Clays and Clay Minerals, Vol. 26, No. 4, pp. 296–298, 1978.

THE CONVERSION OF X-RAY INTENSITY RATIOS TO COMPOSITION RATIOS IN THE ELECTRON PROBE ANALYSIS OF SMALL PARTICLES USING MINERAL STANDARDS

M. A. F. Pyman,* J. W. Hillyer,† and A. M. Posner*

* Department of Soil Science and Plant Nutrition and † Electron Microscopy Centre
University of Western Australia, Nedlands 6009, Western Australia

(*Received 24 January 1978*)

Abstract—X-ray intensity ratios of Si/Al, Si/Fe, and Al/Fe in micron-sized particles of geochemical standards were found to vary linearly with the composition ratio. The same linear relationship was found for samples of the clay minerals kaolinite and illite.

Key Words—Albite, Biotite, Illite, Kaolinite, Orthoclase, Phlogopite.

INTRODUCTION

Analysis of small particles in the electron probe has been open to the objection that many standards are required and that they must be of similar size, shape, and mineralogy to the samples under study (Armstrong and Buseck, 1975; Weeks and Passoja, 1977).

Owing to the difficulty of applying matrix corrections to small particles, it is common practice in microprobe analysis to use ratios of X-ray intensities from two constituent elements (Bayard, 1973; White et al., 1966). Direct proportionality of this intensity ratio to the composition ratio is then assumed. Such proportionality has been found for Ca/Si and Ca/Al ratios for powdered synthetic zeolites (White et al., 1966). Si/Al ratios have been determined by X-ray spectrometry (Scott, 1956) and by electron probe microanalysis using polished specimens with a defocused beam (Takagi and Yamaguchi, 1971). Both found significantly nonlinear relationships which are attributed largely to the relatively high absorption of SiKα by Al. Rowse et al. (1974) found a linear relationship between intensity ratio and composition ratio for standards prepared in resin from mixtures of silica and gibbsite and analysed with a defocused beam. This relationship was then used to analyze particles of kaolinite.

In this experiment we determined the relationship between intensity and composition ratios for Si/Al, Si/Fe, and Al/Fe for micron-sized particles using well-characterized mineral standards. Samples of pure kaolinite and illite were then analyzed similarly and compared to the standards.

MATERIALS AND METHODS

The mineral standards used were albite, biotite, hornblende, orthoclase, phlogopite, and sillimanite. Sources of the standards are detailed in the references. The kaolinite was from Greenbushes, Western Australia, and has been described by Bolland (1975). Sedimentary illite from Mullellorina, South Australia, was provided by Dr. K. Norrish. X-ray powder diffraction identification of the kaolinite and illite was carried out using CuKα radiation on a Phillips vertical goniometer equipped with a graphite curved crystal monochromator.

Approximately 10 mg of sample was hand ground in an agate mortar under butanol. Once the suspension had been thoroughly mixed, a drop was placed on a carbon film on a copper grid. After 5 min the grid was removed, washed in methanol, and dried in air. The grids were then affixed to brass stubs and coated with a 20-nm-thick layer of copper. The specimens were examined in an A.R.L. SEM-Q electron probe microanalyzer equipped with three wavelength dispersive spectrometers. The beam diameter was approximately 0.2 μm with an accelerating voltage of 15 kV and a probe current of 20 nA. Each particle was analyzed for Al, Si, and Fe simultaneously using conditions given in Table 1. Spectrometers were aligned using corundum, quartz, and pyrite for the Al, Si, and FeKα lines respectively. Twenty-five particles of each specimen in the size range 1–5 μm were analyzed at random, each particle analyzed being at least 5 μm from its nearest neighbor. For each particle 20,000 counts were accumulated for Al in 15–50 s. Background corrections were made for every particle by averaging 20-s counts taken for every 10th particle at equal wavelength intervals each side of the peaks; the amount of offset for each element is shown in Table 1. Background count rates were approximately 20 count/s, 2 counts/s, and 2 counts/s for Al, Si, and Fe, respectively.

RESULTS AND DISCUSSION

X-ray powder diffraction analysis of random powder samples and magnesium saturated and glycerol solvated basally oriented aggregates showed the kaolinite specimen to contain no impurities. The kaolin is moderately well ordered. The illite was also pure and belonged to the dioctahedral group.

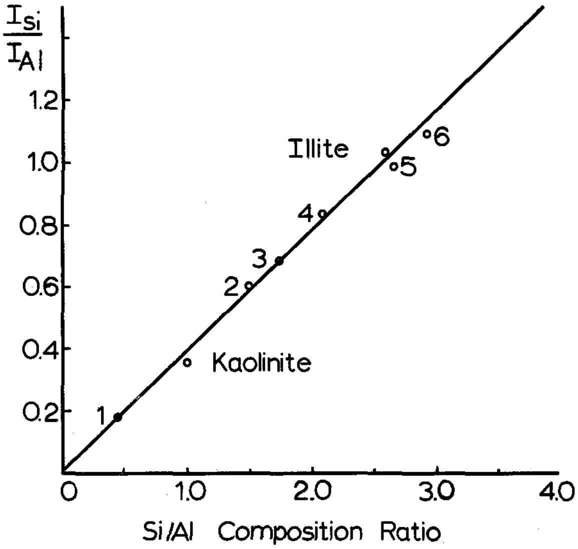

Fig. 1. Si/Al X-ray intensity ratio as a function of composition ratio: 1 Sillimanite 309, 2 Biotite Mica Fe, 3 Biotite V_T 194, 4 Phlogopite Mica Mg, 5 Albite AB1, 6 Orthoclase OR1.

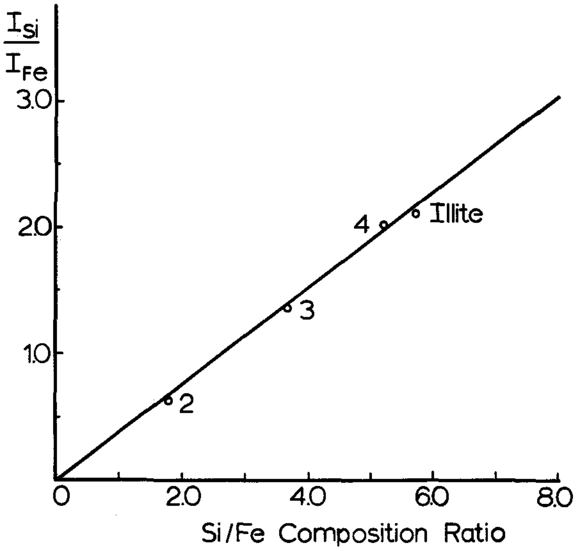

Fig. 2. Si/Fe X-ray intensity ratio as a function of composition ratio. Sample numbers as for Figure 1.

Graphs of intensity ratio against composition ratio for Si/Al, Si/Fe, and Al/Fe are shown in Figures 1, 2, and 3, respectively. The plots are regression lines, the correlation coefficients being better than 0.995 in each case. The coefficients of variation, assuming a normal distribution, are shown for each sample in Table 2. The variation of both the kaolinite (4.7%) and illite (5.8%) Si/Al ratios is similar to the variation of the mineral standards. The large variation for the sillimanite is thought to be due to variation in composition of the mineral. The variation for the Biotite Mica-Fe samples was found to be due to a bimodal distribution.

The results of the hornblende analyses have not been included on the graph because the sample was found to be unstable under the electron beam. The Si count rate appeared to increase with time relative to the Al and Fe count rates. None of the other samples showed this effect.

We would expect that the linear relationship found between the intensity and the composition ratios should hold as long as the particles are smaller than the X-ray emission volume. Assuming a density of 3.0 g/cm^3 and following Reed (1966), the particle diameter required to contain 99% of the SiKα X-ray production is 4.5–5.0 μm. The particle diameters analyzed in this experiment do not exceed these values. Increases in density above 3.0 g/cm^3 and particle size above 5 μm will probably affect the linearity of the relationship. Shifts in wavelength associated with changes of Al coordination number should not make more than a 1–2% difference to the results, when corundum is used to set the wavelength (Sweatman and Long, 1969). Although only silicate minerals have been analyzed in this study, the linear relationship between intensity and composition ratios can be expected to hold for other minerals using the experimental procedure outlined here provided the elements analyzed are major constituents of the mineral.

In view of the varied shape and mineralogy of the standards the linearity of the relationship between in-

Table 1. Spectrometer details.

Element	Crystal	Counter	Window	Background Offset
Al	R.A.P.(100)	Flow Proportional P10 Gas	1µm Polypropylene	0.39nm
Si	P.E.T.(002)	Sealed Proportional Ar Gas	25µm Be	0.13nm
Fe	LiF (200)	Sealed Proportional Xe Gas	25µm Be	0.06nm

Table 2. Coefficients of variation of standards for Si/Al, Si/Fe, Al/Fe.

Standard	No. particles Counted	Coefficient of Variation % Si/Al	Si/Fe	Al/Fe
Sillimanite 309	50	61.7	-	-
Greenbushes kaolinite	25	4.7	-	-
Biotite Mica Fe	25	20.3	24.8	20.3
Biotite V_T194	25	5.4	10.6	9.9
Phlogopite Mica Mg	25	6.0	13.6	10.4
Mullellorina illite	25	5.8	11.9	12.4
Albite AB1	25	8.5	-	-
Orthoclase OR1	25	9.5	-	-

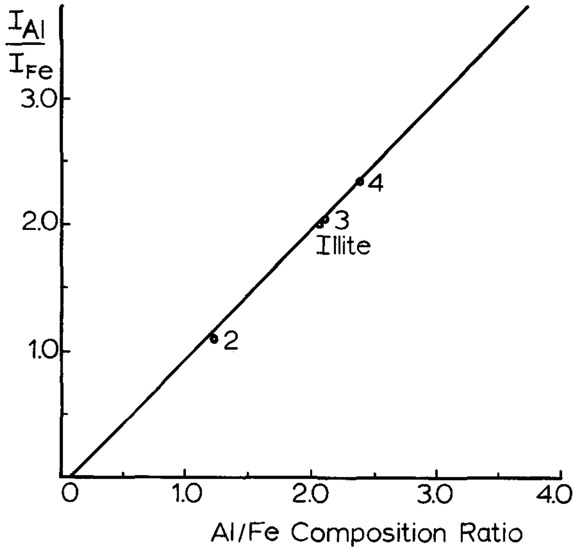

Fig. 3. Al/Fe X-ray intensity ratio as a function of composition ratio. Sample numbers as for Figure 1.

tensity and composition ratios for Si/Al, Si/Fe, and Al/Fe is excellent. Both kaolinite and illite show the same relationship between intensity and composition ratios. This suggests that use may be made of these clay minerals as well as standard minerals for determining composition ratios of specimens without the use of matrix corrections providing that the particle diameter is less than 5 μm. This technique will be well suited to the determination of homogeneity of clay mineral specimens. Calculation of structural formulae of clay minerals normally involves the assumption of complete homogeneity. In specimens where two or more structurally similar but chemically distinct species are present the recognition and analysis of the separate phases will enable studies of mineral properties and provenance to be made with greater confidence.

ACKNOWLEDGMENTS

M. A. F. Pyman gratefully acknowledges the support of a University of Western Australia studentship. We thank Dr. R. J. Gilkes for helpful discussions and for providing the mineral standards used in this study.

DESCRIPTION OF STANDARDS

Albite PSU AB-1: Goldich, S. S., Ingamells, C. O., Suhr, N. H. and Anderson, D. H. (1967) Analysis of Silicate Rock and Mineral Standards. *Can. J. Earth Sci.* **4,** 747–755.

Biotite Mica-Fe: Roubault, M., La Roche, H. de, Govindaraju, K. (1968) Report (1966–1968) on Geochemical Standards. *Sci. Terre (Ann. Ec. Nat. Super. Geol. Appl. Prospect. Minière Univ. Nancy)* **13,** 379–404.

Biotite Basel 1B: Schwander, H. Mineralogisches-Petrographisches Institut der Universität Bernouillanum, CH4000, Basel, Switzerland.

Hornblende Basel 1H: As above.

Orthoclase PSU OR-1: As for Albite PSU AB-1.

Phlogopite Mica-MG: As for Biotite Mica-Fe.

Sillimanite 309: *British Chemical Standards No. 309.* Bureau of Analyzed Samples, Newham Hall, Middlesborough, England.

REFERENCES

Armstrong, J. T. and Buseck, P. R. (1975) Quantitative chemical analysis of individual microparticles using the electron microprobe: theoretical: *Anal. Chem.* **47,** 2178–2190.

Bayard, M. (1973) Application of the electron microprobe to the analysis of free particulates. In *Microprobe Analysis* (Edited by Andersen, C. A.), pp. 323–348. Wiley, London and New York.

Bolland, M. D. A. (1975) *Surface Charge of Kaolinites in Aqueous Suspension*: Ph.D. Thesis, University of Western Australia.

Reed, S. J. B. (1966) Spatial resolution in electron probe microanalysis. In *Optique des rayons X et microanalyse* (Edited by Castaing, R., Deschamps, P. and Philibert, J.) pp. 339–349. Hermann, Paris.

Rowse, J. B., Jepson, W. B., Bailey, A. T., Climpson, N. A. and Soper, P. M. (1974) Compositional elemental standards for quantitative electron microscope microprobe analysis: *J. Phys. E* **7,** 512–514.

Scott, R. K. (1956) Determination of major elements in clays by X-ray spectroscopy. Fall meeting, Refractions Division, American Ceramics Society. Quoted on p. 223 of *X-ray Absorption and Emission in Analytical* Chemistry (Edited by Liebhafsky H. A., Pfeiffer, H. G., Winslow, E. H. and Zemany, P. D.) (1960). Wiley, London and New York.

Sweatman, T. R. and Long, J. V. P. (1969) Quantitative electron probe microanalysis of rock forming minerals: *J. Petrol.* **10,** 332–379.

Takagi, S. and Yamaguchi, G. (1971) Electron probe analysis of oxide minerals with a fine texture: *Proc. 6th Int. Congr. X-ray Opt. Microanalysis*, 761–770.

Weeks, T. J. and Passoja, D. E. (1977) A microprobe analysis of Type X molecular sieve: *Clays & Clay Minerals* **25,** 211–213.

White, E. W., Denny, P. J. and Irving, S. M. (1966) Quantitative microprobe analysis of microcrystalline powders. In *The Electron Microprobe* (Edited by McKinley, T. D., Heinrich, K. F. J. and Wittry, D. B.), pp. 791–804, Wiley. New York, London, and Sydney.

Резюме- Было обнаружено,что отношения интенсивностей рентгеновских лучей для Si/Al, Si/Fe и Al/Fe в частицах микронного размера геохимических эталонов изменяются линейно с изменением отношения составов. Такое же линейное соотношение было обнаружено для образцов глинистых минералов каолинита и иллита.

Kurzreferat- Es wurde herausgefunden, daß das Verhältnis der Röntgenintensitäten von Si/Al, Si/Fe und Al/Fe in mikrongroßen Partikeln geochemischer Standarts linearisch mit dem Aufbauverhältnis variiert. Dieselbe linearische Verwandtschaft wurde in Proben der Tonmineralien Kaolinit und Illit gefunden.