

## REVIEW

# HETEROGENEITIES IN ILLITE/SMECTITE MIXED-LAYER CLAYS: SOME COMMENTS AND RECOLLECTIONS

WILLIAM D. JOHNS

Department of Geological Sciences, University of Missouri, Columbia, USA

Several years ago in Strasbourg, France, at an International Clay Conference (1990), Professor Georges Millot opened the conference with a statement, which can be paraphrased, "That in any natural clay mineral assemblage, no two clay particles are identical in composition".

Although this can be taken to be an exaggeration, it does call vividly to our attention the heterogeneities of structure and composition within even so-called "monomineralic" clay mineral assemblages. Although most of us are aware of the heterogeneous characteristic of clay minerals, it is often disregarded, especially when working with the ubiquitous illite/smectite mixed-layer I/S clays. It seems that we especially forget this character, in attempting to interrelate variations in composition of the I/S series with certain unique physical and chemical properties. This is especially true when attempting to characterize the surface properties of individual particles that comprise an I/S aggregate. This matter will be dealt with a little later.

Many of us, both in academia and industry, have been studying burial diagenesis, where smectite-to-illite transfor-

mations, through mixed-layer intermediates, have received a great deal of attention. The author's interests have centered on the Tertiary (predominantly Miocene) section of the Vienna Basin, which is also an important oil-gas producing area of central Europe. Apart from the interesting geological and economic aspects, the unique availability of continuous subsurface cores of shales rich in I/S, from which large quantities of I/S clays could be extracted, provided sufficient material for various studies. Fig. 1 is taken from data from Horton et al. (1985) for one such profile from Vienna Basin. Here we see the familiar increase in illite in the I/S component with increasing depth in the well profile.

Especially interesting was the reversal in illite content at about 2700 meters depth attributed to anomalously high-Mg pore solutions as well as high bitumen content. However, if we are going to focus attention on this anomaly, then we must likewise wonder about the others. Are we simply seeing the effects of I/S heterogeneity at depth? Accordingly we resampled another set of shales from within each core (about 4

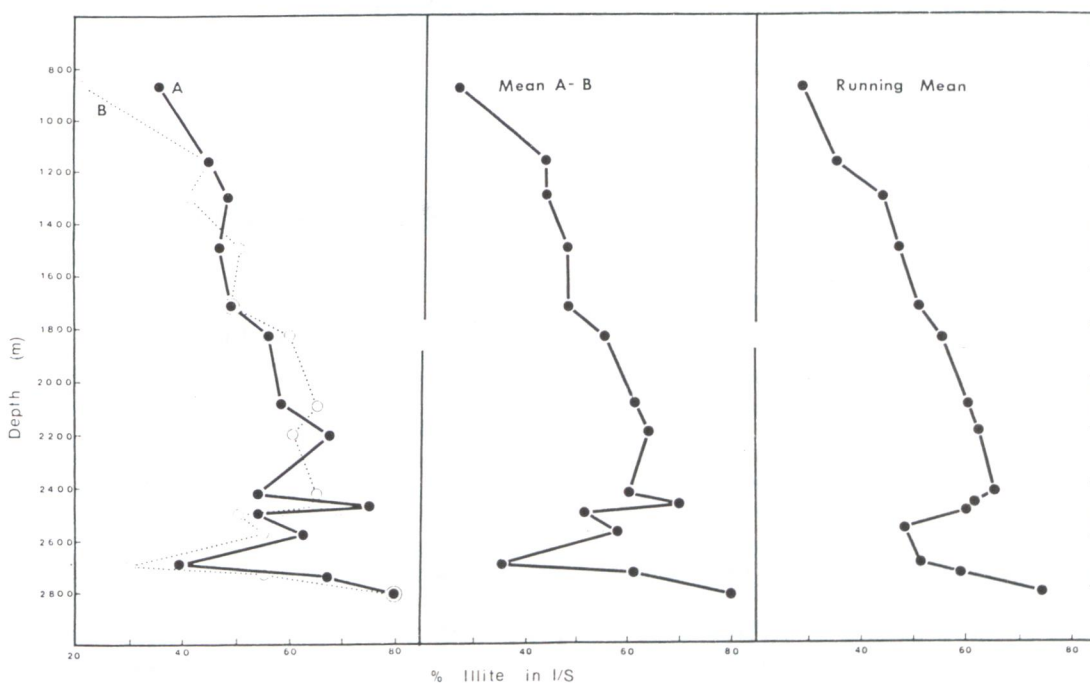


Fig. 1. Illite distribution in I/S phases in Vienna Basin, Austria.





Aggreg. 1		% I
Tr. 1.	II ISSI I I I I I II I III	
Tr. 2.	SSSI IIII I I I I I I III I I I I I	88
Aggreg. 2		
Tr. 1.	SISI I I I I I IIII II ISSIII ISISISISI	
Tr. 2.	IISISISISISI SISI	68

	%	
	S	I
TEM	23	77
XRAY	20	80

Fig. 4. HRTEM analyses for I/S phases from Gulf Coast province, 11,290 ft.

INTERSTRATIFICATION IN MONTMORILLONITE

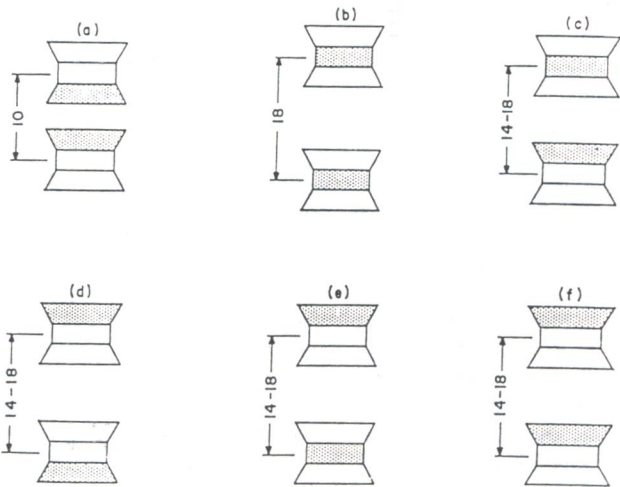
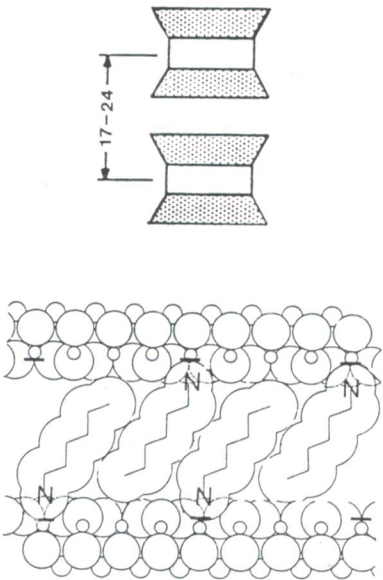


Fig. 5. Montmorillonite particle interfaces; proposed expansion when solvated. Shaded areas indicate sources of layer-charge (From Tettenhorst & Johns 1965, reprinted with kind permission of Elsevier Science, Ltd, The Boulevard, Langford Lane, Kidlington OX5 1GB, UK).

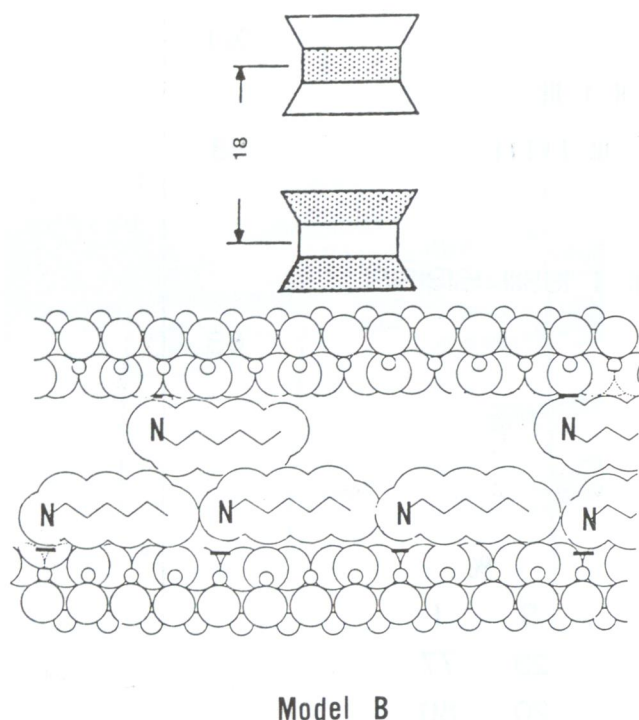
Let us look into this matter further. These heterogeneities can be studied further by means of high resolution transmission electron microscopy (HRTEM). Fig. 2 shows a TEM photo of an I/S separate (GM 7180) from a depth of 7180 ft. in the Gulf Coast province. This sample was prepared using the methods Koester & Vali (1986) where the dispersed I/S was



Model A

Fig. 6. Hexyl ammonium ion configuration complexed between a two high-charge silica sheets.

treated by alkyl-ammonium ion exchange, to irreversibly prop open the smectite layers. Oriented aggregates were then imbedded in epoxy, and thin transparent slices were obtained by microtoming, for viewing at high magnification by HRTEM. The aggregates of stacked silicate layers can be seen; 10 Å separations represent illite layers and 20 Å separations repre-



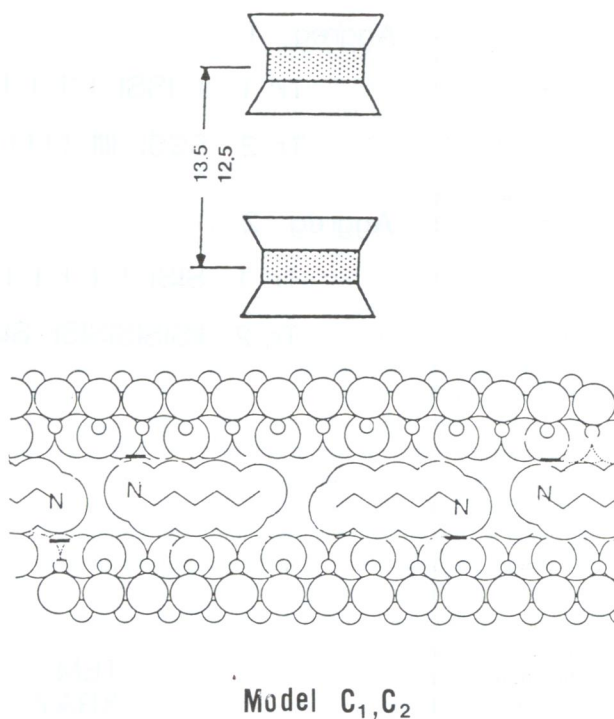
**Fig. 7.** Hexyl ammonium ion configuration complexed between a high-charge and a low-charge silica sheet.

sent smectite layers (Fig. 2). Along different traverses illite (I) and smectite (S) layers were counted. Areas where this differentiation could not be made clearly were ignored. No attempt was made to define the boundaries of individual particles within an aggregate. The results of the analysis after three different traverses for two aggregates are summarized in Fig. 3 for sample GM 7180. The heterogeneity, both along traverses and between aggregates, is apparent. The second aggregate is substantially more illitic than the first aggregate. It is interesting that if we examine enough aggregates (10 in this case) the measured I/S ratio by HRTEM, 28/72, agrees quite favorably to that determined by XRD of 25/75.

Fig. 4 summarizes an analysis for another Gulf Coast I/S from a depth of 11,290 ft. Here less variation in illite content is observed between aggregates. Direct evidence of IS ordering is noted, and direct measurement of 10 aggregates gives an I/S ratio of 77/23, which agrees favorably with the ratio determined by XRD of 80/20, also designated as IS ordered.

Again we can observe directly the heterogeneity of these mixed-layer clays, and how XRD integrates these differences in oriented films. This should be no surprise. Almost five decades ago Bradley & Grim (1948) called our attention to this. They noted that smectite bearing clays, when disaggregated in water disperse into elementary particles. However, when they accumulate as oriented aggregates, they give rise to diffraction phenomena quite different from those of the dispersed state. This phenomenon has been rediscovered recently as we now focus attention on so-called "interparticle diffraction".

There has been a recent revival concerning the nature of particle interfaces which must occur in I/S phases. Fig. 5 summarizes some similar speculation made some years ago (Tettenhorst & Johns 1965), where the focus was on the swelling behaviour at such interfaces. The shaded areas in this figure



**Fig. 8.** Hexyl ammonium ion configuration complexed between two low-charge silica sheets.

indicate the sources, due to ionic substitution, of interlayer charge. Each pair of silicate layers shown illustrate possible juxtaposition of charged interfaces. Today, particularly in the case of illite-rich I/S clays, there is debate about the surface properties, that is, layer charge, associated with the external silicate sheets of contiguous fundamental particles. For example, does the interlayer expansion in 80/20 ordered I/S take place at the interface between normally high-charged illite particles? Are these interfaces bounded by low-charged smectite-like silica sheets, suggesting asymmetrical charge distribution on opposite sides of mica layers? In an attempt to resolve these questions, and based on experience with alkyl-ammonium exchange in smectites and vermiculites (Johns & Sen Gupta 1967), the use of short-chain alkyl ammonium probes to estimate layer-charge was suggested.

Fig. 6 (Model A) depicts an expandable interface between two mica particles, with two high-charge surfaces defining the interface. When treated with hexyl-ammonium ions, these species are exchanged on each interface with the orientation as shown in the lower diagram. The basal spacing can vary between about 17–24 Å, depending on the alkyl chain orientation (related to exact layer charge), and also on the degree of interfingering or interpretation of the molecules.

Fig. 7 (Model B) depicts similarly an interface bounded by a single high-charge and a single low-charge silica sheet. Hexyl ammonium ions, upon replacement in the interface, are likely to assume the orientation and two-layer configuration shown. The basal spacing is about 18 Å.

Fig. 8 (Model C) represents another likely situation, where the interface is bounded by two low-charge smectite-like layers. Our studies indicate a likely 13.5 Å periodicity (Model C<sub>1</sub>) when the single layer complex is formed between monmorillonite-like layers, and a 12.5 Å periodicity (Model C<sub>2</sub>) when beidellitic.



Hexyl-NH<sub>3</sub><sup>+</sup>-I/S (80:20, R=0.5)

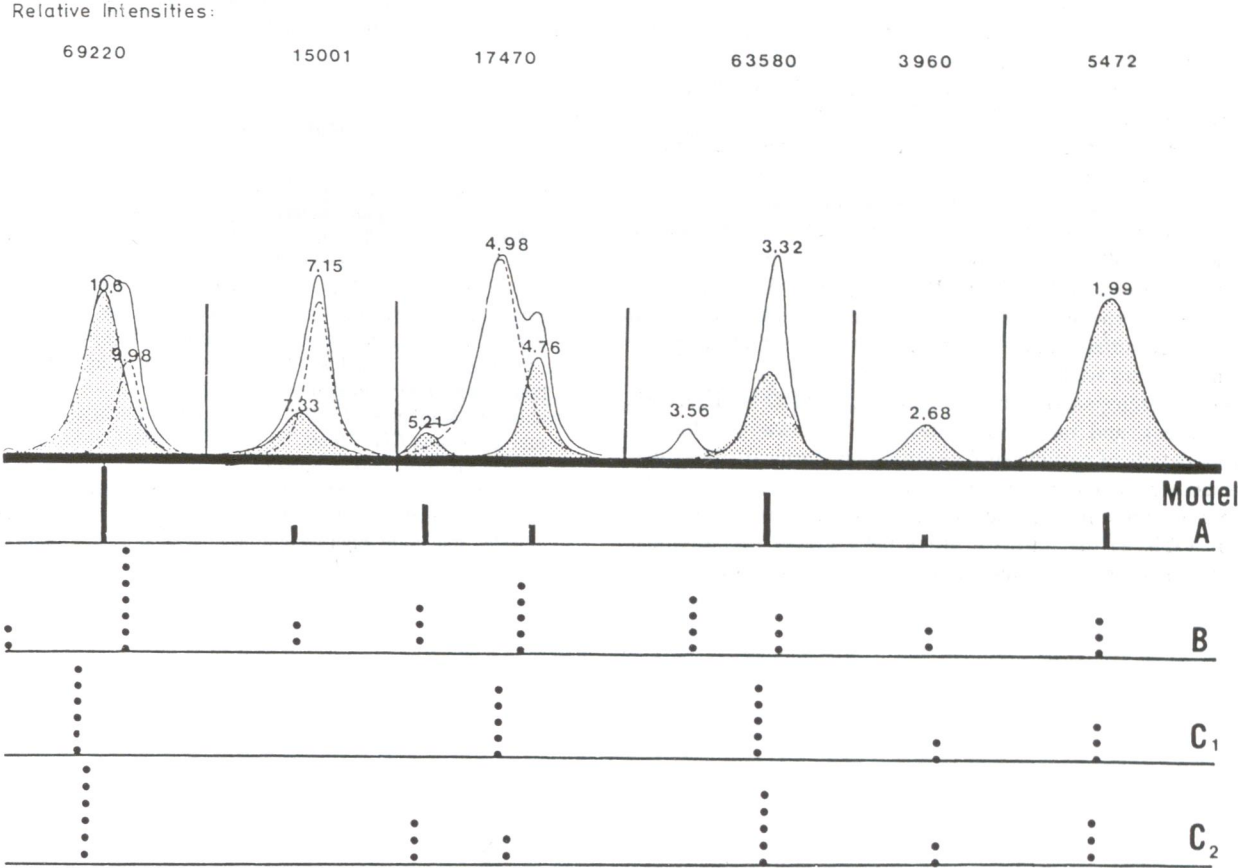


Fig. 9. X-ray diffraction pattern for hexyl-ammonium I/S (80 : 20, Reichweite = 0.5), showing NEWMOD generated diffraction spacings and intensities for different model trials.

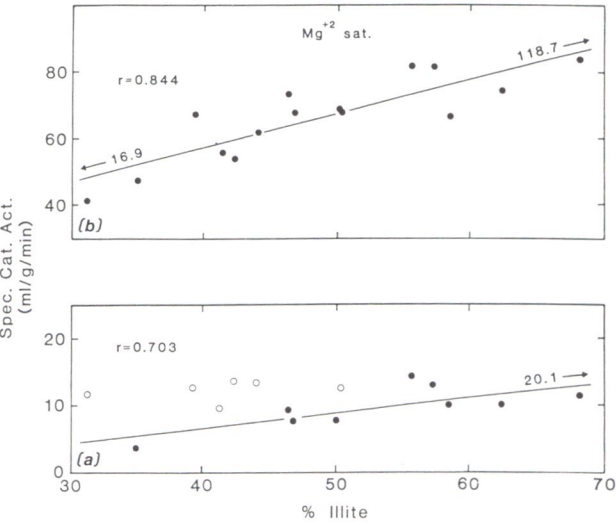


Fig. 10. Correlation between specific catalytic activity and percent illite in I/S phases from the Vienna Basin, Austria profile (From Johns & McKallip 1989, reprinted by permission).

Fig. 9 shows the XRD data obtained for the hexyl ammonium (treated) 80/20 I/S (Reichweite = 0.5) clay from the subsurface of the Vienna Basin of Austria. The deconvolution

Table 1: Modern surface microscopy.

IRS	Infra-Red Spectroscopy
LAMMA	Laser Microprobe Mass Analysis
AES	Auger Electron Spectroscopy
SIMS	Secondary Ion Mass Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
UPS	Ultraviolet Photoelectron Spectroscopy

program coupled with a Scintag automated diffractometer was used to produce the diffraction pattern shown. Note that relative intensities of successive diffraction peaks were not preserved in reproduction. The numbers above each group of peaks gives the relative intensity of the strongest peak of each group, allowing comparison of intensities.

Reynold's NEWMOD program was utilized to generate diffraction profiles representing a variety of Models A, B, C1 and C2 for an 80 illite/20 hexyl-ammonium-smectite (Reichweite = 0.5) I/S clay. The model diffraction peak locations are shown in succession beneath the experimental data (Fig. 9). The observed data indicated by the shaded peaks match closely in position and intensity with that calculated by the NEWMOD method for Model A only. The differences in the

deconvoluted, nonshaded observed peaks can be attributed largely to discrete illite and kaolinite. These data also suggest the presence of a minor amount of model B, that is partly masked by the illite and kaolinite. The experimental data cannot be reconciled with models C1 and C2. It is concluded, therefore, that this I/S clay consists predominantly of illite fundamental particles with expanding interfaces bounded by high-charge silica sheets. Some high-charge (illite)-low charge (smectite) interfaces may also be present.

These conclusions are compatible also with the data of Johns & McKallip (1989) (Fig. 10) where catalytic activity increases as illitization proceeds in the Vienna Basin sequence. This correlation had been interpreted as a progressive transformation of external low-charge surfaces into external illite surfaces of high charge.

In summary we have been interpreting properties of demonstrably heterogeneous bulk aggregates (XRD and surface properties), and have been attempting to draw conclusions about details of particle surface structure. It appears likely that we have gone about as far as possible with this approach. We can now apply the analytical tools of modern surface spectroscopy (Tab. 1) that directly probe the surfaces of individual clay crystallites, providing us with a better understanding of

these surfaces and of ligands or organic species adsorbed on these active silicate surfaces. This will constitute the next important phase of clay mineral surface property research.

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