

## NOTA TÉCNICA

# Cation Exchange Geothermometry: A critique

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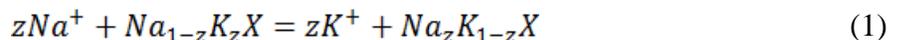
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The geochemical studies of geothermal systems provide insight into the physiochemical processes responsible for their origin and evolution on the basis of the chemical composition of fluids (separated vapor and water) collected from fumaroles, hot springs and drilled wells. Using chemical geothermometers and the conservation of mass, energy and alkalinity, the chemical concentrations are converted to the reservoir conditions to predict the state of water-rock interaction and reservoir processes like boiling, condensation, mixing with other fluids, mineral dissolution-precipitation, etc. (Verma, 2002).

The cation exchange geothermometers (e.g. Na<sup>+</sup>/K<sup>+</sup> ratio) are empirical relations, used to estimate deep geothermal reservoir temperature (Fournier and Truesdell, 1973; Giggenbach, 1981, 1988). Various cation exchange geothermometers have been developed with varying coefficient values in regression equations and/or involving different types of cations.

The word ‘empirical’ has a meaning in natural sciences. It implies that the reason of certain behavior (e.g. Na<sup>+</sup>/K<sup>+</sup> ratio is a function of temperature in hydrothermal systems) is unknown; however, the empirical relation is not violating any existing theory or law of natural sciences. A chemical reaction in any system is governed by the laws of chemical thermodynamics. Thus there is a need to justify that the fact that the observed empirical relations of cation exchange geothermometers are not against the laws of chemical thermodynamics.

The development of Na<sup>+</sup>/K<sup>+</sup> cation exchange geothermometer is based on the following type of cation exchange reaction



where the capital X represents an anion and z denotes the stoichiometric coefficient. The equilibrium constant of this reaction is given by

$$K_{eq} = \exp\left(-\frac{\Delta G_F^{T,P}}{RT}\right) = \frac{(a_{K^+})^z (a_{Na_zK_{1-z}X})}{(a_{Na^+})^z (a_{Na_{1-z}K_zX})} \quad (2)$$

where  $\Delta G_F^{T,P}$  is the difference in the Gibbs’ free energy of formation of the products and reactants at any temperature (T) and pressure (P), subscript (F) stands for formation, (R) is the gas constant, ‘a’ is the activity of respective species. The activity coefficient is considered to unity in case of dilute solutions. Similarly, the activity of solid phases is also considered as unity in developing geothermometers. The equilibrium constant (eq. 2) is reduced to

$$K_{eq} = \left(\frac{[K^+]}{[Na^+]}\right)^z \quad (3)$$

where the square brackets [ ] represent the molal concentration of the species.

Fournier (1989) simplified the equations for various cation exchange geothermometers to the Na<sup>+</sup>/K<sup>+</sup> geothermometers. Then he plotted log (Na<sup>+</sup>/K<sup>+</sup>) versus 1000/T for the cation exchange between albite and

adularia, albite and microcline and Na- and K-montmorillonites together with the geothermometer equations (Figure 1). There is a wide range of values for  $\log(Na^+/K^+)$  at a given temperature and vice versa. For example, at the temperature of 100°C, the values of  $\log(Na^+/K^+)$  vary in the range 0.95 to 2.25 for different equations. Similarly, for a value of  $\log(Na^+/K^+) = 1.00$ , the temperature range is 90 to 410°C. Even if one only considers the geothermometer equations, the temperature range is 90 to 160°C for  $\log(Na^+/K^+) = 1.50$ . It means that one can get a wide range of temperature values using different geothermometer equations for a given ratio of  $Na^+/K^+$ .

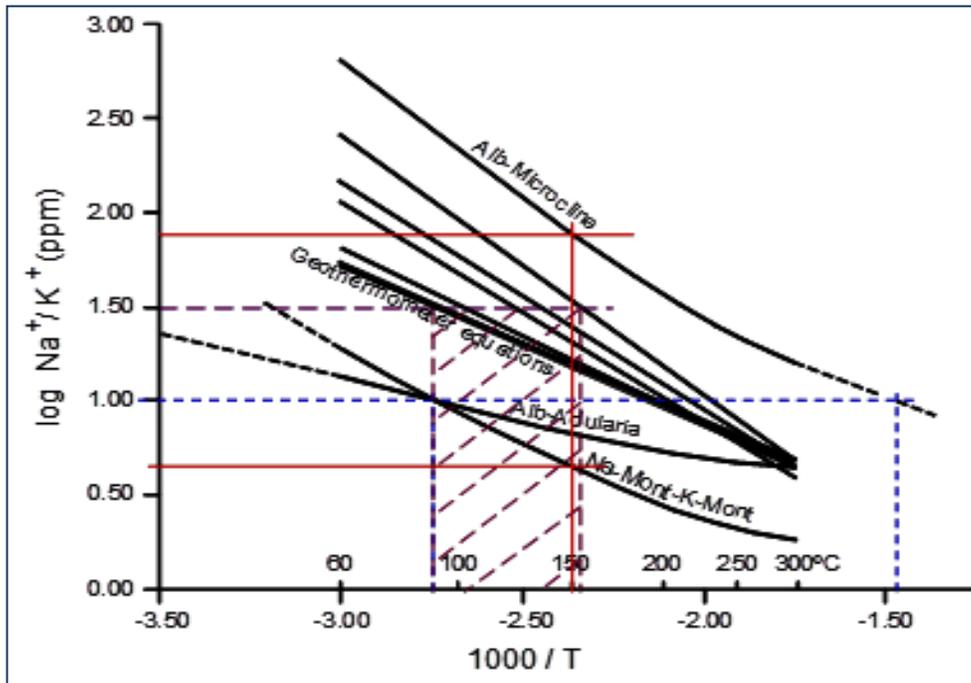
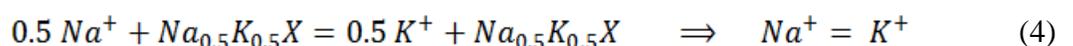


Fig. 1. Variation of  $\log(Na^+/K^+)$  as a function of  $1000/T$  for the theoretical curves for low albite-microcline, low albite-adularia, and Na-montmorillonite-K-montmorillonite together with equations of various  $Na^+/K^+$  geothermometers (modified after Fournier, 1989).

Giggenbach (1981, 1988) extended the cation exchange geothermometry in the triangular plots to illustrate the estimate of reservoir temperature and the classification of geothermal fluids. The fundamental problems of A-B-C triangular plot is that the values (A=1, B=1, C=1) and (A=1000, B=1000, C=1000) fall at the same point. The first point may correspond to rain water whereas the second may be geothermal water.

Let us analyze the above treatment for the development of cation exchange geothermometers on the basis of the laws of chemistry and chemical thermodynamics:

1. There are some materials which have affinity to capture some cation (say  $Na^+$ ) and liberate other (say  $K^+$ ) under certain environmental conditions. These types of reactions are unidirectional for the given environment. Writing a chemical reaction like equation 1 with an “=” sign means that the reaction is in equilibrium (i.e. some reactants form products and an equal amount of products form reactants). Thus an equilibrium exists between reactants ( $Na^+$ ,  $Na_{1-z}K_zX$ ) and products ( $K^+$ ,  $Na_zK_{1-z}X$ ). Clearly, the minerals  $Na_{1-z}K_zX$  and  $Na_zK_{1-z}X$  cannot be the same.
2. The mixed-minerals like  $Na_{1-z}K_zX$  are not pure phase, so their activity cannot be considered as unity.
3. On substituting  $z = 0.5$ , the equation 1 reduces to



It is quite clear that it is not possible, even if  $Na_{0.5}K_{0.5}X$  and  $Na_{0.5}K_{0.5}X$  are different minerals.

4. It is well established in chemistry that a molecule cannot have a fraction of an atom. For example, we cannot write the water molecule as  $HO_{0.5}$ . It means that one atom of hydrogen reacts with half atom of oxygen to form water. An atom is the smallest entity in chemical reactions. So, a mineral molecule cannot be written as  $Na_{1-z}K_zX$  unless “z” is an integer. The second thing is to know the structural formula of the molecule or specie. Thus “z” can be “0” or “1” in this case, and the equation 1 reduces to



5. According to equation 5, the reactants ( $Na^+$ ,  $KX$ ) forms products ( $K^+$ ,  $NaX$ ). We cannot have free ions. It means that equation 5 (or 1) is a partial chemical reaction. Thus there is need to understand, first, the full chemical reaction instead of developing a geothermometer on the basis of a partial chemical reaction.
6. Similarly  $Na^+$  and  $K^+$  are in the solution according to equation 5 (or 1). A solution should be electrically neutral. It means that the concentrations of  $Na^+$  and  $K^+$  are controlled by some anions in the solution. We have to know the effect of controlling anions on the equilibrium constant of the cation exchange reaction.

7. There is no physical unit balance in the equations of cation exchange geothermometers [e.g.  $T(K) = 855.6 / (\log(Na/K) + 0.8573)$ ]. The concentration unit of  $Na^+$  and  $K^+$  is ppm and their

concentrations are not even individually a function of temperature. If anything, their concentrations are functions of temperature and the individual concentration of  $Na^+$  or  $K^+$  will be better geothermometers than those of  $Na^+/K^+$  ratio. There are numbers on one side and a variable with a temperature unit (K) on other side of a cation exchange geothermometer. It is not feasible according to basic physics. Thus, the  $Na^+/K^+$  ratio is a number; it cannot represent the temperature of any system (Verma, 2011).

In summary, the derivation of cation exchange geothermometers is against the basic laws of chemistry and chemical thermodynamics. Historically the foundation of sciences is based on the formulation of theories and laws using experimental evidences (observations). The theories and laws were modified, scrutinized, or abandoned with new evidence. Still some basic laws and theories (e.g. Newton’s laws of motion, thermodynamics, electrodynamics, etc.) have to be validated with any new evidence. For example, Newton’s laws of motion are not valid to describe the motion of small particles with high velocity. These events give birth to quantum mechanics. However quantum mechanics provides the same results as Newtonian mechanics when describing the motion of a large body with low velocity.

Thus we cannot use the “laws of chemistry and chemical thermodynamics” together with the “cation exchange geothermometry” since these are contradictory to each other. We have to abandon the cation exchange geothermometry until we develop a new theory (law) or demonstrate that the cation exchange geothermometry is within the framework of existing theories and laws.

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