state condition (Figure 6). In the case of the two experiments carried out at 90 °C, the kinetic evolution of the basalt and dacite dissolution processes were typified by long reaction times (*t* >11,000 h) to reach a representative quasi-steady state, whereas for the experiment at 150°C, such quasi-steady state conditions were achieved in a slower reaction time (~2000 h). As can be observed in the kinetic patterns of the low temperature experiments, initially fast dissolution of the feldspar minerals between 0 and 4,000 h seems to occur followed by a slow approach to quasi-steady state conditions, typically at reaction times greater than 8,000 h. For the high temperature experiment, the initial dissolution of the minerals occurred between 0 and 700 h, followed by an apparent stabilization at reaction times greater than 1,500 h (Figure 6g).

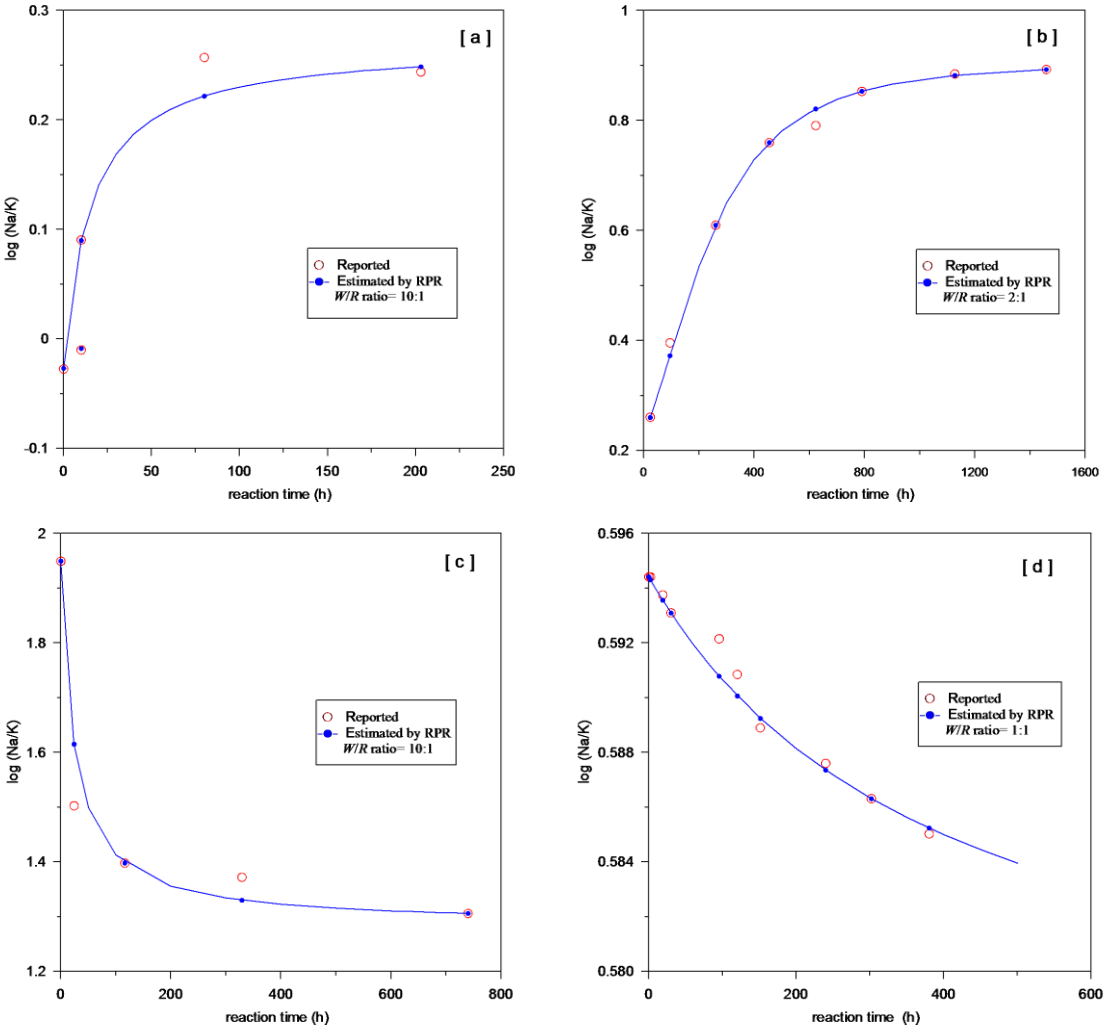

Figure 3: **Geochemical data compiled from previous WRI experiments, and a comparison with the predicted estimates inferred from the RPR models: [a] Savage (1986), [b] Savage et al. (1993), [c] Dickson and Potter (1982), and [d] Zhou and Zhang (2005).**

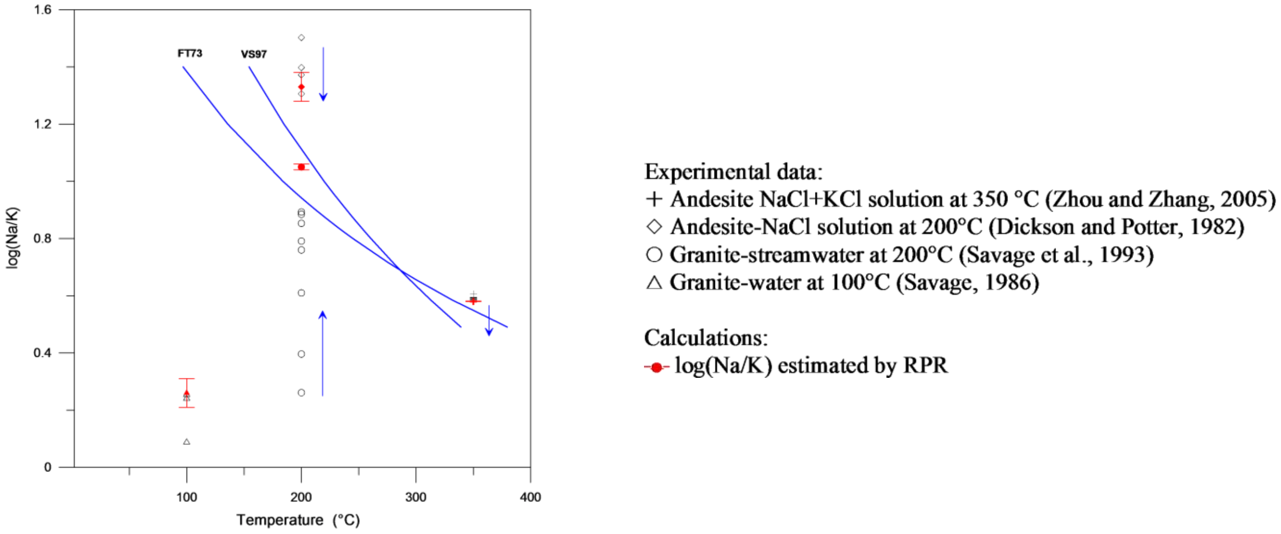

Figure 4: Statistical analysis between the logged data from previous WRI experiments with selected Na/K geothermometers.

Table 2. Summary of the numerical results obtained from all the WRI experimental data.

WRI experiment	Maximum time of experimentation (h)	Temperature (°C)	log(Na/K)$_{GEO}$	log(Na/K)$_{RPR}$	NRRS	%DEV	Reaction time predicted at quasi-steady state conditions (y)
Previous experiments							
a	203	100	1.61±0.32	0.26±0.05	0.034	1.9	n.d.
b	1459	200	1.03±0.12	1.05±0.01	0.002	2.7	37±4
c	740	200	1.03±0.12	1.33±0.05	0.002	4.7	180±1
d	380	350	0.50±0.07	0.58±0.01	0.0004	0.2	270±30
New experiments							
e	17304	90	1.69±0.35	0.72±0.06	0.005	8.8	2098±587
f	11064	90	1.69±0.35	1.08±0.01	0.001	0.5	4619±308
g	2160	90	1.69±0.35	0.83±0.08	0.00001	9.2	507±240

Previous experimental data: [a] Savage (1986), [b] Savage et al. (1993), [c] Dickson and Potter (1982), [d] Zhou and Zhang (2005). New experimental data: [e] basalt-water interaction at 90 °C (this study), [f] dacite-water interaction at 90 °C (this study), and [g] basalt-water interaction at 150 °C (this study).

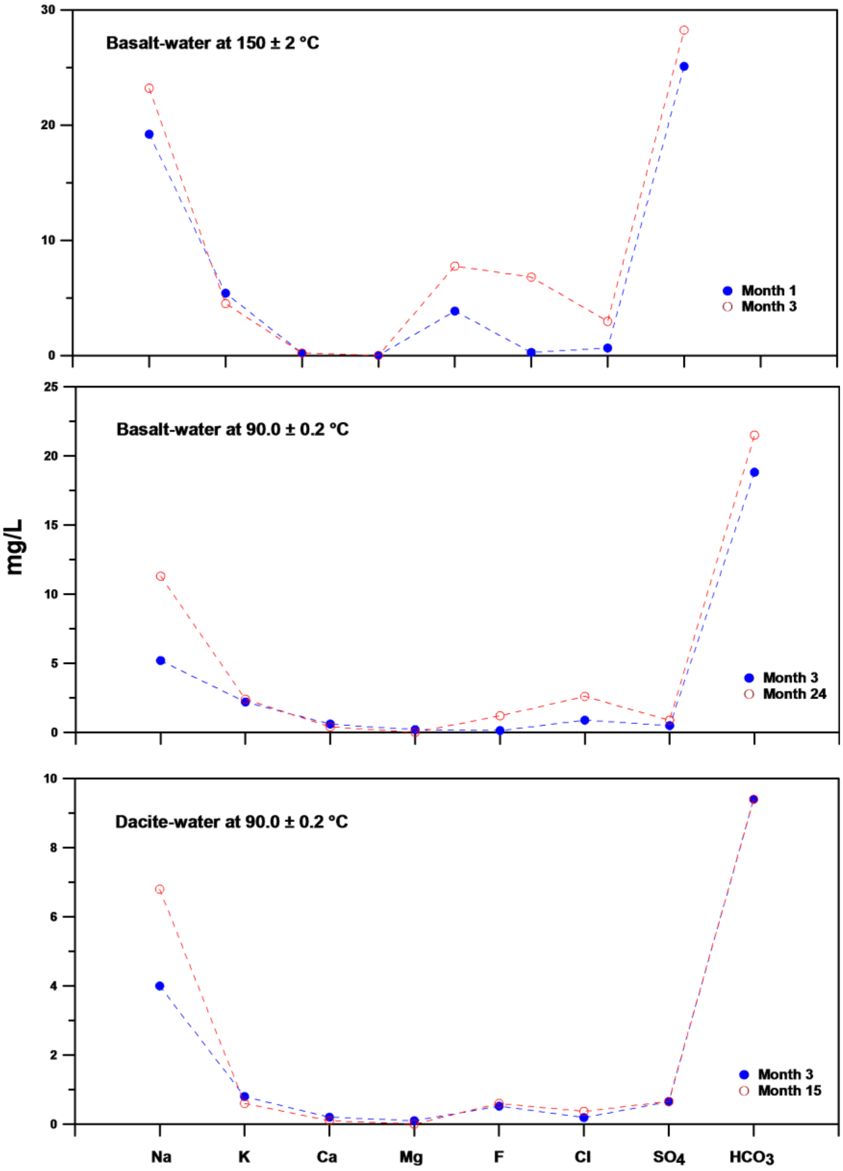

Figure 5: Summary of chemical composition variation in leaching solutions collected in new WRI experiments at 90 and 150°C.

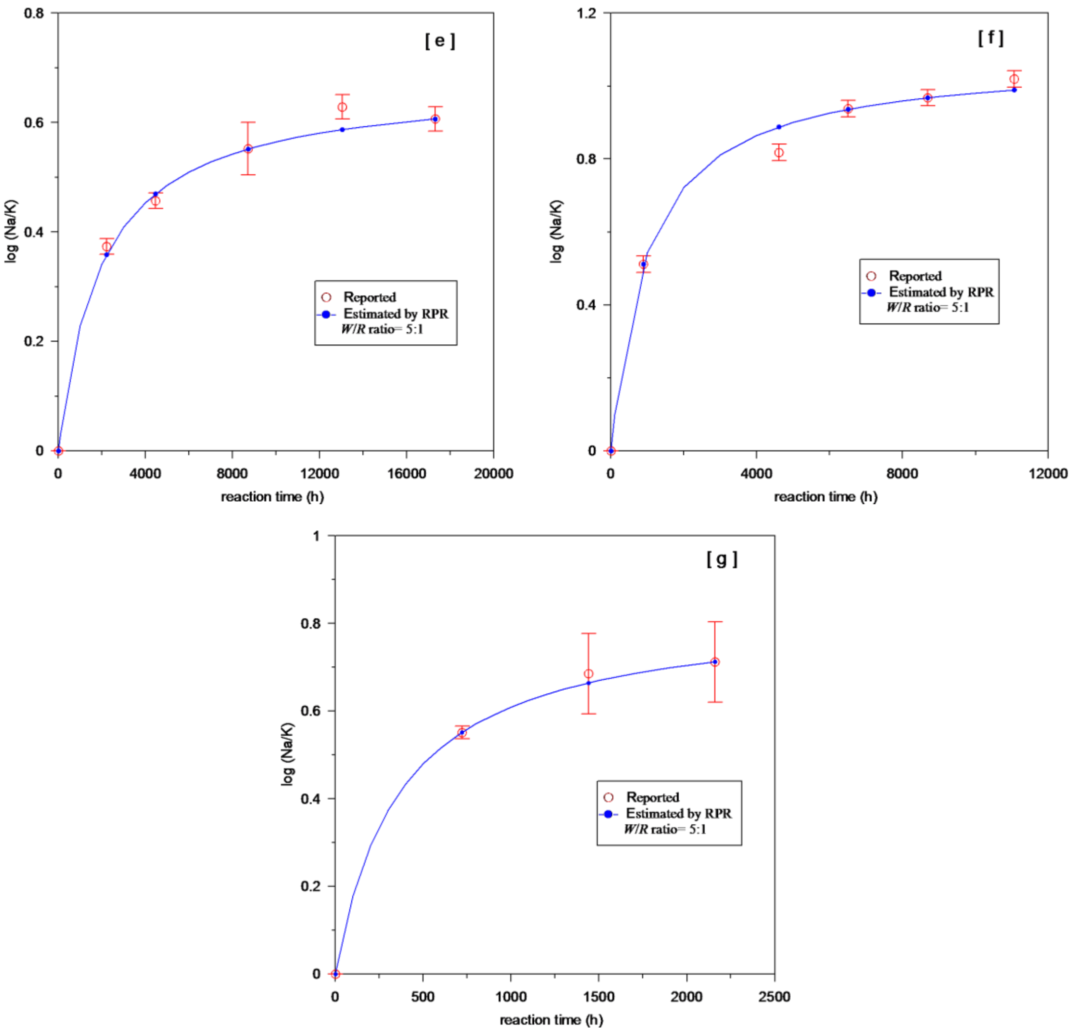

Figure 6: Geochemical data compiled from new WRI experiments from this study, and a comparison with the predicted estimates inferred from the RPR models: [e] basalt-water interaction at 90 °C, [f] dacite-water interaction at 90 °C, and [g] basalt-water interaction at 150 °C.

2.4.3 Application to RPR to New Experimental Data Series

The numerical regression results obtained after a successful application of the RPR are compiled in Table 2. Mean values of 0.72±0.06, 1.08±0.01, and 0.83±0.08 were estimated with good accuracy for the $log(Na/K)_{RPR}$ of the basalt-water (at 90°C), dacite-water (at 90°C), and basalt-water (at 150°C) systems, respectively. All these RPR predictions are graphically shown as solid lines in the plots of Figure 7. The predicting performance and the goodness of the RPR fitting were validated by means of the statistical parameter NRSS, which showed acceptable statistical values of 0.005 for the basalt-water system; 0.001 for the dacite-water system; and $1x10^{-5}$ for the basalt-water system (150°C), as show in Table 2. From this statistical analysis, it was demonstrated in all the WRI experiments that their equilibrium conditions are very far to be reached because the *log(Na/K)* estimates predicted from the RPR models are statistically different from those values inferred from the geothermometry equations (see Figure 7). According to the predictions of the RPR, very long reaction times are actually needed in the three new WRI experiments to achieve the equilibrium conditions (up to 507±240 years for the RPR, as show Tables 2).

2.5 Conclusions

A new geochemometric method based on rational polynomial regression models was successfully developed for describing the kinetic evolution in water-rock interaction experiments. The chemical composition and the reaction time were predicted with high accuracy at quasi-steady state conditions. The method was successfully validated with four WRI experiments previously reported in literature. The key statement for RPR model assumes that *log(Na/K)* calculated from geothermometer equations is the most probable fluid chemical composition under a hypothetical equilibrium conditions between alkali-feldspars and the experimental solution. The geochemometric modelling also was applied to evaluate the kinetic behavior of three new WRI experiments, which were performed to evaluate the solubility of Na and K at 90 and 150 °C for a period of 24 and 3 months, respectively. The geochemometric modelling is a powerful, reliable, and reproducible tool for studying the kinetic and geochemical processes at steady state condition in low-enthalpy geothermal resources. Such methodology together with well controlled WRI experiments could be used in future calibrations of Na/K geothermometer for predicting deep equilibrium temperatures in low-enthalpy geothermal systems.

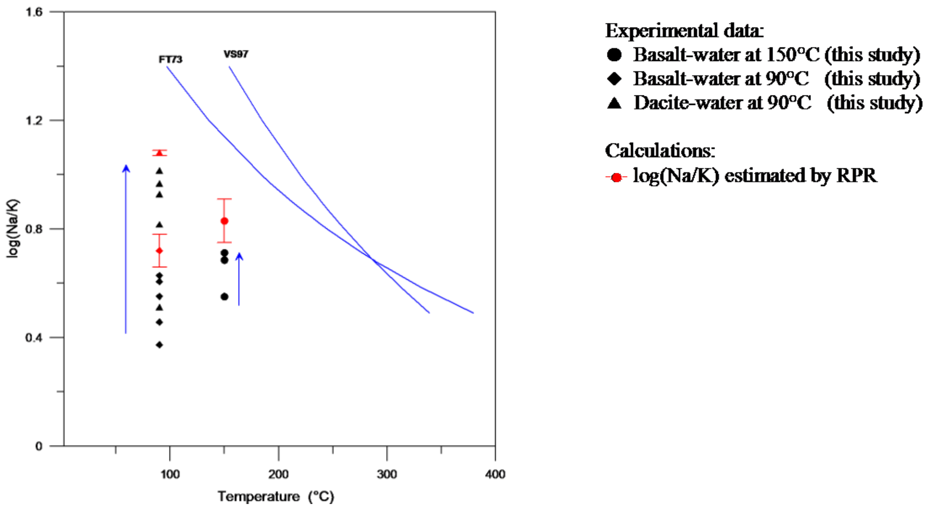

Figure 7: Statistical analysis between the logged data from new WRI experiments with selected Na/K geothermometers.

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