DETERMINATION OF THE CHEMICAL COMPOSITION OF NATURAL ILLITES BY ANALYTICAL ELECTRON MICROSCOPY

Key Words—AEM, Bulk analysis, Illite, Sericite, XRF.

Several methods are available for bulk chemical analysis of clay minerals including wet chemical, XRF and electron microprobe techniques. While these approaches may be satisfactory for many chemical analyses of bulk samples, they necessarily include any mineral impurities that occur within the sample. Such impurities are often detected, but the XRD methods usually employed are not very sensitive. Small amounts of impurities can produce significant variations in bulk chemistry even at levels well below the 5 wt% necessary to assure detection by XRD (Warren and Ransom 1992). Efforts to remove impurities before analysis involve a variety of more or less effective pretreatments, for example, Kittrick and Hope (1963), which are assumed to leave clay mineral compositions unaltered, although this is not well-established. Thus, chemical analyses of clay minerals by conventional bulk methods have significant shortcomings.

During the last decade, the advent of analytical transmission electron microscopy (AEM) has offered a new approach to the analysis of clay minerals, which has the potential to overcome some of the shortcomings of earlier methods. Since AEM is capable of providing data on the scale of single crystals, it should be possible to determine chemical heterogeneities within bulk samples. However, in a previous AEM study of clay minerals dispersed on holey carbon substrates, Mackinnon and Kaser (1987) observed relatively large variations in estimated standard deviations that they attributed to differences in sample thickness, variations in sample composition and, to a lesser extent, variations in sample orientation, thus compromising the determination of intergranular variations. Use of ultramicrotomed samples greatly reduced the effects of thickness and orientation and would therefore, be highly desirable for studies of intergranular compositional variations. Although significant differences were observed between grains on C substrates by Mackinnon and Kaser (1987), AEM analyses were found to bracket values obtained by wet chemical analysis, raising the possibility of obtaining accurate impurity-free bulk chemical analyses of clay minerals using AEM techniques. However, this possibility has not been explored or tested.

In 1987, Eberl et al. characterized a suite of unusually pure sericites (illites) from fractures in hydrothermally altered volcanic rocks in and around the Silverton caldera in the western San Juan mountains of Colorado. The sericites were identified as R ≥ 3-ordered, mixed layer illite/smectites with expandabilities >4 and <14%. The chemical compositions of these illites were determined by bulk methods. The concentrations of MgO, Al_2O_3, SiO_2, Fe_2O_3, CaO and TiO_2 were determined by XRF; K_2O, Na_2O and SrO determined by atomic adsorption spectroscopy (AAS). Since they were unusually pure and had been well characterized, these samples seemed ideal for a comparative study.

MATERIALS AND METHODS

Nine of the 22 samples analyzed by Eberl et al. (1987) (AR1R, LF7, RM3, RM4, RM8, RM13, RM30, RM35A, SG4) were available for this study. Despite their unusual purity, some trace impurities were observed by XRD (Eberl et al. 1987) including jarosite (LF7, RM3, RM8, RM35A), quartz (RM35A, SG4), chlorite (AR1R) and pyrite (RM13). Many of the samples also contained small amounts of dickite and traces of anatase. However, separation of the <2 μm grain-size removed most of the quartz and dickite, and treatment with a Na acetate buffer and dithionite was used to remove sulfates and Fe hydroxides, followed by 1N NaCl exchange. The <2 μm size fraction was then Sr saturated by washing with 0.1N $SrCl_2$ solution. Thus, 7 of the 9 samples used in this study should have been free of impurities detectable by XRD when analyzed by Eberl et al. (1987). The results of the XRF and AAS analyses were used to calculate structural cell contents; TiO_2 was not included because of the presence of trace amounts of anatase and CaO was neglected because it was found to be present in very small quantities.

No further chemical pretreatments were attempted before AEM analysis. The samples were suspended in

Table 1. Composition of Brazilian muscovite: comparison of AEM and EMP analyses. Weight percents (g/100 g) and standard deviations (1 σ).

	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3
EMP	0.89	0.33	37.60	48.86	10.86	0.00	1.59
	0.04	0.08	0.45	0.58	0.39	0.01	0.50
AEM†	0.64	0.46	37.65	48.72	10.53	0.02	1.71
	0.43	0.38	0.87	0.65	0.45	0.03	0.22

† 20 analyses.

Table 2. Comparison of AEM (± 1 σ) and bulk chemical analyses of Silverton sericites (g/100 g).

	ARIR		LF7		RM3		RM4	
	AEM	Bulk†	AEM	Bulk	AEM	Bulk	AEM	Bulk
SiO_2	54.79 ± 1.15	55.08	52.25 ± 1.57	51.94	52.39 ± .86	52.78	53.24 ± 1.55	53.44
Al_2O_3	31.12 ± 1.07	29.92	34.07 ± 1.44	34.88	32.82 ± 1.17	33.25	32.38 ± 1.32	32.81
Fe_2O_3	1.95 ± .84	1.96	2.23 ± .53	2.27	2.67 ± .76	2.10	2.04 ± .64	1.91
MgO	1.58 ± .47	2.02	0.87 ± .43	0.87	0.98 ± .40	1.13	1.60 ± .44	1.62
CaO	0.03 ± .05	<.03	0.09 ± .12	<.02	0.01 ± .02	0.03	0.05 ± .13	<.03
MnO	0.05 ± .07	ND	0.01 ± .02	ND	0.01 ± .03	ND	0.01 ± .03	ND
Na_2O	0.27 ± .32	0.19	0.60 ± .48	0.16	0.23 ± .41	0.14	0.61 ± .49	0.11
K_2O	10.14 ± .94	10.49	9.77 ± .77	10.42	10.61 ± .40	9.82	9.93 ± 1.12	9.93
TiO_2	0.08 ± .07	0.28	0.11 ± .10	0.19	0.28 ± .62	0.75	0.12 ± .41	0.41

† Bulk analyses (Eberl et al. 1987) are normalized to 100 wt% of elements analyzed using AEM.

distilled water and dispersed onto a TEM grid with a c film substrate.

The samples were analyzed using a KEVEX-EDX system with a Be window on a Hitachi H-600 STEM at 100kV in the STEM mode. Analyses were carried out on at least 54 (range 54–67, avg. 58) single grains of the same approximate thickness, isolated in a field of view at a magnification of 20–30,000 X. A nominal raster size of $(1.3 \ \mu m)^2$ was used to minimize volatilization and 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. Analyses were performed assuming "thin film" conditions with k-ratios determined from silicate standards (Cliff and Lorimer 1975). Calibration of k-values was accomplished using 5 non-phyllosilicate electron microprobe (EMP) standards and checked by comparison of AEM and EMP analyses of a standard muscovite (Table 1). Grain thicknesses were estimated by transmitted electron intensities, while grains with similar electron densities were selected visually. Analytical error in AEM analyses of illite has been discussed by Warren and Ransom (1992). All Fe was calculated as Fe_2O_3. No additional trace impurities were observed under the electron microscope.

ANALYTICAL RESULTS AND THEIR IMPLICATIONS

Under the electron microscope, relatively large (>0.05 mμ) platy, mica-like crystals were observed for samples SG4 (Figure 1a) and RM35a. Most of the remaining samples consisted of smaller, lath-like (Figure 1b) and/or platy, mica-like crystals (AR1R, LF7, RM30), although the crystals from some samples (RM4, RM3, RM8, RM13) were less well-developed. Quartz impurities were observed in most samples (AR1R, LF7, RM3, RM8, RM13, RM30), kaolinite (dickite?) in a few samples (AR1R, RM3) and TiO_2 (anatase?) in two samples (RM8, RM35a). Samples RM4 and SG4 were found to be free of impurities.

The results of the AEM analyses are compared with the bulk chemical compositions determined by XRF and AAS (Eberl et al. 1987) in Table 2. Bulk analyses are normalized to 100 wt.% of the oxides analyzed by AEM. Structural formulas of the Silverton sericites (Table 3) were calculated from oxide weight percents (Table 2) on the basis of 22 oxygens and normalized to a total of 12 cations in tetrahedral and octahedral sites.

AEM and XRF and AAS analyses yield similar chemical compositions. The maximum difference for

Table 3. Comparison of structural formulae (full unit cell) of Silverton sericites.

	ARIR		LF7		RM3		RM4		RM8		RM13	
	AEM	Bulk†	AEM	Bulk	AEM	Bulk	AEM	Bulk	AEM	Bulk	AEM	Bulk
Si	6.90	6.90	6.58	6.48	6.64	6.62	6.69	6.68	6.71	6.60	6.78	6.64
Al-IV	1.10	1.10	1.42	1.52	1.36	1.38	1.31	1.32	1.29	1.40	1.22	1.36
Al-VI	3.51	3.32	3.61	3.62	3.54	3.54	3.49	3.50	3.63	3.58	3.53	3.52
Ti^{+4}	0.01	ND	0.01	ND	0.03	ND	0.01	ND	0.00	ND	0.01	ND
Fe^{+3}	0.18	0.18	0.21	0.22	0.25	0.02	0.19	0.18	0.20	0.22	0.14	0.14
Mn	0.01	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND	0.00	ND
Mg	0.29	0.38	0.16	0.16	0.18	0.22	0.30	0.30	0.16	0.18	0.31	0.32
Ca	0.00	ND	0.01	ND	0.00	ND	0.01	ND	0.01	ND	0.01	ND
Na	0.07	0.04	0.15	0.04	0.06	0.04	0.15	0.02	0.17	0.04	0.17	0.02
K	1.62	1.68	1.56	1.54	1.70	1.58	1.59	1.54	1.46	1.46	1.52	1.56

† Bulk, XRF and AAS data from Eberl et al. 1987.

Table 2. Extended.

RM8		RM13		RM30		RM35A		SG4	
AEM	Bulk	AEM	Bulk	AEM	Bulk	AEM	Bulk	AEM	Bulk
53.65 ± .66	52.94	54.15 ± .81	53.22	51.23 ± 2.08	52.50	54.77 ± .79	53.68	52.19 ± .87	51.92
33.34 ± .74	33.96	32.27 ± .77	33.09	36.97 ± 3.16	35.43	33.75 ± .39	34.13	35.54 ± .86	35.79
2.16 ± .35	2.31	1.51 ± .23	1.77	0.50 ± 1.96	0.09	0.88 ± .11	0.95	0.26 ± .12	0.45
0.84 ± .27	0.92	1.66 ± .30	1.71	0.61 ± .74	1.48	1.08 ± .36	1.40	1.01 ± .26	1.05
0.04 ± .06	<.02	0.09 ± .21	0.03	0.20 ± .53	<.03	0.09 ± .08	<.04	0.02 ± .05	<.03
0.01 ± .03	ND	0.02 ± .04	ND	0.01 ± .03	ND	0.01 ± .03	ND	0.60 ± .08	ND
0.72 ± .52	0.16	0.69 ± .72	0.12	0.25 ± .38	0.11	0.53 ± .49	0.15	0.41 ± .31	0.41
9.20 ± .41	9.23	9.53 ± .49	9.74	10.19 ± 1.93	10.00	8.82 ± .40	8.99	10.41 ± .48	9.96
0.04 ± .09	0.45	0.08 ± .08	0.49	0.05 ± .35	0.65	0.07 ± .07	0.65	0.10 ± .07	0.38

Si in tetrahedral coordination is less than 3% while maximum difference in octahedrally-coordinated Al is about 5%. Although the maximum variation of K within the interlayer site is 7%, most of the site occupancies calculated from AEM results are within 3 to 4% of the values obtained from bulk chemistry. Except for sample RM3, the results for octahedrally-coordinated Fe are also similar. The number of $^{VI}Fe^{3+}$ ions calculated for the structural formula of RM3 (Table 3) by Eberl et al. (1987) does not correspond to the chemical analysis published by these authors. Recalculation of the structural formula of RM3 using their data (Table 2) yields 0.24 Fe^{3+}, which agrees with the value calculated from AEM data (0.25 Fe^{3+}, Table 3). The number of Mg ions per formula unit also shows good agreement between AEM and bulk chemistry, but the numbers of Na ions were over estimated for about half the AEM analyses. Energy dispersive X-ray analysis used for the AEM studies does not appear to be a suitable method for the determination of Na in sericites with low Na concentrations due largely to the low X-ray detection efficiency of elements with atomic numbers lower than 12 (Cliff and Lorimer 1975). Clays are known to be inhomogeneous materials. Thus, standard deviations (Table 2) represent real, small scale variations in chemical composition, as well as analytical error.

The Silverton sericites are unusually pure and relatively free of trace impurities. Therefore, the bulk

Table 3. Extended.

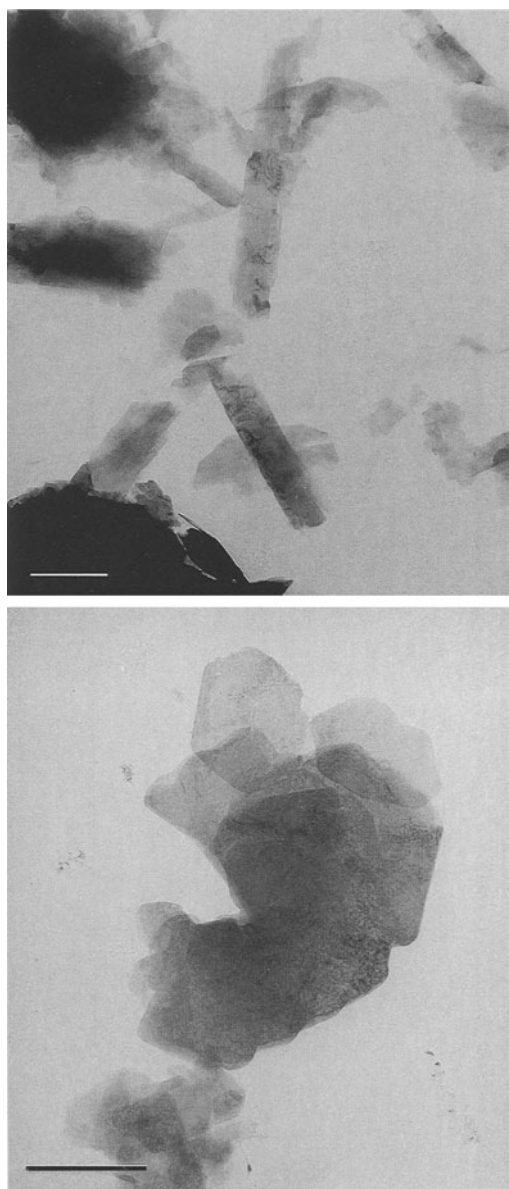| RM30		RM35A		SG4	
AEM	Bulk	AEM	Bulk	AEM	Bulk
6.39	6.54	6.78	6.66	6.54	6.48
1.61	1.46	1.22	1.34	1.46	1.52
3.83	3.72	3.70	3.64	3.77	3.76
0.00	ND	0.01	ND	0.01	ND
0.05	0.00	0.08	0.08	0.02	0.04
0.00	ND	0.00	ND	0.01	ND
0.11	0.28	0.20	0.26	0.19	0.20
0.03	ND	0.01	ND	0.00	ND
0.06	0.02	0.13	0.04	0.10	0.10
1.62	1.58	1.39	1.42	1.62	1.58

Figure 1.   Transmission electron micrographs of illites analyzed in this study: a) SG4; and b) RM30. Scale bar = 1.0 μm.

chemical analyses published by Eberl et al. (1987) provide an adequate estimate of their bulk mineral chemistry. The close agreement of the averages of over 50 individual grain analyses by AEM techniques with the bulk analyses for nine samples from this suite indicates that bulk mineral chemistry (with the exception of Na) can be determined using the analytical electron microscope. The close agreement of K analyses suggests that K diffusion (van der Pluijm et al. 1988) is not a problem for this study.

Thus, it is possible to significantly improve estimates of the mineral chemistry of relatively impure sericites (illites), determined by traditional bulk methods (XRF and EMP), using AEM techniques. Because of the small scale variability of natural illites, AEM analyses of at least 50 grains are necessary to provide adequate analytical precision.

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REFERENCES

Cliff G, Lorimer GW. 1975. The quantitative analysis of thin specimens. J Micros 103:203–207.

Eberl DD, Srodon J, Lee M, Nadeau PH, Northrop HR. 1987. Sericite from the Silverton caldera, Colorado: Correlation among structure, composition, origin and particle thickness. Am Mineral 72:914–934.

Kittrick JA, Hope EW. 1963. A procedure for the particle-size separation of soils for X-ray diffraction analysis. Soil Sci 96:155–164.

Mackinnon IDR, Kaser SA. 1987. Precise elemental analyses of clays using analytical electron microscopy. Clay Min Soc Ann Meeting Prog with Abst. 88 p.

van der Pluijm BA, Lee SA, Peacor DR. 1988. Analytical electron microscopy and the problem of potassium diffusion. Clays & Clay Miner 36:498–504.

Warren EA, Ransom B. 1992. The influence of analytical error upon the interpretation of chemical variations in clay minerals. Clay Miner 27:193–209.