

## Intralayer transitions in phyllosilicates of Martinsburg shale

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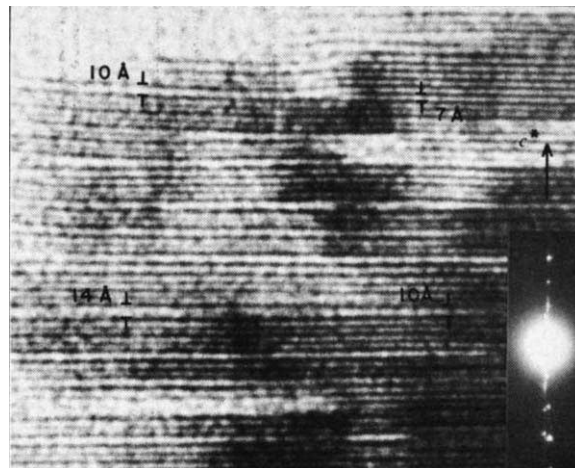
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Phyllosilicates that occur in shales and slates show complex features as generally detected by methods such as X-ray diffraction. Diffraction patterns commonly display features such as broadened and asymmetric peaks which in many cases have been shown to reflect random interlayering of more than one kind of phyllosilicate<sup>1</sup>; for example, illite-smectite and vermiculite-chlorite. Ordered interlayering of more than one phase has also been frequently observed. However, powder diffraction data generally provide insight only into the differences between units of many layers and then they only yield average values. The possibility of variations within individual layers can be investigated using transmission electron microscopy (TEM) and analytical electron microscopy (AEM). We report here on the occurrence of transitions within individual phyllosilicate layers from one trioctahedral structure to another (ferroan lizardite to chlorite) and from trioctahedral to dioctahedral (illite) layers. These variations in structure introduce a new range of complexities into those non-equilibrium phyllosilicate structures which occur in low-temperature sedimentary environments.

The samples studied represent a range between shale and slate and are from the Martinsburg Formation at Lehigh Gap, Pennsylvania. These materials have been studied by various techniques and the phyllosilicates have been shown to consist primarily of a white mica which is transitional from illite (in shale) towards ordered 2M mica (in slate), and chlorite<sup>2,3</sup>.

Samples (made available by Robert Wintsch of Indiana University) were first prepared as thin sections oriented normal to both bedding and cleavage (so that structure layers of clay are normal to the section). Following optical investigations, selected portions were ion-thinned. They were studied using a JEOL JEM-100CX electron microscope which has an approximate X-ray spatial resolution of 300 Å when operated as an analytical electron microscope and a TEM lattice image resolution of 3.4 Å. Phyllosilicate grains were initially imaged in normal TEM mode. Where appropriate, selected-area electron diffraction patterns were obtained, followed by the recording of 00 $l$  lattice fringe images. In most cases a series of through-focus images was taken to obtain the images that truly reflect the local structure. Fringes were found to reflect the true periodicity in focus conditions for highest contrast images. Areas of the sample so characterized were then subjected to AEM analysis. Energy dispersive X-ray spectra only from thinned areas not subject to atomic number, absorption and fluorescence correction factors were compared with those from well analysed standards, using the methods of Cliff and Lorimer<sup>4</sup>, to obtain semiquantitative analyses. The relevant laboratory procedures and techniques have been described elsewhere<sup>5,6</sup>. Final characterization of phases was obtained considering collectively, selected-area electron diffraction patterns, lattice fringe images and AEM data. Comparison of the lattice images to calculated images, however, was not carried out, partly because rapid beam damage precluded obtaining the required images.

Most phyllosilicate grains were found to be a dioctahedral phase which is dominantly 1M illite in shale and 2M muscovite in significant amounts in slate, trioctahedral chlorite, or interlayered illite and chlorite; these are described elsewhere<sup>2,3,7</sup>. Regions of some grains also consist of a phase with 7-Å periodicity and have a composition corresponding to ferroan lizardite, that is, they are trioctahedral phases rich in Mg and Fe

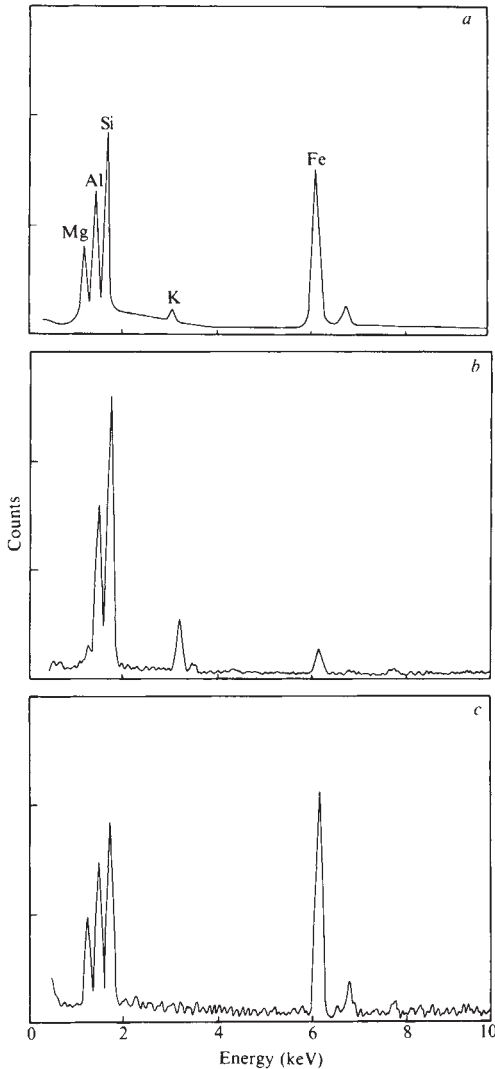


**Fig. 1** Lattice fringe image of an area that shows interlayering of 10-Å illite, 14-Å chlorite and 7-Å ferroan lizardite. The labelled layers illustrate transitions from 10-Å illite to 7-Å ferroan lizardite and to 14-Å chlorite within individual layers. The inserted electron diffraction pattern shows (00 $l$ ) reflections of 14-Å chlorite streaked along  $c^*$  caused in part by random intermixing of 10-Å illite layers. The nonstreaked 10-Å reflections (slightly off angle from the chlorite pattern) are from adjacent illite grains. The specimen is from the transitional sample.

with  $\text{Fe} < \text{Mg}$ . Such grains are found only in samples which do not have a clearly defined slaty cleavage (shales and samples transitional to slates).

Figure 1 is a lattice fringe image of a sequence of phyllosilicate layers which are infrequently encountered but which are the principal subject of this letter. Selected regions are labelled with the appropriate periodicity, showing that there are regions of 14-Å (trioctahedral chlorite), 10-Å (dioctahedral white mica) and 7-Å (trioctahedral ferroan lizardite) structure. These three structures were also identified, in part, through the lattice images of the highest contrast and their characteristic 00 $l$  diffraction patterns (see inset to Fig. 1), which exhibit streaking presumably due to the high degree of disorder seen in the lattice fringe image. Such layers can be seen to randomly alternate in some areas. Such random mixed-layer structures, where trioctahedral and dioctahedral layers are mixed, are unusual. Bailey<sup>8</sup> has recently reviewed the status of various mixed-layer phyllosilicates, for which there is no firm evidence of dioctahedral-trioctahedral mixed-layering, except, perhaps, for the mineral tosudite. The diffraction pattern of the mixed-layer structures illustrated in Fig. 1 shows that the regions of repeat of a given structure type (14-Å chlorite) are large enough to produce coherent diffraction effects. The randomly interlayered units produce diffuseness in the pattern. In some cases, described elsewhere, regular 1:1, chlorite-mica, mixed-layer sequences occur with a periodicity of 24 Å (ref. 7).

The important feature of Fig. 1 is that there are transitions from one structure type to another along individual layers. These are of two types: (1) transitions from ferroan lizardite (7 Å) to chlorite (14 Å). Sequences of layers can be seen where two individual 7-Å layers (serpentine-type structure) change to a single 14-Å chlorite (talc + brucite-type units) layer. Such a transition involves two phases which have, ideally, the same formula, so their presence is not surprising. (2) Transitions along other layers occur from a 10-Å (illite) phase to either a 7-Å (ferroan lizardite) or 14-Å (chlorite) phase. Such a transformation requires change in both chemistry and structure. The 10-Å phase is Al-rich and dioctahedral, but the 14-Å phase is Fe- and Mg-rich and trioctahedral. In addition to a three layer (talc-like) unit, which is common to the trioctahedral 10-Å phase, the latter has an additional brucite layer. The transition therefore involves a change from a dioctahedral to a trioctahedral unit, with insertion of a brucite layer.



**Fig. 2** Energy dispersive X-ray spectra of three different regions: *a*, a type of area shown in Fig. 1 which contains interlayered illite, chlorite and ferroan lizardite (K and high Mg and Fe are characteristic); *b*, illite (high K is characteristic); *c*, chlorite (high Mg and Fe and no K are characteristic). Note that spectrum *a* has characteristics of both spectra *b* and *c*.

Figure 2 shows energy dispersive X-ray spectra from selected areas which are representative of the various structure types. Figure 2*a* is a spectrum from the region for which the kind of lattice fringe image of Fig. 1 was obtained. Figure 2*b,c* shows spectra from other areas of the same sample which yield lattice fringe images (not shown) and other data indicating that they consist of 10- and 14-Å layers, respectively. These two spectra thus serve as standards for the dioctahedral illite (K is characteristic) and trioctahedral chlorite (Mg and Fe are characteristic) layers. The spectrum in Fig. 2*a* displays major amounts of all of these elements, verifying that the 10- and 14-Å layers in Fig. 1 are actually dioctahedral illite (as opposed to trioctahedral 10-Å phases) and trioctahedral chlorite, respectively. If the illite component is subtracted from the polyphase spectrum (Fig. 2*a*), the remaining spectrum must correspond to the 14- and 7-Å layers. Because this composition is nearly identical to that of chlorite, the chlorite (14 Å) and ferroan lizardite (7 Å) must be nearly identical in composition. This confirms the chemical nature of the intralayer and interlayer transitions as described above.

Finally, we note that the intralayer transitions described above are found only where complex interlayered sequences also occur. In addition, they are found only in shales and in samples which are transitional to slate. They clearly represent

non-equilibrium conditions such that given additional time, or increased temperature, or subjected to some other variable which increases reaction rates, they would be caused to anneal away, with the production of stable chlorite or mica. It is just such relatively stable structures which are observed in the slates. Such intralayer transitions may occur quite commonly, however, and their presence adds an additional level of complexity to those phyllosilicate structures which are characteristic of low-temperature, sedimentary diagenesis where chemical equilibrium is difficult to attain.

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## Primitive nephelinitic volcanism associated with rifting and uplift in the Canadian Arctic

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Considerable interest has arisen recently in the nature of plate tectonic events in Arctic Canada and northwestern Greenland during Cretaceous to Recent times<sup>1</sup>. Relatively little is known, however, concerning contemporaneous volcanism, and detailed studies have only been made of the basalts related to the Baffin Bay spreading centre<sup>2,3</sup>, and the Kap Washington peralkaline volcanics associated with regional doming and rifting of northern Greenland during the late Cretaceous<sup>4</sup>. We show here that the Freemans Cove volcanic suite forms a major petrological province of Eocene saturated to undersaturated volcanism in the central Canadian Arctic. This occurrence of basalts, nephelinites and phonolites is an example of intraplate magmatism of the type associated with continental rifting. Emplacement of the rocks has been controlled by graben-like faults formed during the Boreal rifting and Eurekan deformation of the Arctic plate. Magmatism was initiated when extensional deformation was transformed by pre-existing resistant structures into a region of compression and uplift, causing partial melting of metasomatized mantle. Primary nephelinite magmas unusually rich in Ba, Sr, La form a major component of the magmatism.

The Freemans Cove volcanic suite occupies a 40×20 km area of southeastern Bathurst Island (98°10' W; 75°5' N). Sills, dykes and small plugs are intrusive into the Lower Devonian Bathurst Island Formation, the Middle Devonian Disappointment Bay Formation, and a down-faulted block of Cretaceous Eureka Sound Formation<sup>5</sup>.

Igneous activity is confined to the southern portions of the south-east Bathurst Fault Zone<sup>5</sup> an approximately north-south trending system of normal faults. The igneous rocks consist of a suite of tholeiitic, transitional and alkaline basalts, basanites, olivine nephelinites, olivine melilitite nephelinites, phonolites and phonolitic trachytes. Representative compositions of the major varieties are given in Tables 1 and 2. (Samples prefixed N and BI are from the 1973 and 1976 expeditions to Bathurst Island respectively. Compositions presented are of individual samples.)