

## ON THE CORRELATION OF EXPANDABILITY WITH MINERALOGY AND LAYERING IN MIXED-LAYER CLAYS

**Key Words**—Expandability, Illite, Interstratification, Mixed layer, Nomenclature, Smectite, X-ray powder diffraction.

Despite a long history of interest in the chemical and mineralogical constitution of materials commonly designated as dioctahedral mixed-layer clays and their textural relations in natural samples, these topics are still the subject of considerable debate resulting from conflicting physical and chemical data. In part, the controversy is related to the manner in which the constituents of these clays are defined and identified. For example, in 1937, Grim *et al.* proposed that the group name “illite” be adopted as a general category for the micaceous clay mineral constituents of argillaceous sediments. Since that time, the name illite has evolved to where its use now invokes a specific mineral having compositional and crystallographic characteristics that make it distinct from other micaceous minerals (e.g., Hower and Mowatt, 1966; Perry and Hower, 1970; Hower *et al.*, 1976; Środoń *et al.*, 1986). As a result, in the latest report of the Nomenclature Committee of The Clay Minerals Society (Bailey *et al.*, 1984), the mineral illite was provisionally defined on the basis of three criteria, the first specifying it to be composed of non-expandable micaceous layers and the other two establishing specific chemical characteristics that set it apart from related phyllosilicate species, such as muscovite and members of the smectite group.

In practice, however, the first of these criteria is commonly the only one used to detect what is called “illite” in samples designated as dioctahedral mixed-layer clays, which we would rather call 10/17-Å (ethylene glycolated) clay (see below). Similarly, the expandable components of these clays are generally designated as smectite. These working definitions and the synonymous identification of expandability, or lack thereof, with a mineral or group name such as smectite or illite, cause considerable confusion and ambiguity in the development and application of chemical and thermodynamic models to clay minerals and diagenetic processes. The purposes of this communication are fourfold: (1) to propose in accord with the formal definition and classification of minerals (Dana, 1868; Frye, 1981; Nickel and Mandarino, 1987) that illite and the various members of the smectite group be defined and identified strictly on the basis of their chemistry and crystal structure (i.e., properties that are independent of grain size or the physical behavior of the sample in specific solvents), (2) to recommend that the term illite be restricted to the designation of a phase and no longer be used to refer to a non-expandable phyllosilicate layer

of uncertain composition, (3) to suggest that the term mixed-layer clay be restricted to apply only to those clays which can be demonstrated unambiguously to consist of crystallographically interstratified expandable and non-expandable layers, and (4) to advocate a nomenclature to describe so-called mixed-layer clays in accord with their X-ray powder diffraction (XRD) and transmission electron microscopic (TEM) patterns, as for example, 10/17-Å (ethylene glycolated) clay.

Owing to the fine-grained nature of many clay samples, their constituents are commonly deduced solely from scanning XRD patterns, which are used to determine the number of expanded and non-expanded layers in the sample. The interpretation of these data relies on the crystallographic models and working definitions currently accepted by the clay mineral community regarding the compositional and textural relations between the various phyllosilicates thought to be present in the sample. According to the present consensus, the 10-Å dioctahedral phyllosilicate component of a 10/17-Å (ethylene glycolated) clay that does not expand on saturation with ethylene glycol is termed illite, whereas the 10-Å constituent exhibiting basal (001) expansion to 17 Å upon glycolation is called smectite. Unfortunately, in most cases both of these designations are made without benefit of supporting chemical data for the individual phyllosilicate components, and neither provides for the possibility that the presence or absence of non-expanded or expanded layers may be dependent upon factors other than the presence of illite or smectite. Nevertheless, expansion criteria are still considered by many to be diagnostic of the mineralogy of the sample. On the basis of recent documentation of physical phenomena other than mineralogy that can affect clay mineral expandability (see below), it is our contention that the expandability criterion alone is not sufficient to determine reliably either the existence of, or degree of interstratification of smectite or illite layers in a dioctahedral clay sample.

The validity of correlating clay mineralogy with expandability is dependent upon a number of factors: (1) that crystal size or unrecognized physical and chemical properties of the sample do not contribute to its expandability and (2) that layer silicates having 10-Å non-expandable basal spacings other than illite are not present. Although differences in the orientation of ethylene glycol-solvated 10/17-Å clays on XRD mounts

have little or no effect on the relative amounts of expandable and non-expandable material detected by XRD, sample disaggregation, grinding, and interparticle diffraction have been demonstrated to cause increases in the expandability of clay samples that are independent of sample mineralogy (Fenner, 1966, 1967; Blahoslav and Kranz, 1981; McHardy *et al.*, 1982; Nadeau *et al.*, 1984a, 1984b, 1984c; Nadeau, 1985; Ahn and Peacor, 1986; Eberl *et al.*, 1987; Inoue *et al.*, 1987). After saturation with ethylene glycol, a pure single-phase sample of what is considered to be a non-expandable mineral (i.e., illite, chlorite, or "sericite") may exhibit expanded layers in an XRD pattern, provided the sample contains a quantity of ultrathin disarticulated phyllosilicate layers (Nadeau *et al.*, 1984a, 1984b, 1984c; Ahn and Peacor, 1986; Eberl *et al.*, 1987).

A second phenomenon, one that affects smectite expandability and that is not generally recognized, is the development of three-dimensional crystalline order. Mamy and Gaultier (1976, 1979), Plançon *et al.* (1978), and Eberl *et al.* (1986) among others have shown that the expandability of certain smectites is directly related to their stacking sequence. The smectites they studied were fully expandable only if the sample layering was turbostratic. As three-dimensional order was imposed by alternate wetting and drying of the samples, the percentage of expandable layers decreased significantly (see also, Whitney and Northrop, 1988). Other ambiguities arise in the interpretation of XRD patterns in terms of interstratification of expanded and non-expanded layers, if, in fact, illite occurs as a separate phase within pure smectite, or vice versa (Ahn and Peacor, 1986). Hence, in a clay sample, the expandability detected by XRD cannot be correlated reliably with the mineralogy of the sample and it is not necessarily representative of the interstratification of the clay in its natural setting.

In the present clay mineral literature, interparticle diffraction, ordered layering, and the presence of more than one discrete phase in a sample does not appear to have been reconciled satisfactorily with the currently accepted interpretation of XRD patterns or with the prevalent definitions and concepts of clay mineral behavior. We believe that the evidence for the existence of these effects is now strong enough that a re-evaluation is required of the criteria used to identify the constituents of clay samples in which expandability, or lack thereof, is currently used to designate the mineralogy (e.g., smectite, illite, and the various types of so-called mixed-layer clays).

The use of expandability as the sole criterion for identification of a mineral is not consistent with the formalism reviewed in the latest report of the International Mineralogical Association's Commission on New Minerals and Mineral Names (Nickel and Mandarino, 1987). In accord with these guidelines, we recommend that argillaceous material which appears from XRD and/or TEM data to contain both expandable

and non-expandable components be called an  $x/y$ -Å (ethylene glycolated, or otherwise treated) clay (where  $x$  and  $y$  refer to the percentages of non-expanded and expanded basal spacings, respectively), unless other crystallographic and chemical data are available to warrant a more specific mineralogic classification, such as a mixture of two or more phases or an interstratified mineral consisting of expandable and non-expandable layers. As suggested by R. C. Reynolds (Department of Earth Science, Dartmouth College, Hanover, New Hampshire, written communication, 1988), modifiers, such as percent expandable, dioctahedral, trioctahedral, etc., could be used in a preface, leading to designations such as: 40% expandable, dioctahedral 10/17-Å (ethylene glycolated) clay. Unlike the term "mixed-layer clay", this nomenclature carries no necessary connotation of interstratified layering. The term is deliberately ambiguous in this regard, and also with respect to whether or not more than one phase is present in the sample, in order to prevent the association of mineral (and hence chemical) names with a property that is dependent on the physical behavior of the sample. Accordingly, names that are prevalent in the literature and assigned on the basis of the XRD or TEM identification of expanded and non-expanded constituents of what are commonly called mixed-layer clays, such as I/S, ISII, randomly interstratified illite/smectite, regularly interstratified illite/smectite, ordered illite/smectite, would no longer be used unless the mineralogical constituents and their textural relations can be definitely established.

The approach described above should result in objective descriptions of clay mineral samples by circumventing chemical and mineralogical connotations inherent in the present illite/smectite terminology. If our recommendations are adopted, we believe it will encourage development of better and more exact analytical techniques and equipment capable of determining the actual mineralogy of clay samples. As a result of the discussion we trust this communication will generate, we hope that misleading or erroneous interpretations of XRD patterns and TEM photographs resulting from the assumption of a direct correspondence between expandability, mineralogy, and layering can be prevented, or at least minimized, and that a better understanding of phase relations among phyllosilicates will emerge.

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