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FUNDAMENTAL PARTICLES AND THE ADVANCEMENT OF GEOSCIENCE: RESPONSE TO "IMPLICATIONS OF TEM DATA FOR THE CONCEPT OF FUNDAMENTAL PARTICLES"

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Abstract

A scientific response to suggested modifications of the fundamental particles theory for clay minerals, and limitations regarding its usage in the literature, demonstrates that such modifications may be unnecessary, and potentially harmful to communication of research results. The value of this mineralogical model, as well as its physical description of complex clay mineral properties in diagenetic and other environments, would be compromised or unduly restricted by adopting the suggested criteria for its usage. In the absence of a demonstrably superior and confirmed alternative model, it is recommended that the fundamental particle hypothesis have priority within geoscience disciplines, as it provides a quantitative, verified, and independently validated basis from which to evaluated the nature, behavior, and origin of clay minerals in a variety of geological settings.

Keywords: fundamental particles, MacEwan crystallites, mixed layer clays, electron microscopy, X-ray diffraction, illite, smectite, diagenesis, nomenclature of clay minerals.

Sommaire

Cette réponse scientifique aux modifications proposées au concept des particules fondamentales, tel qu'appliqué à l'étude des argiles, et aux restrictions visant son utilisation dans la littérature, démontre que de telles modifications pourraient bien s'avérer inutiles, et pourraient même nuire à la communication de résultats de recherche. La valeur de ce modèle minéralogique, de même que la description physique de propriétés complexes d'assemblages diagénétiques ou autres, seraient compromises ou bien sévèrement limitées si l'on adoptait les critères proposés pour son utilisation. En l'absence d'une alternative prouvée supérieure, il paraît souhaitable de continuer l'utilisation prioritaire du concept de particules fondamentales dans les disciplines géoscientifiques, parce qu'il offre une base quantitative, vérifiée et validée à partir de données indépendantes, par laquelle il est possible d'évaluer la nature, le comportement, et l'origine des minéraux du groupe des argiles dans une variété de contextes géologiques.

(Traduit par la Rédaction)

Mots-clés: particules fondamentales, cristallites de MacEwan, argiles interstratifiées, microscopie électronique, diffraction X, illite, smectite, diagenèse, nomenclature des argiles.

Introduction

This contribution to the debate within the mineralogical sciences about fundamental particles is given at the invitation of the editor. It is a reply to a short discussion regarding implications of high-resolution transmission electron microscopy (HRTEM), as presented by Peacor (1998). The issues considered here include: 1) the need to clearly differentiate between one-dimensional and three-dimensional coherency, 2) the limitations of HRTEM analytical methods and observations, and 3) the failure of HRTEM or other studies to provide an alternative to the fundamental particle model that can be verified and confirmed by experiment or quantitative measurements. The latter issue is central to the discussion, because in the absence of such an alternative, there is no value in severely restricting or eliminating altogether consideration of a verified and confirmed model from the geoscience literature, one that has resulted in major advancements in clay mineralogy, as would result from accepting the proposals put forward by Peacor (1998).

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Merits of the Fundamental Particle Model

The fundamental particle model was established during the mid-1980s (Nadeau *et al.* 1984), and has since then become a paradigm within the field of clay mineralogy (Nadeau 1998a, b). As is often the case during the establishment of a new paradigm, problems in communication arise, in part because there is no formally sanctioned terminology of definitions, which leads to confusion. An important corollary to the fundamental particle model is the phenomenon of interparticle diffraction, whereby apparent one-dimensional coherency can arise from within turbostratic arrangements or aggregates of fundamental particles. Thus, a one-dimensional MacEwan crystallite 15 layers thick composed of different types of clay-mineral layers, say illite and smectite (mixed-layer I/S, which are important mineral components in sediments and soils), can arise from an aggregate of much thinner fundamental particles, where the interfaces of particles behave like smectite interlayers (Fig. 1). The new paradigm causes confusion because a coherent one-dimensional arrangement of layers is no longer a mixed-layered *crystal.* This has been confirmed by independent XRD experiments on samples of bentonite, which show that for I/S, the three-dimensional periodicity (*hkl* maxima) arises from within fundamental particles of illite, whereas the turbostratic dislocations are located at the smectite interfaces

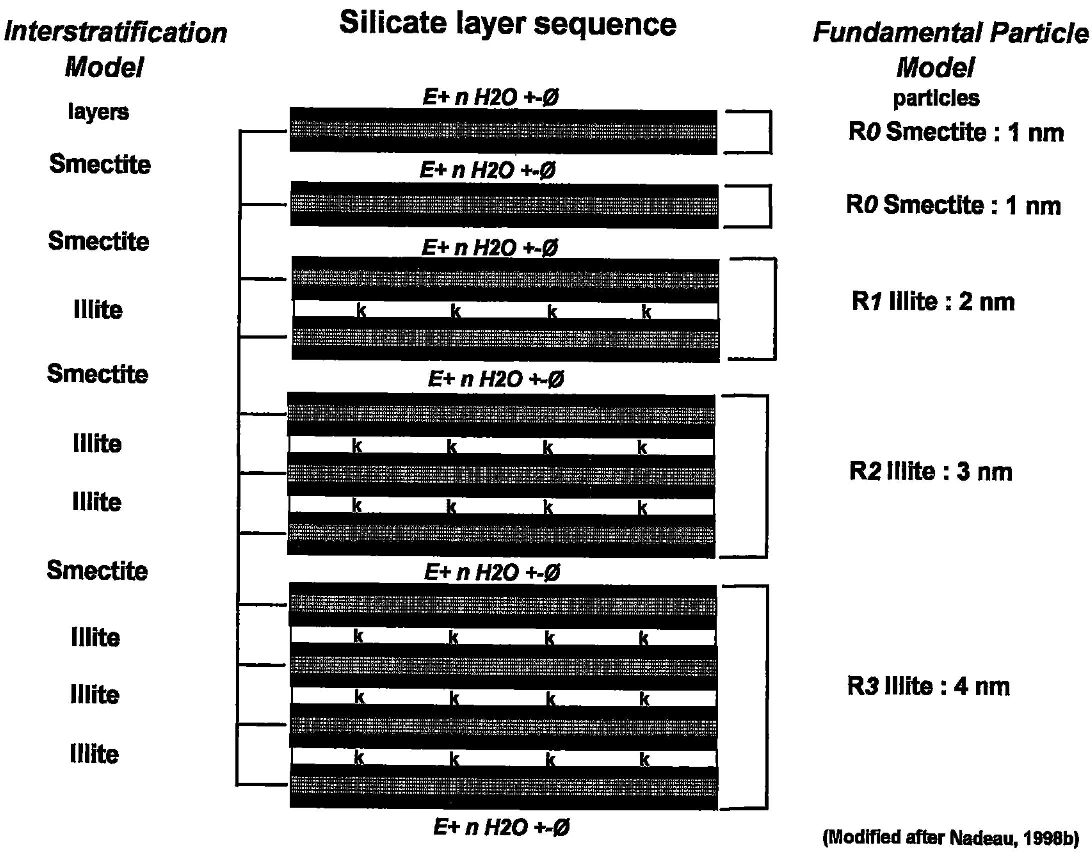

FIG. 1. Silicate layer sequence of mixed-layer illite/smectite based on interstratification within MacEwan crystallites (left) and the fundamental particle model (right). Two-to-one (2:1) silicate layers are represented by two tetrahedral sheets (black) joined by one octahedral sheet (stippled). Exchangeable cations, water, or organic molecules such as ethylene glycol are indicated by E+ n H_2O ± Ø, and planes of non-exchangeable cations within fundamental illite particles or interstratified illite layers are represented by "k". Note that a single 2:1 silicate layer is identical to an elementary smectite particle according to the fundamental particle model, but not to a smectite layer in the interstratification model where the octahedral sheets are taken as the layer boundaries. Note also that three-dimensional turbostratic structural dislocations within the layer sequence are restricted to particle interfaces (smectite interlayers). The proposed taxonomy of particles is from Nadeau (1998b).

(Reynolds 1993). Therefore, the experimental data indicate that the coherent one-dimensional layer-sequences are incoherent across expandable smectite-like layers in three dimensions. It is not surprising, therefore, that confusion exists within the literature regarding the usage of the terms crystal, crystallite, coherent domain, particle, layer, interlayer, illite, smectite, *etc.* Until these issues are addressed specifically within the normal development of nomenclature, such confusion is likely to continue.

A vital issue concerns the advantages and limitations of analytical methods. A hallmark of the fundamental particle model is that it reconciled both XRD and TEM data, mainly from I/S clay separates from samples of bentonite and sandstone, within one interpretive model. Mainly on the basis of HRTEM observations of bulk-rock samples from shales, Peacor (1998) claims that these observations should take precedence over those based on clay-mineral separates because of possible artifactual cleavage of pre-existing crystals during sample preparation. It is shown here that both clay separates and HRTEM of bulk rocks are susceptible to artifactual effects, and that careful evaluation of these factors is required to most effectively extract information from the analytical measurements and observations. Also, clay mineralogists have often placed emphasis on diagenetic studies of bentonites within shale – mudstone sediments, in order to avoid the complex petrology of detrital phyllosilicate components usually found in shales (*cf.* Nadeau & Reynolds 1981).

First, let me deal with the claim that measurements of coherency from clay-mineral separates are not representative of the bulk rock. The fundamental particle model holds that because the sequence of particles within an aggregate is always random, as long as the type and proportion of the fundamental particles present within a specimen remain unchanged, either in the bulk rock or the clay separate, the observed sequence of layers and coherency relationships will be the same. This view was confirmed by detailed experiments on I/S in samples of bentonite, both on the bulk rock and clay separates (Reynolds 1992). Studies of diagenetic I/S from preserved subsurface bulk-rock samples have also shown that important textural relationships are lost owing to collapse of the delicate clay during drying in air (McHardy *et al.* 1982). Observations from a North Sea reservoir sandstone in preserved samples prepared by Critical Point Drying (CPD) methods to remove the interfacial tension effects of drying from a water-saturated state (McHardy & Birnie 1987) show that the diagenetic

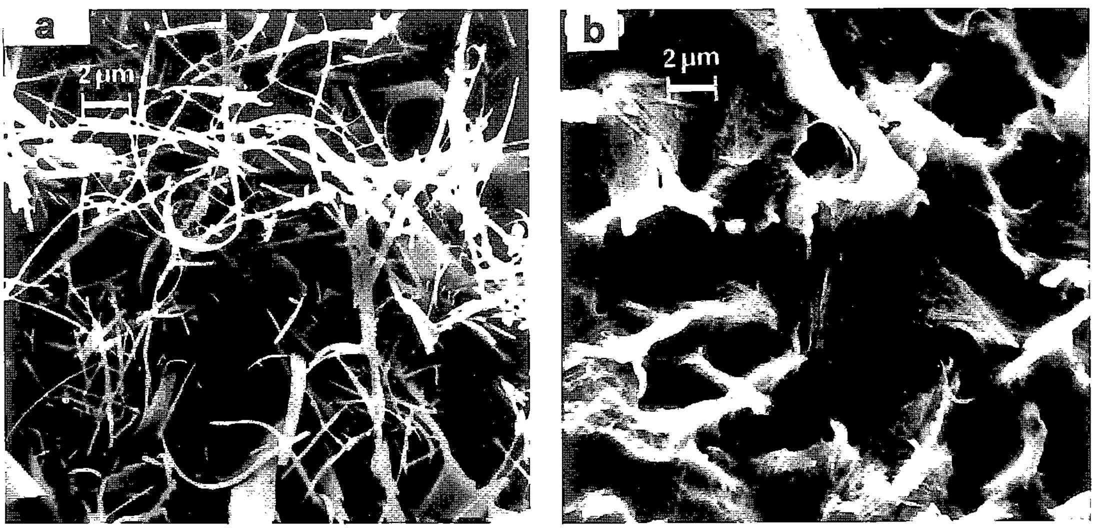

FIG. 2. Scanning electron micrographs of diagenetic illite (R >=1, 10 % expandable layers by XRD) from a preserved, water-saturated sample of the Rannoch Formation, North Sea. (a) Critical Point Dried specimen showing delicate diagenetic textural features of individual illite particles growing within the pore space of the rock; see McHardy & Birnie (1987) for details of the procedure. (b) Air- dried sample showing collapse of the diagenetic clay into aggregated irregular masses of "anastomosing" layers. Note that outlines of some of the individual particles can still be seen on the surface of the masses despite the high degree of basal surface association. In terms of the discussion, (a) is considered representative of the diagenetic fundamental particles of illite in their subsurface growth-habit, and (b) is their artifactual aggregation into MacEwan mixed-layer clay crystallites cause by collapse upon drying in air. Dispersal of fundamental particles from such aggregates during preparation of clay separates does not constitute cleavage of pre-existing three-dimensional mixed-layer crystals, as claimed by Peacor (1998). Micrographs courtesy of W.J. McHardy.

clay consists of separate and individual lath-shaped particles of illite (Fig. 2a), whereas the conventional air-dried specimen shows the effects of collapse of the particles to form masses of irregular aggregates (Fig. 2b). Similar behavior has also been demonstrated for sandstones containing diagenetic smectite (Nadeau 1998c).

So which view is correct? If the specimen is preserved and prepared carefully by CPD methods, the textural relationships indicate that diagenetic "fundamental particles of illite" (Fig. 2a) grew separately and individually by crystallization from solution. Observation of textures from air-dried specimens (Fig. 2b) are not invalid, in that they represent the condition of specimens in the collapsed state, but their artifactual nature is commonly not recognized. Within this limited perspective, here considered analogous to MacEwan crystallites and HRTEM bulk-rock observations, the clay is viewed as irregular masses of "anastomosing" layers. Indeed, if these masses are dispersed back into fundamental particles during preparation of clay-mineral separates, the observer restricted to the air-dried rock specimen perspective would argue that such particles must have been "cleaved" from pre-existing mixed-layered crystals, and as such would claim that the particles are artifactual. My understanding is that all of the bulk-rock HRTEM specimens discussed by Peacor (1998) are from conventional air-dried samples, and this fact may explain, at least in part, the basis for the claims made.

The above discussion, however, does not address the claims of three-dimensional coherency across smectite interlayers by Peacor (1998). Although there are notable exceptions, the majority of smectite samples are turbostratic, in that they show no three-dimensional periodicity (Brindley 1980). The work of Reynolds (1992) regarding the turbostratic nature of smectite-like interlayers confirms, in a much more detailed and precise way, the general experience of mineralogists in studying clay materials containing smectite components. Peacor (1998) claims that turbostratic dislocations in smectite are just an assumption of the fundamental particle hypothesis (although multi-layer fundamental particles of smectite were never ruled out). Even if it is a general assumption, it is no more an assumption than the mixed-layer crystal in MacEwan or Markovian interpretive models. Nevertheless, Peacor's suggestion of more general three-dimensional periodicity of smectite in I/S from shales is extraordinary, and can be addressed by the following arguments: 1) induced three-dimensional periodic collapse of smectite-like interlayers due to ion-milling methods of sample preparation for HRTEM observations, 2) representativeness of HRTEM and lattice-resolution cross-fringes due to electron-beam damage to the specimen, and 3) precipitation of diagenetic illite on pre-existing surfaces of detrital mica or illite in shales, resulting in three-dimensional coherently oriented fundamental particles of diagenetic illite due to a common mineral substrate during epitactic nucleation and growth. These are reviewed in turn.

It has been shown that although smectite layers are generally turbostratically related, three-dimensional periodicity can be induced through interlayer-ion saturation, such as potassium or cesium, and thermal effects due to heating. HRTEM methods of preparation for bulk rocks require that the specimen be sectioned, polished, and subjected to a beam of high-energy ions. This last step is referred to as ion-milling, and involves abrading away an area of the specimen (*cf.* Nadeau & Tait 1987). HRTEM observations are then made on the ion-thinned edges of the specimen. In the high-vacuum environment during this procedure, effects of ion-milling illitic or micaceous specimens could result in potassium fixation in nearby ion-exchange sites, and increase susceptibility to induced collapse of three-dimensional periodicity. Such an effect could also contribute to reported difficulties in distinguishing between illite and smectite layers by HRTEM (Ahn & Buseck 1990).

Secondly, clay minerals, owing to their delicate microcrystalline nature, are commonly susceptible to electron-beam damage. During HRTEM examination, and particularly when lattice-fringe and cross-fringe diffraction features are examined, the specimens generally undergo rapid deterioration within the highly focused beam of electrons. Operators are usually forced to rapidly acquire and record image and diffraction data before the area under examination is damaged beyond recognition. In shale samples, which invariably contain detrital micas, differentiating between the features of incipiently formed diagenetic illite and those within more robust detrital illite and micas may be difficult. Sampling bias of lattice information or HRTEM images in favor of features associated with detrital micas could result, owing to their greater stability during examination.

Thirdly, the presence of detrital micas within shales may establish a pre-existing diagenetic condition that is not dominant in bentonites and sandstones, namely large surface-areas of muscovite that provide energetically favored sites for the nucleation of diagenetic illite. This possible effect can be demonstrated by analogy to cementation by diagenetic quartz in sandstones, where pre-existing grains of detrital quartz provide a preferred surface for epitactic nucleation and growth (*cf.* Bjørkum *et al.* 1998). In sandstones with coatings of microcrystalline quartz, individual crystals of epitactic diagenetic quartz exhibit a common or "coherent" orientation due to the shared nucleation substrate (Fig. 3, after Aase *et al.* 1996). The question can be asked: is the grain of detrital quartz along with its diagenetic overgrowths one crystal, or one large grain of detrital quartz covered by a myriad of individual crystals of diagenetic quartz? Considered as a continuous three-dimensional periodic array, it would be regarded as one crystal, which results in coherency of domains between the detrital quartz and

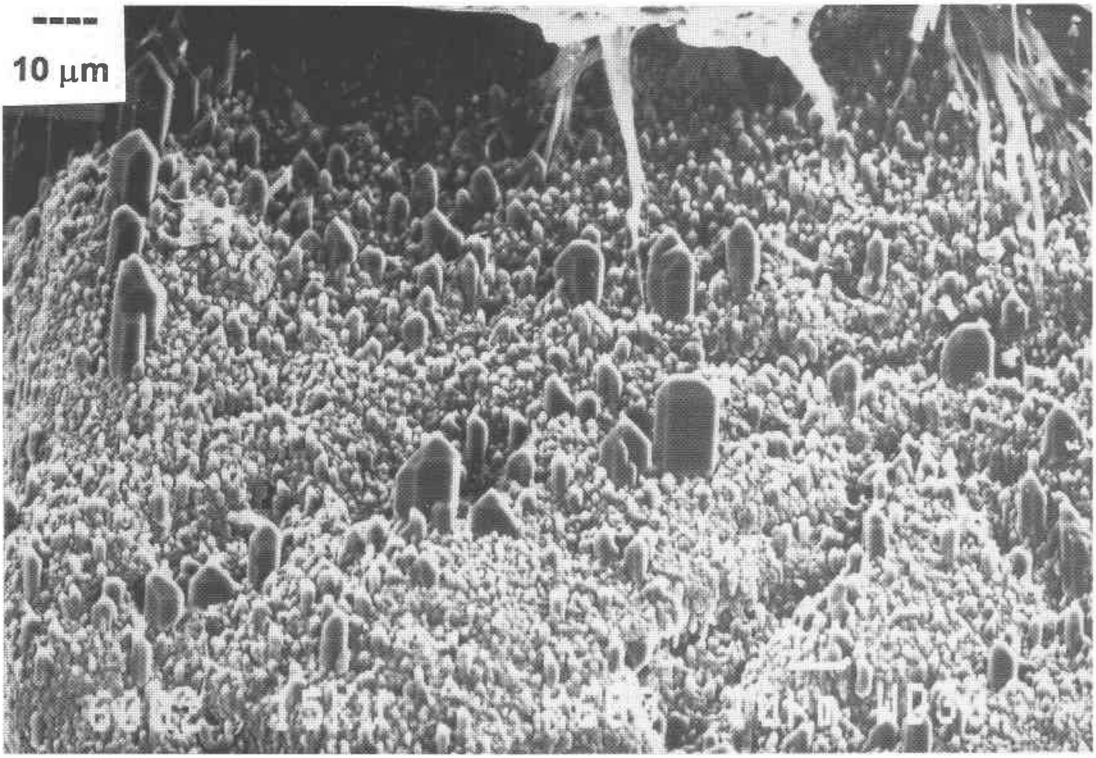

FIG. 3. Diagenetic microquartz crystals, showing common orientation due to the shared substrate of a detrital quartz grain surface during nucleation. Analogous situations regarding nucleation and growth of diagenetic illite on surfaces of detrital mica in shales may result in adjacent particles showing three-dimensional coherency when examined by HRTEM. In such an analogous situation, coherent relationships reported by HRTEM studies do not invalidate the fundamental particle concept, as claimed by Peacor (1998). Micrograph after Aase *et al.* (1996).

diagenetic quartz, as well as among the microcrystals of diagenetic quartz. From a diagenetic point of view, however, the microcrystals of quartz nucleate and grow as separate entities, and as such they contribute individually to the thermodynamic equilibrium of the system through such parameters as surface energy, solubility, and silica saturation. So which view is correct? As is often the case, it depends on one's point of view, and the purpose for which one defines the system. If an analogous situation exists for epitactic growth of diagenetic illite on detrital mica in shales, it could turn out that coherent relationships between fundamental particles of illite and a common substrate result in both views being valid, and not mutually exclusive. Such an explanation can reconcile why HRTEM observations from shales are in apparent conflict with the XRD measurements from bentonites of Reynolds (1992), as discussed by Pevear *et al.* (1997) on the basis of measurements by atomic force microscopy (AFM).

IN CLOSING...

In closing, I would like to address the question "How can we most effectively advance the geosciences?" in light of this discussion. The fundamental particle model has established itself as a powerful paradigm within clay mineralogy. It has contributed to a better understanding of the nature and origin of mixed-layered clays, and it is the only model that can uniformly explain the observed sequence of layers and the geological evolution of layer sequences of these minerals. The recommendation that usage of the term "fundamental particle" be limited only to those circumstances that fit the original definitions used during the initial communication of the model, namely the proposed SAED single-crystal criteria or "test", would severely restrict consideration of the concept as a general interpretive model. This is analogous to requiring a corresponding SAED single-crystal "test" before one could consider MacEwan mixed-layer crystal as an interpretive model, which most researchers would find unacceptable. Despite the substantial research effort represented by HRTEM as well as other studies, no quantitative alternative to the fundamental particle model exists. Until such time as a verified and confirmed alternative is established, the fundamental particle model should have priority. Its usage embodies the best prospects for advancement of geoscience disciplines that must consider the nature and behavior of complex clay minerals in natural systems. Recently, it has also produced important applications in mechanisms of crystal growth (Eberl *et al.* 1998) as well as sedimentary basin analysis (Bjørkum & Nadeau 1998). The proposed "test" of Peacor (1998) would at best place unrealistic burdens on scientific communications, and at worst set back the research community over ten years with no credible way forward.

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