

ILLITIZATION OF KAOLINITE: THE EFFECT OF PRESSURE ON THE REACTION RATE

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Abstract—Studies of the paragenesis of authigenic illite in arkosic sandstones of various regions and ages have revealed that the illitization of kaolinite is an important reaction accounting for the formation of authigenic illite in sandstones during burial diagenesis. The illitization of kaolinite takes place at an intermediate burial depth of 3–4 km, where pressure can reach values of 100 MPa (≈ 1000 bars). The purpose of the present study was to analyze the effect of pressure on the rate of kaolinite illitization in alkaline conditions. Hydrothermal reactions were conducted on KGa-1b kaolinite in KOH solution at 300°C and under pressures of 500, 1000, and 3000 bars for 1 to 24 h. The visual examination of the X-ray diffraction (XRD) patterns indicated a notable influence of pressure on the reaction rate. Molar percentages of muscovite/illite formed at each time interval were calculated from the analysis of two diagnostic XRD peaks, representing the 060 reflections of kaolinite and muscovite/illite. The data were modeled to obtain the initial rate of conversion at each pressure. The results indicated that the initial rate of kaolinite to muscovite/illite conversion is one order of magnitude greater at 3000 bars than at 500 or 1000 bars. Comparison of these data with those in the literature show a faster conversion rate (several orders of magnitude) in an initially high-alkaline solution than in a near-neutral solution.

Key Words—Hydrothermal Reaction, Kaolinite, KOH, Muscovite/illite, Pressure, Reaction Rate, XRD.

INTRODUCTION

Illitization of kaolinite is an important reaction accounting for the formation of authigenic illite in sandstones during burial diagenesis (Hancock and Taylor, 1978; Sommer, 1978; Seemann, 1979; Dutta and Suttner, 1986). The evolution of kaolinite toward illite is caused by a number of different factors such as pH, temperature, pressure, surface area, cation availability, time, and rock/fluid ratio. Velde (1965) was the pioneer in demonstrating that muscovite can be synthesized rapidly from kaolinite and KOH solution. Chermak and Rimstidt (1990) determined experimentally the rate of transformation of kaolinite to muscovite/illite in KCl solution while Huang (1993) reported results on the kinetics of the kaolinite to K-mica conversion in alkaline solution. [In the pure $K_2O/Al_2O_3/SiO_2/H_2O$ system, as in the present case, muscovite and illite are indistinguishable and are grouped as muscovite/illite. For a detailed discussion of mineralogical differences, occurrences, and abundance of muscovite vs. illite see Bailey (1984)]. Huang (1993) found a conversion rate about two to three orders of magnitude faster in an initially highly alkaline solution than in near-neutral solution. Bauer *et al.* (1998) followed the entire reaction of kaolinite in KOH

solutions and described the formation of new phases and their relation to the different liquid/solid ratios. While studies have examined the influence of pH, temperature, and rock/fluid ratio on the illitization rate of kaolinite, none has been devoted to analyzing the influence of pressure on kaolinite illitization. Most reactions reported in the literature were conducted under the water-vapor pressure given by the temperature used in the reactor. Huang (1993) used an external pressure of 500 bars to analyze the transformation of kaolinite into muscovite/illite. However, Huang did not study the influence of pressure but the effect of alkalinity on the illitization rate.

Studying the transformation of kaolinite to illite with increasing pressure is important because the formation of illite *via* illitization of kaolinite takes place at an intermediate burial depth of 3–4 km, where pressure can reach values of 100 MPa (≈ 1000 bars) (Bjorlikke, 1980). The present experimental investigation was conducted in order to examine the influence of pressure on the kinetics of kaolinite illitization under alkaline conditions at a high rock/liquid ratio. X-ray diffraction was used to measure quantitatively the relative amounts of kaolinite and muscovite/illite in the reaction products at each pressure and time. The initial reaction rate was calculated for each pressure and compared with the studies of Huang (1993) and Chermak and Rimstidt (1990). Scanning electron microscopy (SEM) was used to obtain information on the influence of pressure on the morphology and chemical composition of the muscovite/illite particles.

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MATERIALS AND METHODS

Sample preparation

KGa-1b kaolinite, with the chemical formula $(\text{Si}_{3.83}\text{Al}_{0.17})^{\text{IV}}(\text{Al}_{3.86}\text{Fe}_{0.02}\text{Ti}_{0.11})^{\text{VI}}(\text{Ca},\text{Na},\text{K},\text{Mg})_{0.05}\text{O}_5(\text{OH})_4$, was obtained from the Source Clays Repository of The Clay Minerals Society. A small amount of anatase appears as an impurity phase, as observed in the XRD pattern (Figure 1). Each sample was prepared by placing ~100 mg of powdered kaolinite into a gold capsule (30 mm long, 5 mm o.d., 4 mm i.d.) containing 100 μL of KOH solution (2.85 M). The gold capsules were welded shut and weighed before and after hydrothermal treatment to detect leakage during the run. Samples that leaked were discarded. The gold capsules were also flattened after welding to eliminate free space within the experimental volume. The hydro-

thermal experiments were conducted using a stainless-steel hydrothermal reactor in horizontal resistance furnaces. Three batteries of experiments were run: at 500, 1000, and 3000 bars for 1 to 24 h and at a constant temperature of 300°C. The start time began when the desired pressure and temperature values were attained. After the hydrothermal reaction, each capsule was cut open and the solid sample was washed with distilled water, filtered, and dried at room temperature.

Characterization techniques

X-ray diffraction patterns were recorded using a PANalytical X'Pert Pro diffractometer, with Ni-filtered $\text{CuK}\alpha$ radiation, $0.05^\circ 2\theta$ steps, and counting time of 3 s. Selected divergence, antiscattering, and receiving slits were $1/4^\circ$, $1/2^\circ$, and 0.6 mm, respectively. For quantitative analysis of the reaction progress, an XRD

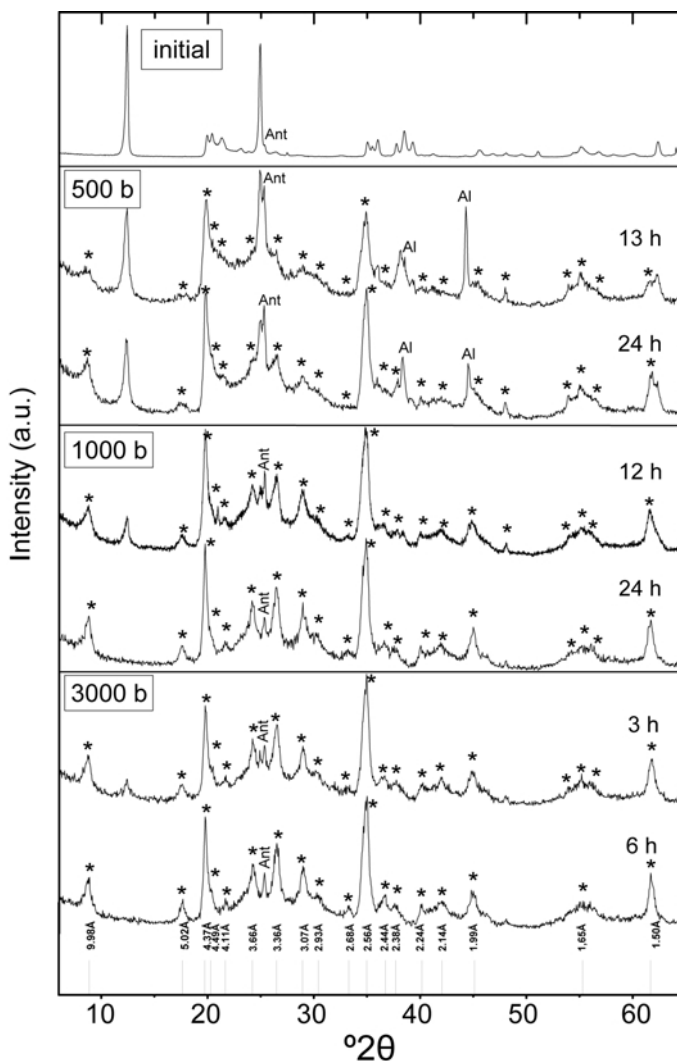


Figure 1. Selected XRD patterns of kaolinite before (top) and after hydrothermal treatment in 2.85 M KOH solution at 300°C at 500, 1000, or 3000 bars for different times. *Reflections from muscovite/illite. Al: Al reflections from the sample holder. Bottom: experimental d values of muscovite/illite synthesized in the present study.

calibration curve was prepared from a series of mixtures containing various proportions of the starting kaolinite and a muscovite/illite that was prepared by complete conversion from kaolinite at 350°C and 3500 bars for 168 h in 2.85 M KOH solution. A 20 mg portion of each composition was mixed thoroughly using an agate mortar, placed on an Al rotating sample holder, and pressed lightly to obtain a flat surface. The XRD patterns were then collected over the 58–64°2 θ range with steps of 0.03° and a counting time of 500 s. Slit selections were the same as given above. This 2 θ range contains the 060 reflections of muscovite/illite at 61.73°2 θ and kaolinite at 62.33°2 θ . The XRD patterns were fitted to two pseudo-Voigt functions using the *ProFit* 1.0c software (Sonneveld and Delhez, 1996), which takes into account the $K\alpha_1/K\alpha_2$ ratio. The ratio $I_m/(I_m+I_k) \times 100$, where I_m indicates the integral intensity of the pseudo-Voigt function fitted to the muscovite/illite reflection at 61.73°2 θ and I_k represents the integral intensity of the pseudo-Voigt function fitted to the kaolinite reflection at 62.33°2 θ , was plotted vs. the nominal wt.% muscovite/illite in the mixtures (Figure 2). The graph of the area ratio vs. the relative quantities of muscovite/illite and kaolinite was linear (least-squares regression analysis gives $y = 3.533 + 0.914x$, $R = 0.994$) due to the similar mass absorption coefficients of both minerals. The areas under the curve of the 060 reflections of kaolinite and muscovite/illite provided, therefore, a direct measurement of the relative quantities of muscovite/illite and kaolinite in a sample containing these two minerals as dominant products. The relative

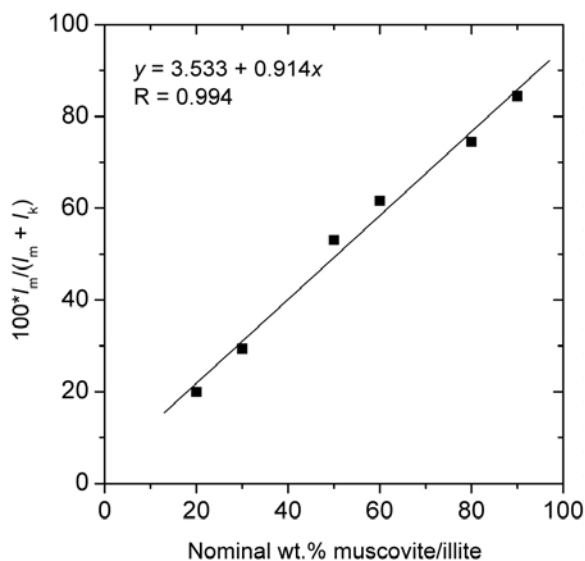


Figure 2. Working curve showing the linear relationship between the 060 area ratios and amount of muscovite/illite in standard mixtures of muscovite/illite and kaolinite. I_m = integral intensity of the pseudo-Voigt function fitted to the muscovite/illite reflection at 61.73°2 θ ; I_k = integral intensity of the pseudo-Voigt function fitted to the kaolinite reflection at 62.33°2 θ .

uncertainty for measuring wt.% of muscovite/illite in the run product was $\pm 5\%$.

Scanning electron microscopy images were recorded using an HITACHI S-4800 FEG-SEM microscope with a field emission gun operating at 20 kV acceleration voltage. The microscope was equipped with an XFlash Detector 4010 (Bruker AXS) for energy dispersive X-ray analysis. The samples were dispersed in ethanol by sonication and dropped on a conventional carbon-coated copper grid.

RESULTS AND DISCUSSION

Influence of pressure on the conversion rate of kaolinite to muscovite/illite

The XRD patterns of samples treated at 500 bars for 1, 4, or 7 h (not shown) exhibited only unmodified reflections of kaolinite, as well as a very broad reflection at $\sim 30^\circ 2\theta$, whereas the XRD patterns of reaction products from the 500 bar treatment at greater reaction times and from 1000 or 3000 bar treatments at all times revealed significant differences (Figure 1). The XRD patterns of the samples treated for 13 and 24 h at 500 bars contained, in addition to the reflections characteristic of kaolinite, a set of new reflections of low intensity and large peak width (although more resolved in the sample treated for 24 h), indicating the incipient crystallization of muscovite/illite (ICDD card 29-1496). The muscovite/illite pattern contained a reflection at 30°2 θ that coincided with that observed at shorter times. The position of the muscovite/illite basal reflection (8.71°2 θ = 10.14 Å) indicates a basal spacing characteristic of 2:1 (TOT) layers with dehydrated interlayer K^+ ions. The 060 muscovite/illite reflection was located at 61.73°2 θ (corresponding to a d_{060} value of 1.503 Å), compared with 62.33°2 θ in the parent kaolinite (corresponding to a d_{060} value of 1.490 Å). The reflections at 4.11, 3.66, 3.07, and 2.68 Å (Figure 1) indicate that the mica polytype formed was 1M at any pressure value.

Increasing pressure to 1000 bars caused the formation of incipient muscovite/illite crystals after 6 h of hydrothermal reaction, as inferred from a broad peak centered at $\sim 8.7^\circ 2\theta$ (not shown). Several low-intensity peaks of a K-F zeolite (ICDD card 38-216) metastable phase were also observed in the XRD patterns of the samples treated for shorter periods. The pattern of the sample treated for 12 h (Figure 1) shows, in addition to low intensity, poorly resolved kaolinite reflections, the whole set of reflections corresponding to muscovite/illite (ICDD card 29-1496). After 24 h, the XRD pattern displayed muscovite/illite reflections exclusively.

When pressure was increased to 3000 bars, muscovite/illite reflections were observed after only 3 h (Figure 1), coexisting with poorly defined kaolinite reflections. After 6 h of reaction, only muscovite/illite reflections were observed in the XRD patterns.

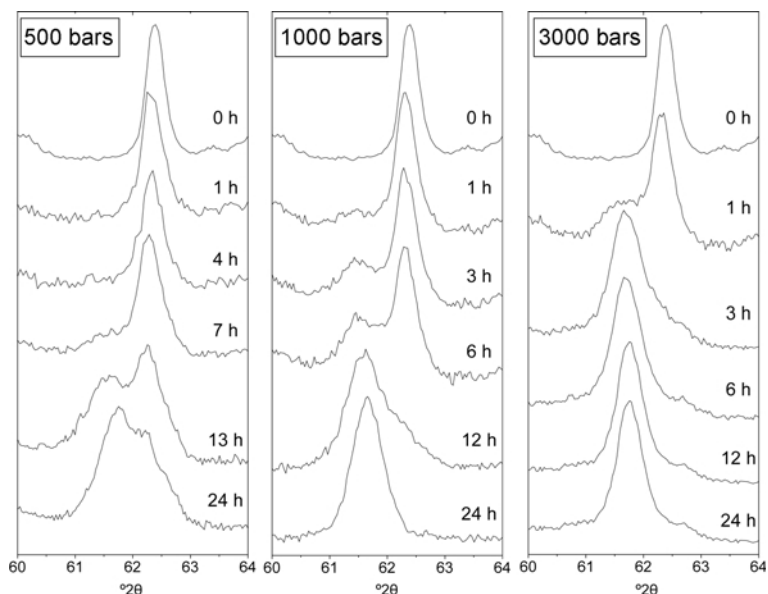


Figure 3. Selected XRD patterns showing the behavior of the 060 reflections of kaolinite and muscovite/illite at 300°C and 500, 1000, or 3000 bars, with increasing reaction time.

Increasing reaction time to 12 and 24 h (not shown) failed to change the structural reflections of muscovite/illite, while the basal reflections were more intense and narrower, mainly due to the increase of coherent thickness.

These results show a clear dependence of the reaction rate on pressure. At the lowest pressure used in this study, 500 bars, the first muscovite/illite crystals appeared after 13 h of reaction. When the pressure was raised to 1000 bars, signs of muscovite/illite crystals appeared after 6 h of reaction and, finally, at 3000 bars, clear reflections of muscovite/illite were observed after only 3 h.

Two diagnostic peaks were chosen to measure quantitatively the relative amounts of kaolinite and muscovite/illite in the reaction products. A peak at $62.33^\circ 2\theta$ is the 060 reflection of kaolinite while the neighboring peak at $61.73^\circ 2\theta$ is the same reflection as in the muscovite/illite structure. The muscovite/illite peak increased as the kaolinite peak decreased with increasing reaction time (Figure 3), but the changes occurred at different times depending on pressure. The wt.% of muscovite/illite in each sample was estimated from the integrated intensities of both reflections, as explained in the Materials and Methods section, and converted to mole fractions of muscovite/illite (X_{illite}) and kaolinite ($X_{\text{kaolinite}}$) (Table 1). The influence of pressure on the amount of muscovite/illite formed is clearly observed in the plot (Figure 4a) of muscovite/illite mole fraction vs. reaction time for each pressure. These data were modeled using an initial rate method similar to that of Huang (1993), who studied the reaction kinetics of kaolinite to muscovite/illite in KOH solution at 500 bars and different temperatures. Huang (1993) carried out a

polynomial fitting of the data to an empirical equation for each temperature, following Chermak and Rimstidt (1990), who studied the reaction kinetics of kaolinite to muscovite/illite in KCl solution. The data reported here, however, fitted better to an exponential growth function (solid lines in Figure 4a), which, because it implies no specific reaction mechanism, was used exclusively to estimate the influence of pressure on the reaction rate. The initial rates (dX_{illite}/dt at $t = 0$) were calculated by differentiating the empirical equations and the results revealed a strong dependence on pressure (Figure 4b). The initial rate of conversion of kaolinite to muscovite/illite was one order of magnitude greater at 3000 bars

Table 1. Experimental results for conversion of kaolinite to muscovite/illite with KOH solution at 300°C and 500, 1000, and 3000 bars.

Pressure (bars)	Time (h)	X-ray peak ratio (illite/(K + illite))	X_{illite}
500	7	0.13	0.09
	13	0.50	0.39
	24	0.67	0.56
1000	1	0.09	0.06
	3	0.31	0.23
	6	0.43	0.33
	12	0.78	0.70
	24	1	1
3000	1	0.36	0.27
	3	0.88	0.83
	6	0.95	0.94
	12	1	1

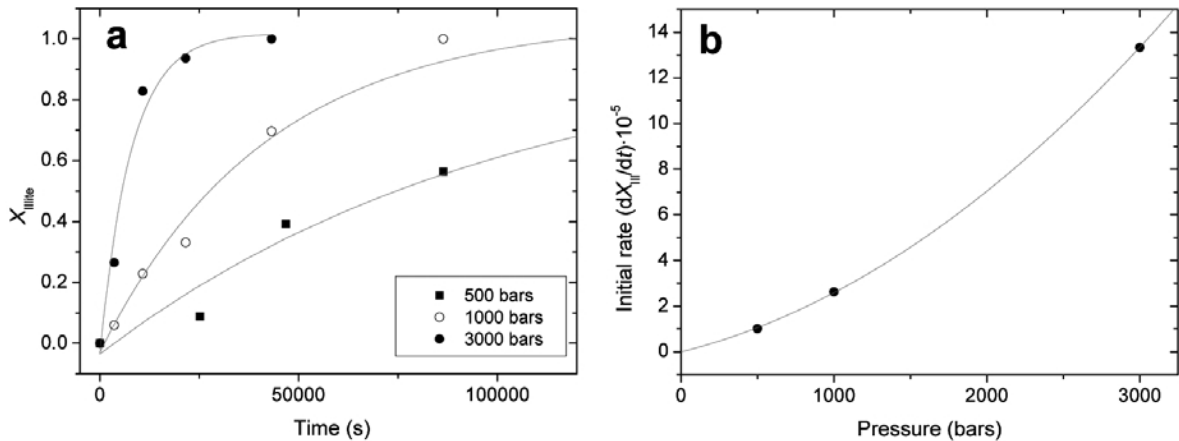


Figure 4. (a) Data points: mole fraction of muscovite/illite grown from kaolinite hydrothermally treated at 500, 1000, or 3000 bars vs. reaction time. Solid lines: exponential growth function obtained from the fitting of the experimental data points for each pressure. (b) Initial reaction rate as a function of pressure for kaolinite to muscovite/illite conversion.

than at 500 or 1000 bars. Comparison of these data with those presented by Huang (1993) for the same P - T conditions shows a slightly smaller value for the initial

rate in the present case, although the order of magnitude is the same for both sets of data ($2.36 \times 10^{-5} t^{-1}$ vs. $1.01 \times 10^{-5} t^{-1}$), the difference probably being due to

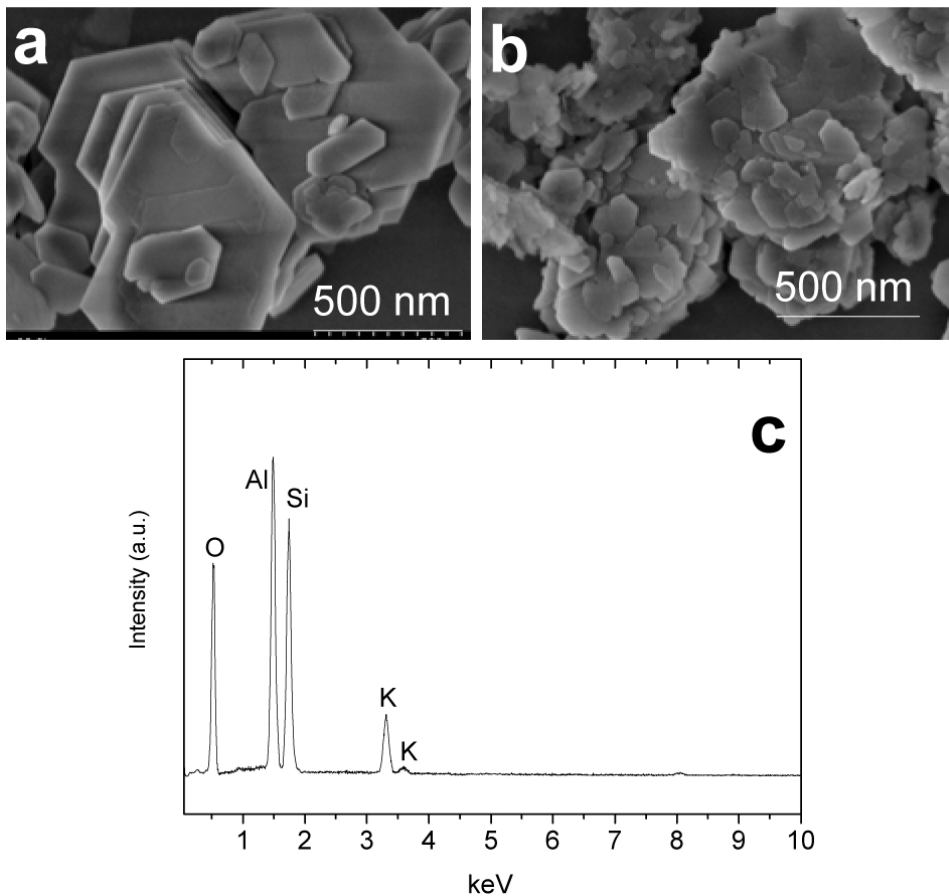


Figure 5. (a,b) SEM images showing the hexagonal morphology of the starting KGa-1b kaolinite particles and the packing of muscovite/illite layers, with poorly defined edges, obtained after hydrothermal reaction in KOH solution at 300°C and 1000 bars for 24 h. (c) EDX spectrum of the muscovite/illite particle shown in part b.

the differences in the experimental setting. In addition, the experiments presented in the present study confirmed the faster conversion rate (several orders of magnitude) in an initially highly alkaline solution than in a near-neutral solution ($17.1 \times 10^{-8} \text{ t}^{-1}$ at 307°C), as is the case in the experiments of Chermak and Rimstidt (1990).

Morphology of the reaction products

The starting kaolinite appeared as well defined hexagonal particles, with diameter in the range 100 to 1000 nm (Figure 5a). Muscovite/illite particles obtained from the hydrothermal treatments (Figure 5b) displayed a morphology which still resembled that of the hexagonal parent kaolinite; the platelets showed very irregular edges and their average size decreased with respect to that of kaolinite. The EDX spectra (Figure 5c) were recorded in a number of muscovite/illite particles. The average atomic % of Al, Si, and K was 41.57, 41.68, and 16.75, respectively. These results indicate a very similar number of Si and Al atoms, which is compatible with a chemical formula close to that for muscovite ($\text{K}(\text{Si}_3\text{Al})\text{Al}_2\text{O}_{10}(\text{OH})_2$). The K content appeared slightly greater than that expected for muscovite, which may be due to the presence of residual K on the particle surfaces not removed during washing.

CONCLUSIONS

Pressure exerts a notable influence on the kaolinite to muscovite/illite conversion rate. The initial rate of conversion of kaolinite to muscovite/illite was one order of magnitude greater at 3000 bars than at 500 or 1000 bars. In addition, the conversion rate in an initially alkaline solution was several orders of magnitude quicker than in a near-neutral solution (Chermak and Rimstidt, 1990).

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REFERENCES

- Bailey, S.W. (1984) Crystal chemistry of the true micas. Pp. 13–60 in: *Micas* (S.W. Bailey, editor). Reviews in Mineralogy, **13**, Mineralogical Society of America, Washington, D.C.
- Bauer, A., Velde, B., and Berger, G. (1998) Kaolinite transformation in high molar KOH solutions. *Applied Geochemistry*, **13**, 619–629.
- Bjorlikke, K. (1980) Clastic diagenesis and basin evolution. *Revista del Instituto de Investigaciones Geológicas. Diputación Provincial, Universidad de Barcelona*, **34**, 21–44.
- Chermak, J.A. and Rimstidt, J.D. (1990) The hydrothermal transformation rate of kaolinite to muscovite/illite. *Geochimica et Cosmochimica Acta*, **54**, 2979–2990.
- Dutta, P.K. and Suttner, L.J. (1986) Alluvial sandstone composition and paleoclimate. II. Authigenic mineralogy. *Journal of Sedimentary Petrology*, **56**, 346–358.
- Hancock, N.J. and Taylor, A.M. (1978) Clay minerals diagenesis and oil migration in the Middle Jurassic Brent Sand Formation. *Journal of the Geological Society of London*, **135**, 69–72.
- Huang, W.L. (1993) The formation of illitic clays from kaolinite in KOH solution from 225°C to 350°C. *Clays and Clay Minerals*, **41**, 645–654.
- Seeman, U. (1979) Diagenetically formed interstitial clay minerals as a factor in Rotliegend sandstone reservoir quality in the North Sea. *Journal of Petroleum Geology*, **1**, 55–62.
- Sommer, F. (1978) Diagenesis of Jurassic sandstones in the Vicking Graben. *Journal of the Geological Society of London*, **125**, 63–67.
- Sonneveld, E.J. and Delhez, R. (1996) *ProFit 1.0c*, Philips Electronics NV, The Netherlands.
- Velde, B. (1965) Experimental determination of muscovite polymorph stabilities. *American Mineralogist*, **50**, 436–449.

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