

THE EFFECT OF CHEMICAL PRETREATMENTS ON THE COMPOSITION OF NATURAL ILLITE

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INTRODUCTION

In order to remove impurities, natural illite is often subjected to chemical pretreatments before analysis, the assumption being that such pretreatments have little or no effect on the composition of illite. Bulk analyses are sometimes reported before and after pretreatment (Aja et al. 1991) but, because the contribution of the impurities to the bulk composition is unknown, the possible effects of chemical pretreatments on the composition of illite cannot be assessed. Recently, Rosenberg and Hooper (1996) have shown that analytical transmission electron microscopy (ATEM) techniques, which exclude impurities, can be used to determine the bulk compositions of relatively pure illite by averaging the analyses of at least 50 crystals per sample. This approach can be applied to impure illite in order to determine the effect of chemical pretreatments on the composition of natural illite.

A considerable body of chemical data exists for the illite samples selected for this study. However, it is difficult to make comparisons because different samples from the same locality may not have the same composition and because varying methods of sample preparation and degrees of pretreatment have been employed to remove impurities. The purpose of this study is to compare the chemical compositions of identical samples before and after a uniform set of treatments using a well-defined analytical procedure.

MATERIALS AND METHODS

Five natural illites—Goose Lake (GL) (Grim and Bradley 1939; Gaudette et al. 1966), Beavers Bend (BB) (Mankin and Dodd 1963; Gaudette et al. 1966), Fithian (F) and Marblehead (MH) (Gaudette 1965; Gaudette et al. 1966) and Silver Hill (SH) (Hower and Mowatt 1966)—were selected for this study. Four of these illites (BB, MH, F and SH) are considered to be standard illites by Środoń and Eberl (1984) inasmuch as they are widely known and often used in published studies; all 4 are mixtures of I and ISII (Środoń 1984; Środoń and Eberl 1984). GL and BB (Routson and Kittrick 1971; Sass et al. 1987), MH (Aja et al. 1991) and F (Routson and Kittrick 1971) have been further

characterized and used as starting materials in experimental studies.

The untreated samples were prepared for ATEM analysis by suspension of mg quantities in distilled water and dispersion onto a TEM grid with a carbon-film substrate. Larger quantities of GL, BB, MH and F were disaggregated by shaking in 2% K₂CO₃ solutions for up to 8 h. SH could not be disaggregated by this method; it was ground in a ball mill containing a 1 M KCl solution for 3 d. The illites were then washed in distilled water and treated for the removal of carbonates (acetate buffer procedure), organic matter (H₂O₂ procedure) and iron oxide coatings (citrate-dithionite procedure) using the methods of Kittrick and Hope (1963), which are based on the work of Jackson (1956) and Mehra and Jackson (1960). These treatments were modified in that Na salts were replaced by their K equivalents to avoid Na contamination in the interlayer site. The samples were then saturated with K⁺ using 1 M KCl solution, followed by washing in distilled water to remove excess salt; size-separated to retain the 0.2–5 μm size fraction by gravity settling and centrifugation; and dried at 60 °C. Milligram quantities of the treated illites were then suspended in distilled water and dispersed on a TEM grid with a carbon-film substrate for ATEM analysis.

The samples were analyzed using a KEVEX-EDX system with a Be window on a Hitachi H-600 scanning transmission electron microscope (STEM) at 100 kV in the STEM mode. Analyses were carried out at 1000 cps and 30% deadtime on at least 50 individual grains (range 50–59) of the same approximate thickness, isolated in a field of view at a magnification of 20–30,000 ×. A nominal raster size of (1.3 μm)² was used to minimize diffusion; count time was 60 s (live time). Under these conditions, alkali loss was not anticipated (Mackinnon and Kaser 1987) and was not observed even during repeat analyses of the same grain; K/Si and Al/Si ratios remained constant during the course of the analyses (Yates 1993). Under the electron microscope, all of the samples appear to consist of a single illitic phase.

Analyses were performed assuming “thin film” conditions with *k*-ratios determined from silicate stan-

Table 1. Comparison of average structural formulae (half unit cell) of natural illite samples before and after pretreatments. Numbers of atoms and standard deviations (1σ).

	Goose Lake		Beavers Bend		Silver Hill		Marblehead		Fithian	
	UTr† (59)§	Tr‡ (54)	UTr (55)	Tr (51)	UTr (50)	Tr (51)	UTr (55)	Tr (52)	UTr (52)	Tr (51)
Si	3.56 0.15	3.55 0.10	3.29 0.07	3.37 0.13	3.33 0.16	3.32 0.18	3.53 0.03	3.44 0.13	3.35 0.13	3.36 0.09
Al	2.00 0.21	2.05 0.19	2.37 0.14	2.11 0.26	1.97 0.24	2.10 0.29	1.96 0.06	2.12 0.21	2.09 0.16	2.18 0.16
Fe	0.24 0.06	0.22 0.05	0.19 0.06	0.30 0.15	0.37 0.17	0.32 0.28	0.09 0.01	0.13 0.08	0.31 0.13	0.24 0.07
Mg	0.17 0.05	0.17 0.07	0.14 0.05	0.20 0.08	0.28 0.17	0.24 0.12	0.39 0.04	0.29 0.10	0.19 0.06	0.21 0.08
Ca	0.04 0.02	0.03 0.01	0.01 0.00	0.03 0.01	0.03 0.02	0.03 0.01	0.03 0.01	0.03 0.01	0.06 0.02	0.03 0.01
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.11 0.14	0.08 0.10	0.00	0.04 0.05
K	0.49 0.09	0.49 0.09	0.72 0.05	0.66 0.05	0.63 0.04	0.65 0.07	0.61 0.03	0.67 0.06	0.50 0.09	0.49 0.07

† UTr = Untreated.

‡ Tr = Treated.

§ Number of grains analyzed.

dards (Cliff and Lorimer 1975). Calibration of k -values was accomplished using 5 non-phyllsilicate electron microprobe (EMP) standards and checked by comparison of ATEM and EMP analyses of a standard muscovite (Rosenberg and Hooper 1996). Grain thicknesses were estimated by transmitted electron intensities; grains with similar electron densities were selected visually. All iron was calculated as Fe_2O_3 .

ANALYTICAL RESULTS AND THEIR IMPLICATIONS

The results of the ATEM analyses are compared in Table 1. Peak integrals were converted to oxide wt% using the k -ratios and normalized to 100%. Structural formulae (Table 1) were calculated from these weights percent on the basis of 11 O atoms and normalized to a total of 6 cations in tetrahedral and octahedral sites.

None of the samples analyzed can be considered to be K-saturated because suspension of grains in distilled water in preparation for ATEM analysis removes some K from smectitic edges of fundamental illite particles (Yates 1993). K-contents reported in bulk analyses of these illites also probably reflect some degree of K undersaturation due to sample preparation procedures.

The chemical compositions of all 5 illites are unchanged after chemical treatments within the precision (1σ) of the analyses. Furthermore, the standard deviations before and after treatment remain about the same for the GL, SH and F illites. Thus, the assumption that chemical treatments do not, in general, affect the chemistry of illites appears to be justified.

However, the scatter of the analytical data for Si, Al, Fe and Mg in MH and, to a lesser extent, in BB illite (Table 1), increases considerably after treatment,

although the standard deviations after treatment are similar to those of the other samples. The increased degree of scatter in BB and MH illites cannot be due to the effects of pretreatments on smectitic components because these illites are the least expandable ($\leq 5\%$; Gaudette et al. 1966); GL that is 25–30% expandable (Gaudette et al. 1966) and, thus, has a significant smectitic component, shows no increase in scatter after treatment. The significance of this observation is unknown, but it suggests that some change has taken place in these samples and, therefore, that ATEM analyses before and after treatment may be necessary to assure that chemical treatments have not altered illite compositions.

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