

Formation of Illite in the Natural $K_2O-Al_2O_3-SiO_2-H_2O$ System in the Hydrothermal Clay Deposit of the Bobae Mine, Korea

보배광산의 열수변질 점토광상의 $K_2O-Al_2O_3-SiO_2-H_2O$
계에서의 일라이트 형성

Chang Oh Choo (추창오) · Soo Jin Kim (김수진)

Department of Geological Sciences, Seoul National University, Seoul 151-742, Korea
(서울대학교 지질학과)

ABSTRACT: Thermodynamic data of mineral reactions were used to construct a phase diagram for the formation of illite from andalusite at one bar and 325 °C in the hydrothermal alteration. Based on chemical compositions, the free energy of formation of illite coexisting with andalusite was calculated by assuming the ideal mixing in a binary system consisting of muscovite and pyrophyllite components. For illite with structural formula $K_{0.86}Al_{2.93}Si_{3.03}O_{10}(OH)_2$, its free energy of formation is -1147.727 kcal/mole at the condition under consideration.

The stability area of illite is more narrow than that of end-member muscovite and prefers lower activity of silica. Illite was formed by hydration of andalusite while pyrophyllite decomposed. Illitization took place preferentially at margin and/or along fractures of andalusite.

요약 : 열수변질작용동안에 수반되는 광물간의 열역학적인 반응관계를 통해 325 °C 와 1 바에서 광물의 상 안정다이어그램을 작성하였다. 홍주석과 공생관계에 있는 일라이트를 백운모와 엽납석 두가지로 이루어지는 이성분계의 이상적 혼합모델을 가정하여, 화학분석치로부터 생성자유에너지를 계산하였다. 구조화식이 $K_{0.86}Al_{2.93}Si_{3.03}O_{10}(OH)_2$ 인 일라이트의 생성자유에너지는 위 조건에서 -1147.727 kcal/mole이다.

일라이트의 안정영역은 이상적 백운모 단성분보다는 훨씬 좁게 나타나며, 실리카의 활동도가 백운모보다는 낮다. 일라이트는 엽납석이 분해되는 동안에 홍주석이 수화되어 형성된 것으로 홍주석의 가장자리나 균열을 따라 일라이트의 형성이 우세하게 일어났다.

INTRODUCTION

Kim et al. (1991) reported that hydrothermal illite occurs in the Bobae mine, Kimhae area, Kyungsangnam-do, Korea. The sericitic alteration zone is subdivided into three subzones; (1) illite-andalusite, (2) illite-pyrophyllite, and (3) illite-albite subzones. According to their fluid inclusion study and mineral assemblage, the temperature of formation of the main ore body is in the range 270-330 °C. The illite-andalusite subzone found in the upper part of the ore body is characterized by greenish white and pale pink colors. Illite in

this subzone is well-crystallized and corresponds to $2M_1$ polytype. But the mineral reaction in each subzone has not been studied yet. Illitic minerals exhibit grain coarsening and increase of crystallinity with rising temperature through all the alteration subzones. This phenomenon supports the so-called Ostwald ripening, that is, reduction of the free energy of surface of smaller crystals enforces them to dissolve to form larger stable crystals.

Knowledge of thermodynamic properties at various conditions is of importance in a phase equilibrium study concerning mineral reactions.

A large amount of experimental data has been accumulated on stability of minerals at a wide range of temperature, pressure, and chemical composition of solid phases and fluids. If thermodynamic data of species of interest are known, we come to assess which species are to be stable and what conditions are required to keep equilibrium under consideration. Many studies on hydrothermal equilibria are powerful tools for thermodynamic assessment of mineral reactions or formations (Sverjensky et al., 1991; Evans, 1965; Montoya and Hemley, 1975; Hass and Holdaway, 1974; Hemley et al., 1980; Velde, 1965; Huang and Keller, 1973). But, a considerable care must be paid to a quantitative application of experimental data on mineral stability because much works do not represent true equilibrium or the synthetic phases differ appreciably from natural minerals.

Most of previous phase equilibrium studies on the natural system have concentrated on geothermal areas where direct information about fluid chemistry and temperatures of co-existing assemblages can be easily obtained (Bishop and Bird, 1987; Aagaard and Helgeson, 1983; Bird and Norton, 1981; Capuano and Cole, 1982; Parry et al., 1984; McDowell and Eberls, 1980; Lonker et al., 1990). Little has been studied on clay deposits because it is difficult to get basic information, especially about temperature of formation and thermodynamic data of clay minerals forming a solid solution.

In this paper, we attempted to construct a phase diagram for the illite-andalusite subzone in the natural $K_2O-Al_2O_3-SiO_2-H_2O$ system using chemical data by the electron microprobe analyses and temperature data from fluid inclusion, and to interpret the formation of illite from andalusite.

EXPERIMENTAL

The samples analysed were collected from illite-andalusite subzone at the top of the ore body. Major minerals of this subzone are illite, andalusite and quartz. Average temperature

of formation of minerals was measured as 325 °C (or 623 K) from the fluid inclusion study ignoring pressure effect. Chemical analysis was done on polished thin section at 15kV with beam current of 10mA and beam diameter of 10 μ m using an electron microprobe. Total Fe was assumed to be ferrous. The polarizing microscope and back-scattered electron image (BEI) by a scanning electron microscope were used for the texture observation.

Thermodynamic data of illite were calculated from chemical data by electron microprobe analysis assuming ideal mixing with a binary system consisting of muscovite and pyrophyllite components. Calculation of the free energy of mixing and configuration entropy should be taken into account for a mineral forming a solid solution. All the thermodynamic data were calculated at one bar and 623 K. The free energy of reactions were used to construct a phase diagram. Detailed procedures for calculation of the thermodynamic data will be described in the following section.

THEORETICAL BACKGROUND

Calculation of the standard free energy of formation at temperature of interest is prerequisite for the phase equilibrium study in which changes of the free energy of reaction are used to calculate the equilibrium constant and to construct phase stability diagrams. Since minerals forming a solid solution have various cations in exchangeable sites, consideration of the free energy of mixing should be made. Methods of calculating the free energy at various conditions were derived from many authors (Gaskell, 1981; Nordstrom and Munoz, 1985; Navrotsky, 1985, 1986; Ganguly and Saxena, 1987). At one bar and temperatures of interest, the free energy of mixing can be formulated as follows.

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (1)$$

Since ΔH_{mix} term becomes zero for ideal mixing of a binary system, equation (1) reduces to

$$\Delta G_{\text{mix}} = -T\Delta S_{\text{mix}} \quad (2)$$

There are two contributions to the entropy of a solid solution, that is, the thermal contribution, S_{th} , and the configurational contribution, S_{conf} . If there is no volume change or heat change during mixing, then the only contribution to ΔS_{mix} is the change in configurational entropy. In statistical thermodynamics, entropy is related to randomness by the Boltzmann equation.

$$S = k \ln \omega \quad (3)$$

where k is Boltzmann's constant and ω is the degree of randomness. Assuming that A and B mix to form a solid solution and that all configurations of A and B atoms are equally probable, the number of distinguishable ways of arranging the atoms on the atomic sites which is ω_{conf} is defined as follows.

$$\omega_{conf} = (N_A + N_B)! / N_A! N_B! \quad (4)$$

where N_A is the number of A atoms and N_B the number of B atoms. Using Stirling's approximation ($\ln N! = N \ln N - N$) and the relationship $N_a k = R$ and $N_b k = R$ where R is the gas constant and N_a and N_b are atoms (Avogadro's number) per mole, the configuration entropy can be obtained.

$$\Delta S_{conf} = -R(X_A \ln X_A + X_B \ln X_B) \quad (5)$$

Since ΔS_{conf} equals ΔS_{mix} , ΔS_{conf} can be used to calculate the free energy of mixing. Because total configuration entropy in a mineral should sum up contributions to each site in which atomic substitution occurs, it can be formalized as follows.

$$\Sigma \Delta S_{conf} = \Sigma [-\nu R(X_A \ln X_A + X_B \ln X_B)]^{site} \quad (6)$$

where ν denotes numbers of mole of sites occurring substitution and R stands for gas constant. Configuration entropy should have positive values. From equation (2) and (6), the free energy of mixing can be written as follows.

$$\Delta G_{mix} = \nu RT[X_A \ln X_A + X_B \ln X_B]. \quad (7)$$

The total free energy of formation of minerals forming a solid solution with the binary system in ideal mixing is

$$G_{total} = (X_A G_A + X_B G_B) + \Delta G_{mix} \quad (8)$$

where the first term with parenthesis explains mechanical mixture to which mixing of two free energy function contributes and the second term represents chemical mixing. For example, the total free energy of formation of natural illite composed of muscovite and pyrophyllite components at 623 K can be written as follows.

$$G_{f, 623} = (X_{mus} G_{mus, 623} + X_{py} G_{py, 623}) + \Delta G_{mix} \quad (9)$$

The free energy of formation of each species is used to calculate equilibrium constants and reaction boundaries of minerals. Using the free energy of reaction, the equilibrium constant can be calculated as follows.

$$\Delta G_r^\circ = -RT \ln K \quad (10)$$

where ΔG_r° represents the standard free energy of reaction, i.e., total free energy of products minus total free energy of reactants.

RESULTS AND DISCUSSION

The illite-andalusite-quartz assemblage is observed in the upper part of the ore body. Rock specimens are shown in Figure 1. Anda-

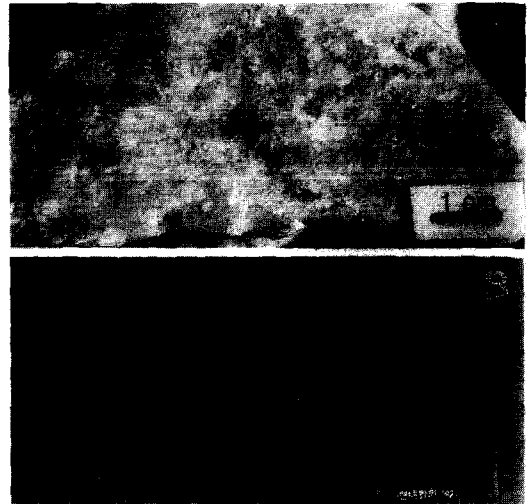


Fig. 1. Typical rock specimens of the illite-andalusite subzone. (A) Rock specimen (sample B10-2) showing andalusite (white) and illite (grey). (B) Rock specimen (sample B36) showing that quartz occurs in a lenticular form in the matrix of andalusite with a small amount of illite.

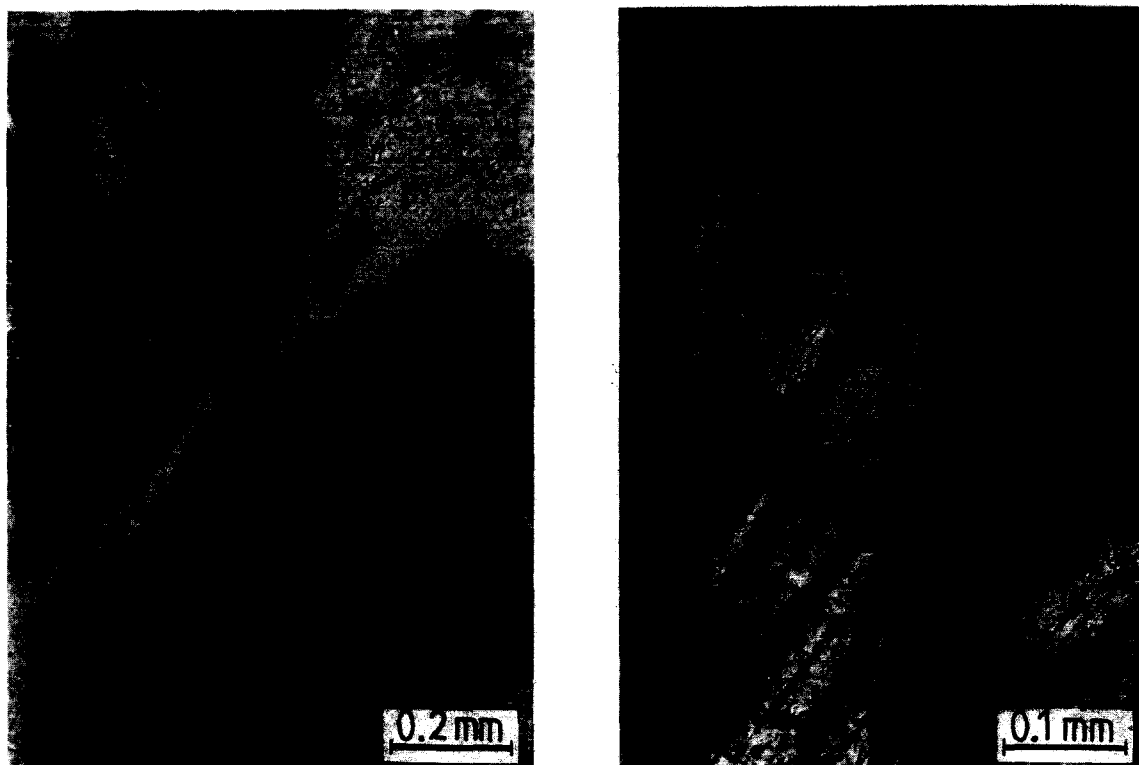


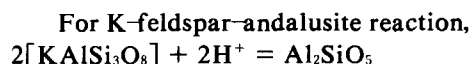
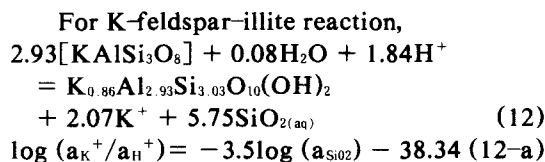
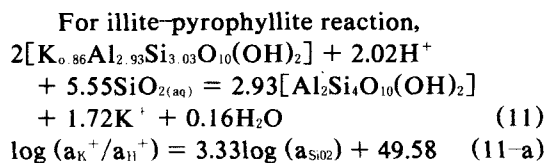
Fig. 2. Microphotographs showing the replacement of andalusite (a) by illite (i). (A) Radiating andalusite is replaced by illite. (B) Andalusite is replaced by illite along its margin and fractures.

illite has generally radiating or rarely tabular morphology which is somewhat different from that formed in regional metamorphism. Illitic minerals replace andalusite at the margin and/or along fractures of andalusite (Fig. 2). Quartz is ubiquitous in this zone. Illite is well-crystallized and corresponds to $2M_1$ polytype.

Chemical composition of minerals were obtained by the electron microprobe (Table 1). The structural formula of illite is $K_{0.86}Al_{2.93}Si_{3.03}O_{10}(OH)_2$. The free energy of formation of illite can be calculated considering the free energy of mixing and configuration entropy as described above. Thermodynamic data calculated for each species involved are given in Table 2. Equations involving possible reactions can be represented for the system $K_2O-Al_2O_3-SiO_2-H_2O$ at 1 bar and $325^\circ C$ (or 623 K), neglecting pressure effect. Equilibrium constant at 623 K is calculated using the equation as below.

$$\Delta G_{r,623}^{\circ} = -RT \ln K \quad (10-a)$$

where $\Delta G_{r,623}^{\circ}$ represents change of the standard free energy of reaction at 623 K. It is assumed that aluminium is conserved in minerals during all reactions. Possible reactions can be written as follows.



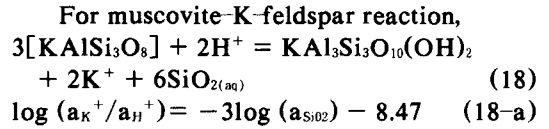
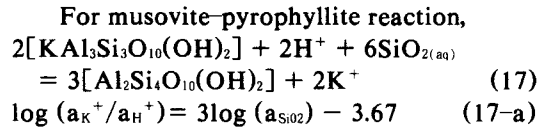
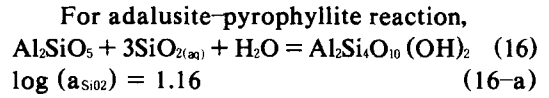
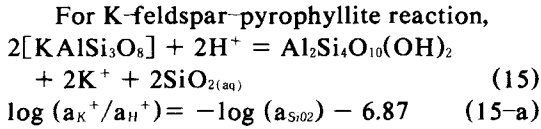
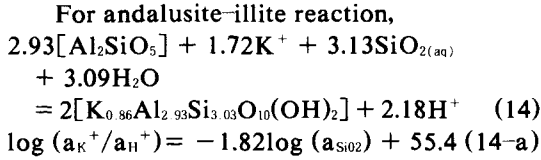
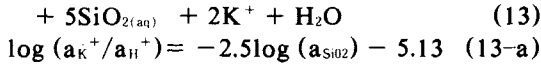


Table 1. Electron microprobe analyses of illites coexisting with andalusite.

| | S2-1 | S2-2 | S2-3 | S2-4 | S2-7 | S2-8 | Avg. |
|--|--------|--------|--------|--------|--------|--------|--------|
| SiO ₂ | 45.814 | 46.283 | 46.713 | 46.840 | 46.065 | 46.470 | 46.364 |
| Al ₂ O ₃ | 38.219 | 38.837 | 38.598 | 38.442 | 38.795 | 34.981 | 37.979 |
| TiO ₂ | 0.076 | 0.038 | 0.072 | 0.106 | 0.165 | 0.655 | 0.185 |
| Cr ₂ O ₃ | 0.151 | 0.109 | 0.052 | 0.050 | 0.049 | 0.023 | 0.072 |
| FeO | 0.394 | 0.205 | 0.314 | 0.165 | 0.208 | 1.226 | 0.419 |
| MgO | 0.004 | 0.000 | 0.012 | 0.000 | 0.000 | 1.339 | 0.226 |
| MnO | 0.000 | 0.073 | 0.000 | 0.040 | 0.019 | 0.011 | 0.024 |
| CaO | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Na ₂ O | 0.483 | 0.497 | 0.596 | 0.506 | 0.481 | 0.385 | 0.491 |
| K ₂ O | 10.120 | 10.463 | 9.990 | 10.285 | 10.544 | 10.330 | 10.289 |
| Total | 95.261 | 96.505 | 96.347 | 96.434 | 96.326 | 95.420 | 96.049 |
| Numbers of cations on the basis of O ₂₀ (OH) ₄ | | | | | | | |
| Si | 6.041 | 6.031 | 6.076 | 6.093 | 6.0116 | 6.156 | 6.069 |
| Al(IV) | 1.959 | 1.954 | 1.924 | 1.907 | 1.984 | 1.844 | 1.931 |
| Σ(Tet) | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 | 8.000 |
| Al(VI) | 3.981 | 4.025 | 3.993 | 3.987 | 3.988 | 3.617 | 3.932 |
| Ti | 0.008 | 0.004 | 0.007 | 0.010 | 0.016 | 0.065 | 0.018 |
| Cr | 0.016 | 0.011 | 0.005 | 0.005 | 0.005 | 0.002 | 0.007 |
| Fe ⁺² | 0.043 | 0.022 | 0.034 | 0.018 | 0.023 | 0.136 | 0.046 |
| Mg | 0.001 | 0.000 | 0.002 | 0.000 | 0.000 | 0.264 | 0.045 |
| Mn | 0.000 | 0.008 | 0.000 | 0.004 | 0.002 | 0.001 | 0.003 |
| Σ(Oct) | 4.048 | 4.071 | 4.042 | 4.034 | 4.034 | 4.086 | 4.051 |
| Ca | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| Na | 0.123 | 0.126 | 0.150 | 0.128 | 0.122 | 0.099 | 0.125 |
| K | 1.702 | 1.743 | 1.658 | 1.707 | 1.757 | 1.746 | 1.719 |
| Σ(Int) | 1.826 | 1.869 | 1.808 | 1.834 | 1.878 | 1.844 | 1.843 |
| Layer charge | | | | | | | |
| Tet. | -1.959 | -1.954 | -1.924 | -1.907 | -1.984 | -1.844 | -1.931 |
| Oct. | 0.151 | 0.208 | 0.131 | 0.080 | 0.115 | 0.158 | 0.124 |
| Int. | 1.826 | 1.869 | 1.808 | 1.834 | 1.878 | 1.844 | 1.843 |
| Total | 0.019 | 0.061 | 0.015 | 0.008 | 0.010 | 0.058 | 0.036 |

Table 2. Thermodynamic data calculated at 1 bar and 325 °C.

| Species | Data sources |
|--|--------------|
| 1. Illite: $K_{0.86}Al_{2.93}Si_{3.03}O_{10}(OH)_2$ | |
| $X_{mus} = 9.4815(X_K)(X_{Al})^2_{oct}(X_{Al})_{tet}(X_{Si})^4 = 0.8626$ | |
| $X_{py} = (X_V)(X_{Al})^2_{oct}(X_{Si})^4 = 0.0261$ | |
| $\Delta G_{mix} = -3.093$ kcal/mole | |
| $G_f = -1147.727$ kcal/mole | (4) |
| 2. Others | |
| Muscovite: $G_f = -1289.667$ kcal/mole | (1) |
| Pyrophyllite: $G_f = -1230.534$ kcal/mole | (1) |
| K-feldspar: $G_f = -882.989$ kcal/mole | (1) |
| Andalusite: $G_f = -572.936$ kcal/mole | (1) |
| $SiO_{2(aqueous)}$: $G_f = -203.67$ kcal/mole | (2) |
| $H_2O_{(water)}$: $G_f = -56.485$ kcal/mole | (1) |
| K^+ : $G_f = -44.418$ kcal/mole | (3) |

(1) Helgeson et al. (1978), (2) Walther and Helgeson (1977), (3) NBS data (1982), and (4) this study

Using equilibrium constants of above reactions, an activity-activity diagram was constructed at one bar and 325 °C (or 623 K). The diagram is given in Figure 3. The stability of minerals involved can be explained from this figure. The stability area of pyrophyllite is relatively wide at values of $\log(a_K^+/a_{H^+})$ and $\log(a_{SiO_2})$, which is ascribed to the composition of a solid solution in illite. The hatched area corresponds to the difference of the stability area between illite and end-member muscovite in which activity of pyrophyllite varies from 0.026 (at solid line) to zero (at broken line). The boundaries of reactions calculated by considering the mixing free energy are regarded as reasonable because they meet precisely at one point, that is, invariant point. Kaolinite can not be seen here since it is metastable at this condition. As activity of muscovite in illite increases to 1.0, the univariant boundary between muscovite and pyrophyllite components shifts to the area with higher activity of silica and lower activity of potassium, which is designated as the broken line. In this case, the stability area of end-member muscovite becomes wide, whereas that of pyrophyllite becomes very much narrow and also that of K-feldspar be-

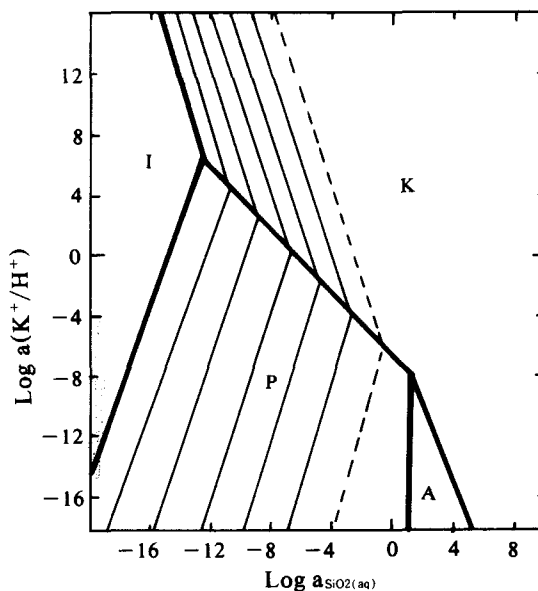
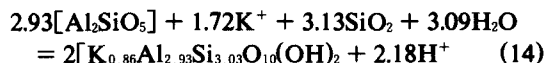
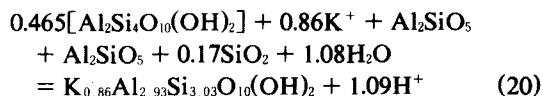


Fig. 3. Logarithmic activity diagram constructed at 1 bar and 325 °C. Abbreviations are as follows: andalusite (A), illite (I), K-feldspar (K), pyrophyllite (P). Bold solid lines are equilibrium boundaries of reaction. The broken line is the reaction boundaries between end-member muscovite and pyrophyllite, and between end-member muscovite and K-feldspar. The whole area lying in the left side to the broken line corresponds to the stability area of end-member muscovite. The hatched area is equivalent to the difference of stability area between end-member muscovite and illite.

comes slightly narrow. The invariant point shifts depending on activities of muscovite and pyrophyllite components in illite. If illite with $a_{mus} = 0.863$ changes to end-member muscovite with $a_{mus} = 1.0$, the invariant point of illite (or end-member muscovite)-pyrophyllite-K-feldspar changes, that is, $\log(a_K^+/a_{H^+})$ decrease from 6.5 to 5.5 and $\log(a_{SiO_2})$ increases from 12.5 to 0.8. Conversely increase of $\log(a_K^+/a_{H^+})$ and decrease of $\log(a_{SiO_2})$ must be necessary in order that illite can be stable with respect to muscovite.

Possible reactions of formation of illite by alteration of andalusite and pyrophyllite can be expressed, respectively.





The reaction boundary between illite and andalusite can not be drawn at the present condition because of thermodynamical instability of this reaction. Considering the fact that illite, andalusite and quartz coexist, it is probable that pyrophyllite is consumed to form illite. It seems likely that andalusite and silica still exist as remnants during the reaction. Such a possibility can be supported by the experiment by Hemley (1959) in which the assemblage mica-aluminosilicate-quartz would become stable with the breakdown of pyrophyllite. With the same value of silica activity, andalusite is more stable than pyrophyllite at higher temperatures above at least 340 °C (Walther and Helgeson, 1977). Therefore reaction (20) is more responsible for the present case. Formation of one mole of illite requires hydration of andalusite involving 1.08 mole of H₂O (water). Log (a_{SiO₂}) should decrease to form illite while log (a_{K⁺}/a_{H⁺}) increases.

CONCLUSIONS

For a mineral forming a solid solution whose thermodynamic data are unknown, the free energy of formation can be calculated based on chemical compositions and mixing functions. Such an approach is much accurate than a routine calculation for simple end-members. According to the phase diagram constructed in this work, the stability area of illite consisting of muscovite and pyrophyllite components is more narrow than that of end-member muscovite, indicating that the illite formation favors lower activity of silica. Formation of illite from andalusite requires hydration. In addition, increase of activity of potassium and decrease of activity of silica are essential for the formation of illite from andalusite. Illitization preferentially took place at the margin and/or along fractures of andalusite.

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