

Water Rock Interaction [WRI 14]

Estimating the reactive surface area of minerals in natural hydrothermal fields: preliminary results

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Abstract

We estimated variation of reactive surface area (RSA) of minerals in the Galician (Spain) geothermal field using the chemical composition of fluids as input data. Our methodology is based on reconstructing the fluid composition according to a reaction progress schema that uses the fractional degree of advancement of the mass-transfer process. RSA of the principal mineral is estimated by using a transposed reaction rate that introduces experimental kinetic rate constants. We found that over the entire reaction process, RSA of feldspars and biotite varied by 2–4 orders of magnitude, thereby explaining the changes observed in CO₂ partial pressure and fluid pH.

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1. Introduction

Fluid – rock interaction controls many environmental and geological processes occurring at the Earth's surface. The quantification of these processes is important in most treatments of global element cycles, notably carbon dynamics and in the challenging areas of geothermal resource evaluation and CO₂ geological storage. The comparison of laboratory derived rates to field scale studies is difficult due to the fact that most laboratory-derived rates are 2-5 orders of magnitude higher than field derived rates [1, 2]. Given the complexity of evaluating reactive transport processes [2, 3], the majority of the investigations apply mass balance isotopic concepts like the water-rock ratio; whereas fluid flow and T-xCO₂ equilibrium are rarely evaluated in a kinetic framework under natural conditions. In this work, we attempt to estimate variations in the mineral reactive surface area using chemical fluid composition as input data.

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We developed an original methodology for quantifying this variable in a natural context and assumed that the evolution of chemical fluids is the signal response to the water-rock interaction as it intrinsically incorporates timescale and reservoir properties (porosity, permeability, water/rock ratio). For long time of residence (>10000 years) and larger space scale (> 150 km²), we assume that fluid composition is mainly driven by reactivity than fluid dynamics (porosity, permeability).

The Galician geothermal field was chosen because of its relatively homogenous geological setting and co-genetic fluid evolution with a wide range of pCO₂ partial pressure at emergence. Two Variscan granites generated by an anatexis process characterize this area [4]. Based on petrographical modal abundances, we estimated that the main mineralogical paragenesis is constituted by silicate minerals in the following proportions: quartz 35%, K-feldspar 20% albite 35%, biotite 10% and muscovite 1%. Accessory minerals like calcite and clays, mainly kaolinite, generally fill secondary porosities in the rock fractures [5]. Water from springs and boreholes was collected using polypropylene falcon tubes previously cleaned with nitric acid. Samples were filtered at 0.45µm for major elements and at 0.01µm for trace elements and acidified with HCl or HNO₃.

2. Fluid Chemistry

The Galician geothermal field is characterized by Na-HCO₃ waters, with an emergence temperature ranging from 15° to 57°C, pH varying from 9.5 to 5.8 and ionic salinity from 6 to 78 mmol/kg [5]. The observed variations in pH, alkalinity and estimated PCO₂ partial pressure were used to evaluate a 'continuous' fluid-rock process. The fluid saturation state (S.I.), estimated by PhreeqC geochemical code [6] using wateq4f.dat thermodynamic database, reveals saturation with respect to kaolinite and quartz. This indicates that all major cation activity (Ca²⁺, Mg²⁺, Na⁺, K⁺) is controlled by the dissolution of granite parent minerals while silica and aluminum activity is controlled by the solubility of neogenic mineral phases. The deep fluid temperature estimated using silica geothermometers [7, 8] falls within an average temperature of 110±10°C for all the sampling points. The pCO₂ partial pressure at equilibrium, estimated from alkalinity and pH using PhreeqC software, indicates that pCO₂ partial pressure increases linearly from 1 to 10⁵ Pa as the sum of major cations increases from 10⁻⁵ to 10⁻² mol/L.

3. Modeling the mineral reactive surface area

The Galician geothermal field shows evidence of simultaneous mineral dissolution and precipitation. The rate of mineral dissolution reaction 'R', corresponding to the amount of matter released to the fluid by unit of time, can be expressed by the following equation [9]:

$$R = S \cdot \bar{R} \quad (1)$$

Where: R is the "*in-situ*" rate of dissolution (in mole per unit of time) representing the mineral dissolution rate under Galician geothermal field conditions, \bar{R} is an absolute rate of dissolution expressed in (mole·m⁻²·sec⁻¹), estimated by laboratory experiments and representing the maximum dissolution rate per unit of mineral area, while S is the reactive surface area (m²). In a multi-mineral system, fluid-rock reactions can be described by a series of mass balance equations for each of the relevant mineral phases in relation to the reaction rate. The rate of dissolution can be expressed as:

$$\frac{dn}{dt} = v \cdot R \quad (2)$$

Where n is the molar concentration, v is the matrix of the stoichiometric coefficient and R is the *in situ* rate. Bearing in mind the transformation of the system from state 0 to a state 1, operating variables become a specific function of the advancement of the reaction ζ [10] resolved in a time-independent space. Practically, ζ was estimated, for every sampled point, by the sum of the major no-controlled cation activities ($\zeta = [\text{Na}] + [\text{K}^+] + [\text{Ca}] + [\text{Mg}]$).

Considering temperature, pressure, volume and reaction progress ζ of each specific reaction as an independent variable, the system can be easily solved by:

$$n_{j, \text{end}} - n_{j, \text{start}} = \int_{\zeta=0}^{\zeta=1} \left(\sum_i \frac{\partial n_{j,i}}{\partial \zeta_i} \right) d\zeta \quad \text{with : } 0 \leq \zeta \leq 1 \quad (3)$$

Where $n_{j,i}$ stands for the molality of the j^{th} aqueous solute in the i^{th} reaction, ζ represents the overall reaction progress and ζ_i is the fractional reaction progress related to the i^{th} reaction. Since the solute concentration of Eqn 2 is known in the compositional space $0 \leq \zeta \leq 1$, the system is now solved for R and Eqn. 2, in the reaction progress mode, becomes:

$$\frac{dn}{d\zeta} = v \cdot R_{\zeta} \quad (4)$$

The evolution of major cation concentrations as a function of the reaction progress ζ is reported in Fig.1.

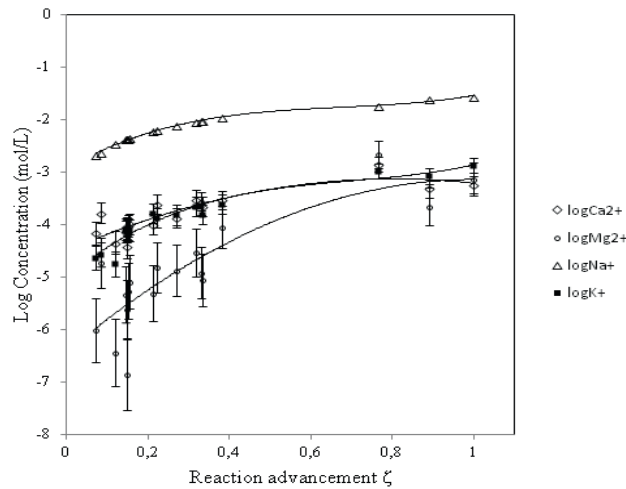


Fig. 1. Evolution of the cation concentration as a function of the reaction progress ζ .

The transposed reaction rate, R_{ζ} , can be estimated by :

$$R_{\zeta} = S_i \cdot \overline{R}_i \left(\frac{dt}{d\zeta} \right) \quad (5)$$

The *in-situ* dissolution rate R , related to the concentration of a specific aqueous species as a function of the reaction advancement, corresponds to the partial derivative of the concentration species as function of ζ , while the absolute rate of dissolution \bar{R} is a kinetic function of the reaction affinity and dissolution constants depending on pH, temperature and chemical composition. Values of selected mineral absolute rates, \bar{R} , are reported in Scislewski and Zuddas [12]. If R and \bar{R} are calculated independently as a function of the reaction advancement, the reactive surface area S also becomes a function of the reaction advancement ζ (Eqn.5).

4. Results and Conclusions

We estimated the reactive surface area (RSA) using the *in situ* dissolution rate of Eqn. 1 and found a progressive change throughout the process. All the investigated RSA progressively increased throughout the water-rock interaction process. Albite and K-feldspar RSA systematically increased by two orders of magnitude while biotite RSA increased by more than 4 orders of magnitude. Our results show a higher variation in biotite RSA throughout the entire CO₂-water-rock interaction process. The determining role played by biotite in the global granite hydrothermal alteration process was earlier proposed [11] in the Cornwell Carnemellis granite. The results of this work are in agreement with the long term and a large-scale evolution of crust-water interaction and quantify previous estimations based on Sr isotopic ratios [13, 14].

Our original modeling approach indicates that the RSA is not a constant parameter, contrary to what is generally assumed in current modeling. Our preliminary findings indicate that CO₂ mineralization in granite hydrothermal fields is mainly driven by silicate minerals and especially by biotite, whereas calcite dissolution contributes only negligibly to the global budget. The kinetic approach used in this study offers a reliable geochemical methodology for estimating the evolution of mineral reactivity, taking into account ratio of RSA of different minerals in natural water-rock interaction systems.

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