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Thermodynamic interpretation of Na-K-Ca geothermometer in the natural water system

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A cation-chloride concentration diagram showing the stability of minerals in natural water system at elevated temperatures is constructed. The curves on this diagram showing the equilibrium between aqueous solution and minerals commonly occurring in nature generally satisfy the empirical Na-K-Ca relationship obtained by FOURNIER and TRUESDELL (1973). This indicates that the chemical composition of natural waters is largely controlled by minerals commonly occurring in nature.

INTRODUCTION

It has been well known that the atomic Na/K ratio in natural waters is related to temperature (WHITE, 1965, 1968; ELLIS, 1969, 1970). This relationship has been also experimentally obtained (ORVILLE, 1963; ELLIS and MAHON, 1967; HEMLEY, 1967). This is interpreted by albite-K feldspar-aqueous solution equilibrium (WHITE, 1965; ELLIS, 1970; FOURNIER and TRUESDELL, 1973). Recently, FOURNIER and TRUESDELL (1973) showed that the ratio Na/K of solution generally yields the temperature much higher than actual temperature and in addition to the concentrations of Na and K the concentration of Ca has to be considered in order to estimate the temperature of natural water. They called the relationship of the concentrations of Na, K and Ca with temperature "Na-K-Ca geothermometer".

In the present paper, it is attempted to interpret the Na-K-Ca geothermometer thermodynamically on the basis of mineral-water equilibrium.

THERMODYNAMIC CALCULATION AND DISCUSSION

It is common in the natural water system that Na^+ constitutes the most dominant cation. Among anions, Cl^- and HCO_3^- are dominant in general. At elevated temperatures considered in the present paper, pH is generally less than seven as will be deduced later. In this pH range H_2CO_3 is considered on the basis of its dissociation constant (RYZHENKO, 1963) to be contained

in the solution more than HCO_3^-. Therefore, the concentration of HCO_3^- is assumed to be neglected in comparison with Cl^-. Thus the following electroneutrality relation is approximately established in the aqueous solution.

$$m_{Na^+} \doteqdot m_{Cl^-} \qquad (1)$$

where m is molality.

HELGESON (1967) constructed activity diagram depicting chemical equilibrium among minerals and aqueous solution at elevated temperatures (Fig. 1). At three phase equilibrium points (albite-sericite-K feldspar and albite-sericite-Na montmorillonite) of $Na_2O-K_2O-SiO_2-Al_2O_3-H_2O$ system at elevated temperatures (Fig. 1),

$$a_{Na^+}/a_{H^+} = \text{constant} \qquad (2)$$

For these points, the relation between pH and the concentration of Cl^- can be derived from equations (1) and (2). Thermochemical data were taken from HELGESON (1969) for the construction of the diagram. Figure 2 shows that silicate mineral assemblages comprise pH buffer system and pH decreases with increasing concentration of Cl^-.

In the similar manner described above, the relation between the concentrations of K^+ and Cl^- is derived (Fig. 3). In this case, $\log m_{K^+}$ increases with increasing $\log m_{Cl^-}$.

If calcite is in equilibrium with the aqueous solution, the relation between pH and the concentration of Ca^{2+} can be obtained from the
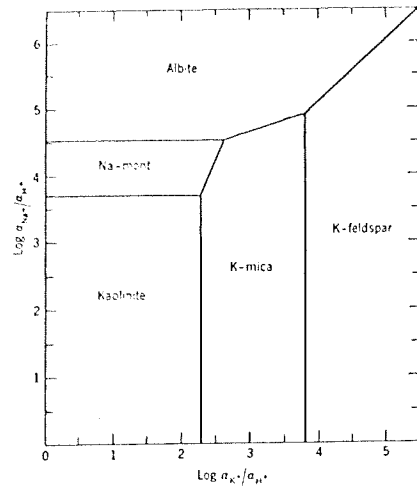
Fig. 1. *Activity diagram depicting chemical equilibrium among minerals and aqueous solution at 300°C (after HELGESON, 1967). The activity of water is taken as unity. Quartz is present.*
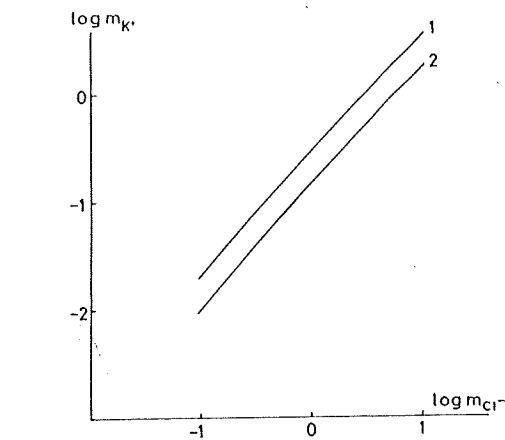

Fig. 3. *The variation of concentration of K^+ with that of Cl^- in aqueous solution in equilibrium with the silicate mineral assemblages at 250°C.*
1: *Albite-sericite-Na montmorillonite-quartz*
2: *Albite-sericite-K feldspar-quartz*

Fig. 2. *The variation of pH with concentration of Cl^- in aqueous solution in equilibrium with the silicate mineral assemblages at 250°C.*
1: *Albite-sericite-Na montmorillonite-quartz*
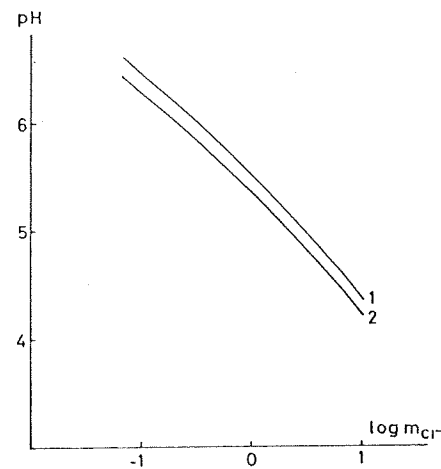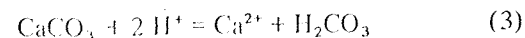2: *Albite-sericite-K feldspar-quartz*

following equilibrium.

$$CaCO_3 + 2 H^+ = Ca^{2+} + H_2CO_3 \qquad (3)$$

The equilibrium constant for this reaction is expressed as,

$$K = a_{Ca^{2+}} \cdot a_{H_2CO_3} / a_{H^+}^2 \qquad (4)$$

This equation shows that activity of Ca^{2+} is related to pH, concentration of H_2CO_3 and temperature. Because pH is related to the concentration of Cl^- for the equilibrium curves 1 and 2 in Fig. 2, the relation between the concentrations of Ca^{2+} and Cl^- can be derived for calcite-albite-sericite-K feldspar-quartz (curves 4 7 in Fig. 4) and calcite-albite-sericite-Na montmorillonite-quartz equilibrium (curves 5 and 8 in Fig. 4) with constant $m_{H_2CO_3}$. The range of $m_{H_2CO_3}$ in the solution in equilibrium with calcite is assumed to be 10^{-2} to 10^{-1}. The other equilibrium curves for the assemblage including Ca minerals are also drawn (Fig. 4). These assemblages are wairakite-albite-sericite-K feldspar-quartz (curve 3), Ca montmorillonite-albite-sericite-Na montmorillonite-quartz (curve 6), Ca montmorillonite-albite-sericite-K feldspar-quartz (curve 9) and anhydrite (curve 10). The effect of solid solution on the equilibrium curves is not considered because of the lack of thermochemical data of solid solution.

FOURNIER and TRUESDELL (1973) showed that $\log m_{Na^+}/m_{K^+} + 4/3 \log m_{Ca^{2+}}/m_{Na^+}$ is constant at constant temperature over 100°C. This value is about 0.8 at 250°C.

$$\log m_{Na^+}/m_K + 4/3 \, \log m_{Ca^{2+}}/m_{Na^+} = 0.8 \qquad (5)$$

Substitution of m_{Na^+} for m_{Cl^-} can be approximately made. The concentration of K^+ is expressed as a function of that of Cl^- (Fig. 3).
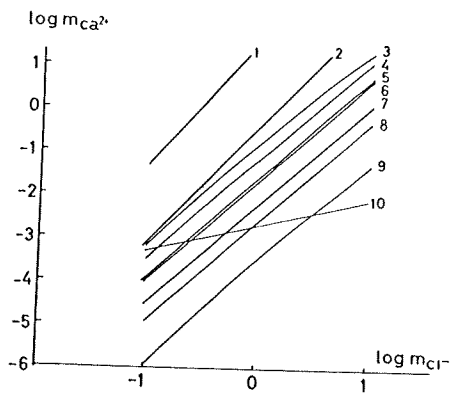
Fig. 4. The variation of concentration of Ca^{2+} with concentration of Cl^- in aqueous solution in equilibrium with a given mineral assemblage at 250°C.

1: Equilibrium curve based on albite-sericite-Na montmorillonite-quartz-aqueous solution equilibrium and Na-K-Ca relationship obtained by FOURNIER and TRUESDELL (1973).

2: Equilibrium curve based on albite-K feldspar-aqueous solution equilibrium and Na-K-Ca relationship obtained by FOUNIER and TRUESDELL (1973).

3: Wairakite-albite-sericite-K feldspar-quartz.

4: Calcite-albite-sericite-K feldspar-quartz ($m_{H_2CO_3} = 10^{-2}$).

5: Calcite - albite - sericite - Na montmorillonite - quartz ($m_{H_2CO_3} = 10^{-2}$).

6: Ca montmorillonite-albite-sericite-Na montmorillonite-quartz.

7: Calcite-albite-sericite-K feldspar-quartz ($m_{H_2CO_3} = 10^{-1}$).

8: Calcite - albite - sericite-Na -montmorillonite - quartz ($m_{H_2CO_3} = 10^{-1}$).

9: Ca montmorillonite-albite-sericite-K feldspar-quartz

10: Anhydrite ($m_{SO_4^{2-}} = 10^{-3}$).

Therefore, the empirical relation obtained by FOURNIER and TRUESDELL (1973) is changed into,

$$\log m_{Ca^{2+}} = 2 \log m_{Cl^-} + 6(\log \gamma_{Na^+}/\gamma_{K^+}) + k \quad (6)$$

where k is −0.9 and 1.0 for albite-K feldspar and albite-sericite-Na montmorillonite—quartz equilibrium, respectively and γ_i denotes activity coefficient of i species. These curves are drawn in Fig.4. The slopes of the curves of 1 and 2 are nearly the same as those of the other curves calculated.

It is very notable that curves for the common mineral assemblages at elevated temperatures (calcite - albite - sericite - K feldspar-quartz

($m_{H_2CO_3} = 10^{-2}$) and wairakite-albite-sericite-K feldspar-quartz assemblage) are close to the curve 2 in position. To the contrary, the curve for the mineral assemblage, albite-sericite-Na montmorillonite-quartz, derived from the Na-K-Ca relationship obtained by FOURNIER and TRUESDELL (1973) is quite different in position from the other curves calculated and the Ca^{2+} concentration in the solution in equilibrium with this mineral assemblage is higher than Na^+ concentration under high salinity conditions.

In conclusion, these results indicate that the chemical composition of natural water at 250°C is largely controlled by such minerals commonly occurring in nature as albite, K feldspar, sericite, calcite, wairakite and quartz.

Limited condition is treated in the present paper. Wider physicochemical and geologic environments have to be treated in order to interpret precisely the natural water composition.

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