

BOOK REVIEWS

Illite, by Alain Meunier and Bruce Velde. Springer, 286 pp. [ISBN 1-881208-13-3]. Price \$109

To my knowledge, this is the first book ever written which is entirely devoted to illite, and the first broad compendium of illite affairs since our chapter ‘Illite’ was published twenty years ago (Środoń and Eberl, 1984). Being such a rare bird, this book deserves the attention of all friends of illite. However, the title is misleading. It should read ‘Illite from a very personal perspective’. This is not a balanced review of all published data on illite or all concepts of the nature of illite and its origin. Instead it is a passionate presentation of a personal viewpoint. Of the references cited, 20% of the 370 are by the authors or their students. Other references are often used only as sources of data, which are interpreted without referring to or discussing the original interpretations; this is legitimate. The book is interesting and stimulating, but it seems to be addressed to experienced illite students, who are most able to read it critically.

The book is not easy to follow. It seems to have been written in a hurry, not critically reviewed, and not edited properly. Be prepared not to find several of the cited references in the reference list (some of them are non-existent, e.g. Eberl and Środoń (1984) cited on p. 4, or Środoń *et al.* (1987) cited on p. 111), to find some listed twice (Gharrabi *et al.*, 1998), different versions of names (e.g. Loucks on p. 22 vs. Louks in the reference list), misleading references to figures (2.13 on p. 91), mistakes in equations (p. 146), and very poor table and figure captions.

There is a consistent failure to explain the symbols used, which makes the figures and tables very difficult to follow. Figure 2.24 is a good example of this shortcoming. Several figures are reproduced twice without good reason and sometimes in different versions (Zat 1139 XRD pattern on pp. 17 and 99, two patterns on pp. 49 and 82, 11 and 78, *etc.*), while others such as Figure 3.12 are incomplete. Whole paragraphs have been repeated (p. 51 vs. 52; 168 vs. 169).

Worse than that, the contents of the tables and figures cannot be trusted. In Tables 2.3 and 2.34 and associated figures, the fundamental particle thickness listed as measured from HRTEM images is in fact the coherent scattering domain (mixed-layer crystal) thickness calculated from the fixed cations content assuming constant $0.89/0_{10}(\text{OH})_2$ charge of illite layers, which is taken from the last column of Table 3 in Środoń *et al.* (1992).

Table 3.1 represents another case. The caption implies a data set from a cited paper, while the percentages of low- and high-charge smectite are the

authors’ interpretation, not fully consistent with the criteria listed below the table.

The Beavers Bend illite is characterized on p. 20 as PCI $2M_1$, while in Figure 1.3 it is identified as a mixture of PCI and dominant illite-smectite. In reality this sample may contain a paragonite-like mineral, but additional tests would be needed to verify this. One mixed-layer mineral is presented in Figure 4.27, but two are discussed in the related text. The caption for Figure 4.31 suggests comparison of Sr-saturated and oxidized K-saturated forms of the same samples, while in the figure, the patterns are marked differently. Thus some of the authors’ speculations are based on incorrect or questionable data.

The language is an additional obstacle. In many places, the authors’ thoughts are not easy to follow, e.g., on p. 23: “These shifts in the monoclinic direction from 2:1 layer to 2:1 layer stacking which form polytypes.” This is partly caused by the authors’ vague style, and partly by their English, but this is difficult to understand given that Bruce Velde is an American. Editing by a native English speaker would have helped this book greatly. In general, the editorial level is miserable and well below the standard of CCM.

However, if a dedicated reader does not give up too early, he will be rewarded and find a coherent vision of illite seen from several perspectives. These ideas of illite are based on an impressive volume of the authors’ own work and their interpretations of other people’s data. This vision is disputable on many points, but confronting it is a very stimulating process and potentially beneficial for an experienced reader. The following are some of my own confrontations.

I found Chapter 1 particularly difficult to accept, mainly because it relies so heavily on the peak-decomposition technique of Lanson and Velde (1992). This technique has been presented in the introduction as the dominant ‘method’ achievement of clay research in the last decade. However, even when it was born, it was known that this approach, based as it is on the use of symmetric Gaussian shapes, is methodologically incorrect because the low-angle clay peaks are very asymmetric due to the shape of LpG^2 factors in this 2θ range. Moreover, NEWMOD, which can be used to fit a composite pattern with proper shapes of expected mineral components, was already in broad use at that time. Since then, V. Drits and his collaborators have demonstrated in a series of papers how the composite clay peaks can be fitted precisely using simulated peak shapes. They also established the criteria of reliable fit that entails fitting more than one angular range and at least two XRD patterns of the same sample in different

states (e.g. glycolated and air-dried) using the same set of structural and compositional parameters. This is because even if realistic shapes are used, the solutions are not unique for one pattern and one angular range.

Drits *et al.* (1998) showed that crystal-thickness distributions of clays, and in particular illite and illite-smectite, are most often lognormal. Using this type of distribution in XRD simulation, illite peak shapes can be modeled very precisely.

Another common shape of particle-size distribution curves is asymptotic and for the example XRD pattern of the Le Puy illite, interpreted in Figure 2.10 as a mixture of illite-smectite plus illite, this can be modeled as illite with an asymptotic distribution of crystal thickness (D. Eberl, unpublished). Indeed, this illite is essentially non-swelling and not a mixed-layer clay.

A further example of misinterpretation concerns sericite (p. 16). Silverton sericites are classified using the authors' criteria as WCI (non-expandable) illites, while the original authors had presented an extensive documentation of their expandability including the change from illite-smectite into illite-vermiculite characteristics, depending on the interlayer cation and the relative humidity. These examples demonstrate how misleading the Gaussian peak decomposition technique can be. In my opinion, the sooner its proponents follow the lead of Bruno Lanson and switch to the rigorous approach of pattern modeling, the better for clay science.

My second major reservation concerning Chapter 1 is the erroneous presentation of the fundamental particle approach (pp. 38–39). An illite particle is not two layers, but any number of layers permanently bound by fixed cations. A mixed-layer crystal and not fundamental particle is an equivalent of a coherent X-ray domain. The illite fundamental particle is not necessarily $1M$ and indeed is often $1Md$, *i.e.* contains rotational defects $n \cdot 60^\circ$ and/or $n \cdot 120^\circ$.

The strong aspects of Chapter 1 are, in this reviewer's opinion, the sections on layer charge and on thermodynamic stability of illite.

Chapter 2 reads much better. The summary of illite generation in soils is worth reading and thinking about because this is still one of the most enigmatic aspects of the illite rock cycle. The authors' evidence seems quite convincing. One would still like to see ultimate proof, based on K-Ar dating, for example. This is because of the danger of eolian contamination, which was demonstrated to be a serious problem even in temperate European climatic conditions (Šuchá *et al.*, 2001). One can learn a lot from the next section, on the formation of illite in weathered granites, which is the field studied extensively by the authors.

I found the section on sedimentary (lacustrine) illites less rewarding. This is a French speciality, most of the occurrences described being from various French Tertiary basins. It is clear from all the XRD data published in these papers that lacustrine illites are not

$2M_1$ as stated by the authors on p. 78 about Le Puy illite, but $1Md$, with numerous $n \cdot 60^\circ$ rotational defects. Indeed, in Le Puy illite there is an admixture of the $2M_1$ polytype, which is probably detrital. That would explain the always greater than stratigraphic K-Ar dates of this mineral obtained by N. Clauer (pers. comm.). The origin of lacustrine illites is not so obscure any more since the excellent study of Hay *et al.* (1991) on the Searles Lake in California.

The section on diagenesis presents an interesting hypothesis that a smectite is formed first from the detrital clay assemblage, a problem worth considering even though the stable isotope study of Yeh and Eslinger (1986) seemed to indicate otherwise. The statement on p. 83 that R1 ordering 'begins, by definition, at 50% smectite' is incorrect. R1 ordering appears gradually and most commonly R0-R1 transition is observed at ~40–35%S (e.g. data from Šuchá *et al.*, 1993, reproduced by the authors on p. 98). It is never observed at 50% in the diagenetic sequences. In other words, the stage of a regular rectorite-type mineral is never observed. Rectorite is a rare mineral of hydrothermal origin. This late appearance of R1 is interpreted as a result of nucleation and growth of illite. By the time all smectite monolayers disappear, a condition of R1 ordering, some illite particles managed to grow and the population also contains particles thicker than 2 nm, thus %S < 50. An additional reason is a restricted size of the mixed-layer crystals. The smectitic edges of such crystals are not accounted for in XRD measurement, which makes the composition more illitic (e.g. ISIS crystal will be recognized as 40%S).

The comments on the role of a vermiculitic precursor in the illitization process refer to an old dispute which is worth continuing. It is a plausible hypothesis but hard evidence is still lacking. Perhaps the present-day XRD pattern-modeling approach of Drits *et al.* will solve this problem definitively.

The section on illite crystallinity (p.85) is very old-fashioned, presenting the state of the knowledge from decades ago. The students of illite crystallinity today use angular measures, not mm, and calibrate their data using interlaboratory standards. Techniques for interpreting illite crystallinity measurements in terms of mean crystal size and of extracting crystal-size distributions from XRD peak-shape analysis became available years ago (Drits *et al.*, 1998). This information, lacking in the text, can be found in the attached glossary.

Page 92 brings a refreshing statement that the compositional variability of mixed-layer crystals can be different from that predicted by the Markovian statistics. The problem could be investigated by HRTEM. For now, the Markovian hypothesis holds well because these models produce very satisfactory fits of XRD data.

The model of illitization presented in Figure 2.20 violates our knowledge of the successive layer arrange-

ments during the illitization process. It is well established that R1 ordering evolves gradually into R2, R2 into R3 *etc.*, which implies longer and longer sequences of illite layers. The transition of R1 to R2 cannot be explained by solid-state transformation and for this exact reason the dissolution and growth hypothesis was born in the 1980s. Interestingly, the authors never mention R>1 minerals in their text, as if they were unaware of their existence. The evolution from 50%S to illite is characterized as the alleverdite-to-illite transition.

The chapter on hydrothermal systems deserves attention for several reasons. The authors pose, and try to answer, a very intriguing question: can illite-smectite form without a smectitic precursor? They offer very convincing evidence of the instability of muscovite with respect to illite in hydrothermal environments. Finally they draw our attention to particular mineralogy of the boiling zones produced by montmorillonite to beidellite plus saponite reaction. This was an eye-opener for me, perhaps also an explanation of rare occurrences of rectorites which are hydrothermal, ordered beidellite-paragonite minerals.

The section on K-Ar dating is valuable, because it makes the reader aware of the complexity of this problem and underlines the role of illitization mechanism in the K-Ar data interpretation. The authors believe that the illitization proceeds through continuous ripening, *i.e.* dissolution of smaller illite particles and crystallization of bigger ones (p. 131). Indeed, several authors, including myself, suggested such a mechanism in the 1980s. It appeared later that the measured crystal-thickness distributions, broadening in the course of illitization, cannot be reconciled with the ripening mechanism but can be explained by continuous nucleation and growth of illite (Środoń *et al.*, 2000), which has grave consequences for the interpretation of K-Ar dates. Hopefully, one day, we will discover who was right and learn how illites evolve.

The interpretation of Glassman *et al.* (1989) of K-Ar data presented on p. 135 demonstrates well how much caution is needed in this field. The authors interpret older ages of coarser fractions as indicative of continuous nucleation mechanism. However, the original authors warned of the possibility of detrital contamination and reported in their table a 410 Ma age of a mica separated from one of the samples. It is easy to calculate that a few percent of such mica (quantity undetectable by XRD) will affect the measured Paleogene ages of the fine fractions. Thus the alternative explanation of such data is detrital contamination, increasing in coarser fractions. The same comment applies to the Balazuc example (pp. 182–187). It seems that in such cases the Ockham razor should be applied rigorously: only if the detrital contamination is excluded beyond any doubt, then the interpretation of K-Ar data in terms of a reaction mechanism is justified.

The section on kinetics of illite formation reflects well the state of this subject, *i.e.* a general confusion. A

good example is the treatment of Whitney and Northrop (1988) data. On p. 147 we learn that the system should be interpreted as a three-component structure of low- and high-charge smectite plus illite and not a two-component of smectite and illite. This sounds convincing, but then the %I determinations of Whitney and Northrop cannot be trusted because they were obtained for the two-component model. Instead, these data are used to follow the reaction progress (Fig. 3.1) and to calculate the kinetic parameters on Figure 3.7. On top of that, on p. 147 we learn about up to 11% illite in R0 reaction products, on p. 158 we read that no illite is present, and on p. 159 that 8% illite layers are detectable. It seems prudent to say that the kinetic models of illitization based on data of such quality should be looked at with a great caution.

Chapter 4, on applications, reads well and offers a valuable summary of the authors' vast experience in this field. The section on geothermal resources repeats and broadens interesting information presented earlier (section 2.3). The next section offers a valuable synthesis of information on the diagenesis in the Paris Basin. The section on organic *vs.* mineral maturity brings a stimulating review and intriguing data on the reaction of the two indicators to short pulses of temperature (Fig. 4.18). Unfortunately % illite data (a) refer to the eastern Paris Basin and the reflectance data (b) to an individual well, and the authors have documented earlier the presence of local thermal anomalies in the basin. For this reason, (a) and (b) may represent different thermal regimes, which would not allow for direct comparison. The following chapters present a very convincing demonstration of the usefulness of illite structural characteristics (polytypes and defects) in prospecting for metal deposits.

The section on soils offers evidence of the effect of agricultural practices on soil potassic clays. The Chinese case is very convincing. Other detailed interpretations may be questionable because soils are particularly complex clay systems, so the conclusions based on the decomposition technique are particularly risky. Also, the authors seem to ignore the role of clay aggregation. Different chemical treatments (*e.g.* oxidation) may destroy clay aggregates to different extents and liberate clay crystals, which may have profound effects on relative peak intensities (*e.g.* enhancing the discrete mica peak). Nevertheless, the chapter offers a valuable introduction into the fascinating field of illite behavior in soils. Also, the last chapter on nuclear waste disposal brings stimulating new ideas concerning this important application of clays.

The glossary attached at the end of the book is surprising in a couple of respects. First, it correctly presents fundamental particles, which was not the case in Chapter 1. Secondly, half of it is devoted to the presentation, in some detail, of the modeling of XRD effects from mixed-layer crystals, *i.e.* a rigorous

approach to identifying clay mixtures, which in the book is avoided and substituted by the Gaussian decomposition technique.

One closes this book with the impression that if this glossary was put in front and then followed, this would have been a better book. But even in its current state, it is worthy of careful study. With all its pitfalls, this book offers a vision which makes you think about illite, its intriguing nature, properties and potential applications to solving geological and technical problems.

ACKNOWLEDGMENT

Douglas McCarty improved the English of this review.

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- Zeolite Science and Technology* by the same editors (Auerbach *et al.*, 2003), I had high expectations of this accompanying volume on layered materials, and in general I was not disappointed.
- The contents of the book can be roughly divided into two sections, the first of which, in six chapters, describes clays and their modifications. The second part, comprising five chapters, describes other layered materials such as layered double hydroxides, zirconium phosphate and phosphonates, manganese oxides, *etc.*
- Chapter 1 (Carrado) gives a general introduction to clay mineralogy and clay mineral structures, at a level appropriate for those who are not experts in the subject. An overview follows of the most common characterization techniques used in the study of clay minerals such as X-ray diffraction, infrared spectroscopy, nuclear magnetic resonance, N₂ adsorption and desorption, cation exchange capacity and surface acidity. The chapter concludes with a short introduction to the use of clay minerals in catalysis, a topic dealt with more extensively in Chapter 6.
- Chapter 2 (Park and Sposito) focuses on the molecular modeling of clay mineral structures and their surface chemistry to provide molecular-scale details of, *e.g.* surface reactions. Even though molecular modeling is based on physical concepts (quantum mechanics) and the use of mathematics, the mathematical descriptions have been kept to an absolute minimum, whilst still demonstrating what can be achieved. It clearly shows the power of modeling in the description of spectral information and visualization of what is actually happening on a clay surface. More detailed information on the use of molecular modeling can be found in the recently published Clay Minerals Society Workshop Lectures volume (Kubicki and Bleam, 2003).
- Chapter 3 (Ruiz-Hitzky, Aranda and Serratos) focuses on the modification of clays through interaction with organic molecules. The sorption of organic molecules, with different types of functionalities, on clay surfaces strongly influences the properties of these clay surfaces and can therefore be used in a variety of applications. This chapter firstly describes the interactions of organic cations and neutral organic molecules on 2:1 clays followed by a section on the intercalation of kaolinite with organic molecules and adsorption on palygorskite and sepiolite. Also in this chapter there is a general overview of the relatively new area of nanocomposites formed through the interactions between clay and polymers. Finally, descriptions of some applications of organoclays as selective adsorbents, in membranes, as supports for organic reactions and heterogeneous catalysts, in photoactive materials and as ionic and electric conductors are given.
- Chapter 4 (Johnston, Boyd, Teppen and Sheng), which seems to be somewhat out of line with the general emphasis of the book, describes the chemical mechanisms involved in the interactions between clay surfaces and the nitroaromatic compounds. The environmental

JAN ŠRODOŇ

Institute of Geological Sciences PAN
Senacka 1, 31-002 Kraków
Poland

Handbook of Layered Materials, edited by Scott M. Auerbach, Kathleen A. Carrado and Prabir K. Dutta. Marcel Dekker Inc, New York, Basel, 2004, 646 pp. [ISBN 0-8247-5349-6]. Price \$195

In present-day chemistry a whole range of layered materials exists but only a few of them are as widely used as those described in this book. As the authors suggest, this book is intended to give a general background and does not imply an up-to-date review of the existing literature. Having bought *Handbook of*