

## BOOK REVIEWS

**Cristallochimie des Argiles Kaoliniques et Applications.** Bulletin de Minéralogie, Vol. 105, part 5, (1982), pp. 413–581, published by the Société Française de Minéralogie et de Cristallographie, and available as a separate number, 180 F. Available also from Masson Publishing USA, 133 E. 58th St., New York, New York 10022, \$20.95.

This issue of the Bulletin de Minéralogie contains 17 comprehensive reviews presented at a seminar held in Paris, November 12 and 13, 1981. All articles are in French with the exception of an introductory lecture in English by R. F. Giese which summarizes his work on electrostatic energy calculations for the kaolin minerals. Abstracts, which are often quite detailed, are given in French and English. Many of the papers summarize work which has been in progress over the last ten years on the crystallography, mineralogy, geology, and applications of kaolin minerals in the paper, ceramic, and other industries. A striking feature of almost all the contributions is the great attention given to the role of structural disorder and how it affects properties and applications of kaolin minerals. These studies are remarkable also for the close collaboration which has existed between those working in universities, in government-sponsored laboratories, and in industry, so that the same or similar materials have been studied by different groups using different techniques.

The character of the contents will be indicated by reference to some of the topics covered. C. Tchoubar *et al.* at Orléans summarize and extend their work on the X-ray diffraction effects produced by structural disorder in kaolinite. M. M. Mestdagh *et al.* at Louvain (the collaboration extends into Belgium) discuss the role of structural iron on the crystallinity of kaolinite, particularly from the standpoint of electron spin resonance spectra. The effect of iron in causing displacements of vacant octahedral sites and thereby modifying the interlayer bonding is discussed. A related topic is presented by M. Cruz-Cumplido *et al.* who relate crystallinity with the hydroxyl infrared spectra and the cohesion energy of kaolinites which they studied by hydrazine intercalation. Similar topics are discussed by D. Bonnin *et al.* in a survey of work using

electron paramagnetic resonance, Mössbauer, and EXAFS techniques.

Two papers by J. Yvon *et al.* and J. M. Cases *et al.* (the same four authors for both papers) discuss the crystal-chemical and morphological characteristics of the industrially important kaolin clays of the region of Charentes. Again the role of Fe(III) replacing Al is emphasized as is the presence of K, some of which may be present in interstratified layers. The clays of the Paris basin in the region of Provins are discussed by M. Thiry who relates their characteristics to the conditions of sedimentation. The relatively high cation-exchange capacity of disordered kaolinites may be correlated with smectite interstratification. J. Lemaître *et al.* address the age-old question of the thermal transformation of metakaolin to mullite and suggest two reaction paths, one involving segregation of silica and alumina, the other a transformation without segregation. The role of mineralizers on these reactions is discussed.

Many other interesting papers must be passed over in this short review. Industrial applications are considered by J. Yvon *et al.* of kaolinitic clays in the rubber industry, by J. F. Delon *et al.* on the use of kaolin clays in ceramic materials for the building industry, and by J. F. Delon and five collaborators on the use of the Charentes clays for paper coating. In all of these papers extensive data on the mineralogical and chemical characteristics of the clays in relation to their applications are given. I have only the highest praise for this issue of the Bulletin; clay mineralogists having any interest in kaolinite cannot fail to find many topics of considerable interest and possibly may improve their acquaintance with the French language at the same time.

G. W. BRINDLEY

**Hydrothermal Chemistry of Zeolites**, by R. M. Barrer. Academic Press, London and New York, 1982. 360 + ix pages, \$57.50.

Typical of Professor Barrer's work, *Hydrothermal Chemistry of Zeolites* is an excellent book. One of its outstanding features is its coverage of *very* recent developments in zeolite chemistry, for example, the synthesis and properties of aluminum phosphate molecular sieves, announced in 1982 by Union Carbide Corporation, and the apparent resolution of the Lowenstein-rule controversy by Exxon workers who reported magic-angle spinning  $^{29}\text{Si}$  NMR studies of a siliceous zeolite A, also in 1982.

In the volume's preface the author emphasizes that this monograph is devoted essentially to zeolite synthesis and states that "... improved chemical knowledge of these complex crystallizing systems will, it is hoped, help to design ways of making more and more of the large number of novel zeolites which so far have been constructed only as models." In addition, and perhaps even more significant in this reviewer's opinion, are the ten or so natural zeolites which have not been made synthetically. Thus, it appears that zeolite synthesis as a science is essentially non-existent; nonetheless, this reviewer shares Professor Barrer's hope, but, having spent more than

25 years in this field, he is not optimistic enough to expect systematic zeolite syntheses such as one finds in synthetic organic chemistry to become a reality for some time to come.

This monograph brings together for the first time an overall, well-organized summation of what has been learned about zeolite crystallization and related subjects. Chapter 1, on the occurrence, classification, and properties, presents an overview of zeolites including natural zeolite formation, zeolite topology and classification, molecular sieving properties, catalytic applications (necessarily brief), and an excellent summary of zeolitic cation exchange. Chapter 2, on the hydrothermal chemistry of silicates, contains a detailed thermodynamic treatment of the phase equilibria and stabilization of porous crystals by guest molecules. It also discusses the role of water solubility of oxides involved in zeolite formation. Chapter 3 gets into the practical aspects of zeolite synthesis and discusses the various forms of aluminum and silicon oxide derivatives which are the principal starting materials. This chapter covers such recent work as  $^{29}\text{Si}$  MAS-NMR studies of species in solution. Chapter 4 delves into the region of

zeolite crystallization and the most challenging and formidable areas of nucleation and crystal growth. The author's coverage of the kinetics of crystal growth is excellent. This chapter also contains a section on "Organic Bases in Zeolite Synthesis" which treats thoroughly the use of alkylammonium and quaternary ammonium ions. Such work has led to the synthesis of a large number of new zeolite phases, synthetic analogs of several natural zeolites, and, of great significance, zeolites with Si/Al ratios exceeding those of any known natural species.

Chapter 6 reviews "isomorphous" replacement of tetrahedrally coordinated ions or atoms by other similarly coordinated elements, the most obvious being the replacement of Si by Al. This brings up the Lowenstein-rule controversy mentioned above, and Professor Barrer performs an outstanding service in thoroughly reviewing the very recent literature on this subject. This chapter also reviews the aluminum phosphate molecular sieves alluded to above. With regard to many similar framework-substituted compounds, Professor Barrer is rather forthright in stating, "... iron, certain rare earth elements and boron can replace Si or Al, but the structures are not zeolites. The evidence of significant framework substitution by B(III), Fe(III), Cr(III), Zr(IV) or Ti(IV), under the

low-temperature aqueous alkaline conditions normally used in zeolitization, is incomplete and ambiguous." Chapter 7 treats the salt-bearing "tectosilicates," which are of lesser interest to many people concerned with the most important applications of zeolites. These materials tend to be "stuffed" with salts and therefore generally are unable to take up the types of molecules usually sorbed and/or catalyzed by normal zeolites.

In addition to a subject index, the volume contains a substance index which is very useful, especially for locating information on a specific zeolite or zeolite family. Readers who have had some experience with zeolite synthesis and the hydrothermal chemistry of silica and silicates can appreciate what a difficult task Professor Barrer undertook in putting this book together. The number of variables encountered in this field is really overwhelming, and the author has done a commendable job in achieving some degree of order in a chaotic field. This reviewer would not recommend the book to the beginner, but for those who have some knowledge of zeolites in general and who have lived, to some extent at least, with the frustrations of zeolite synthesis, this book is a blessing.

GEORGE T. KERR

## ERRATA

In the paper by Dyrek, Klapayta, and Sojka (Volume 31, Number 3, 223–229), the first word of line 4 of the Abstract should read "decreased" instead of "increased." The three foreign-language translations of the abstract should be corrected in a similar manner.

In the note by Novich and Martin (Volume 31, Number 3, 235–238), the coefficient of variation equation on p. 235 should read as follows:

$$CV = 100\bar{d}[\Sigma (ld - \bar{d})^2/(n - 1)]^{1/2}.$$

The authors of these articles regret the inconvenience caused to the readers.