

Analytical transmission electron microscopy in the study of diagenetic clay minerals

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Invited review lecture—extended abstract

As discussed by Lorimer (this volume), the several advantages of analytical electron microscopy over conventional electron probe microanalysis are particularly appropriate to the study of clay minerals. First of these is greatly improved spatial resolution which is partly the result of very small excitation volumes in the ultra-thin rock sections normally used. It is thus possible to obtain analytical data from single crystals of micrometre dimensions—a necessity for most clay mineral research. In many cases this level of resolution is required simply to avoid contamination by oxides and hydroxides as well as by other clay minerals.

This analytical advantage should also be seen in light of the additional information provided by transmission electron microscopy—high resolution textural detail and crystal structural data from selected area diffraction patterns and lattice images.

No technique, however, is without its problems. In this laboratory we have determined *k* values (see Lorimer) from a number of mineral standards, mostly large mica crystals first analysed by microprobe. We have encountered some difficulties due to contamination during ion-beam sample preparation and also cases of apparent standard heterogeneity. As with other microbeam methods, loss or migration of volatile elements such as Na can constitute a problem. Taken together with uncertainties of sample thickness and geometry in the beam, we conclude that analysis in TEM is much more time-consuming and somewhat less reliable than by conventional electron microprobe. The advantages of vastly increased resolution and excellent textural and crystal-structural information, however, greatly outweigh these negative aspects.

Ireland *et al.* (1983) applied these techniques to

glaucanites and illites in sandstones and shales of the Lower Cretaceous Glaucanite Sand Formation, Alberta. Authigenic kaolinite and detrital micas were also analysed. Table 1 lists means and standard deviations for 29 glaucanites and 44 illites [Fe(II)/Fe(III) ratios determined by wet chemical methods on a number of separated concentrates and these values assumed throughout].

Table 1 Mean glaucanite and illite data from Ireland *et al.* (1983). TEM oxide analyses recast as mica formulae assuming 22 oxygens. Fe(II)/Fe(III) ratios determined separately.

	Glaucanites (29)		Illites (44)	
	Mean	Standard Deviation	Mean	Standard Deviation
Si	7.28	0.13	6.92	0.24
Al tetrahedral	0.72	0.13	1.09	0.24
Al octahedral	1.79	0.62	3.37	0.24
Ti	0.02	0.01	0.03	0.02
Fe trivalent	1.35	0.50	0.25	0.12
Fe divalent	0.34	0.13	0.06	0.03
Mn	0.004	0.007	0.002	0.005
Mg	0.46	0.07	0.42	0.12
Ca	0.05	0.01	0.05	0.02
Na	0.01	0.03	0.08	0.09
K	1.49	0.14	0.97	0.28
Octahedral total	3.97	0.06	4.13	0.13
Interlayer total	1.55	0.14	1.10	0.28

From the octahedral totals it is clear that glaucanite and illite both approximate very closely to true dioctahedral structures. Little variation at all is seen within the illite population whilst that in the glaucanite population can be attributed to extensive Al(III) for Fe(III) octahedral substitution. Ireland *et al.* (1983) showed this variation to be more systematic (i.e. much less scatter) than in populations of published analyses obtained by conventional methods of analysis, presumably because

contamination by other phases had been largely avoided.

Whittle (1986) and Curtis *et al.* (1985*a, b*) presented the findings of a study of grain-coating chlorites in sandstones. Once again, the majority of analyses conformed well with ideal mineral formulae (this time trioctahedral, Al-rich chlorites). A number of samples, however, exhibited compositional variation outside that reasonably to be expected for the chlorite structure. Curtis *et al.* (1985*a, b*) showed that this could be interpreted as a mixing curve between trioctahedral smectite and chlorite. Ireland (1982) obtained lattice images from one sample that indicated interstratification of approximately 1.0 and 1.4 nm layers, entirely consistent with the analytical data.

Since these published investigations, we have looked at clay minerals in a number of other sediments and also continued efforts to reduce errors in analytical methodology. Our findings still show that authigenic clay minerals have compositions which conform closely to ideal phyllosilicate structures. Chemical variation is less than the classical literature might suggest. It would thus appear that analytical TEM is the only method which, by virtue of its excellent spatial resolution, can routinely avoid contamination by other phases and hence yield sound compositional data for clay minerals from sedimentary rocks of various kinds.

It is interesting to note other recent work (i.e. not utilizing analytical TEM) which suggests that 'fundamental' clay particles may be exceedingly small and be of relatively non-variable composition (Nadeau *et al.*, 1984; Lee and Peacor, 1983). All these findings tend to indicate that clay alteration mechanisms proceed via dissolution and replacement rather than by structural modification, as has been the generally accepted interpretation of reactions such as the important smectite-illite conversion in mudrocks during burial.

References

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