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Book Review

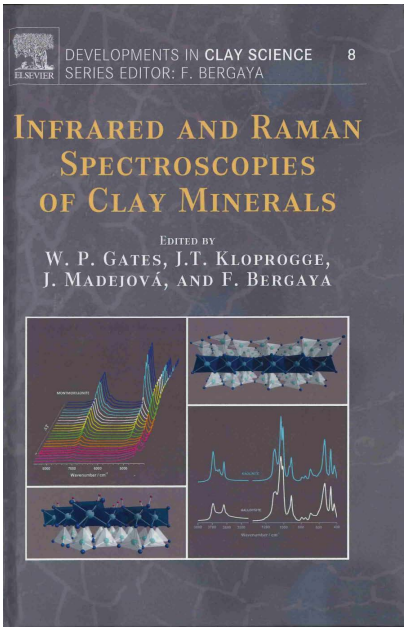
Book Review: Infrared and Raman Spectroscopies of Clay Minerals, Volume 8, Developments in Clay Science, 1st Edition. Edited by Will Gates, J. Theo Kloprogge, Jana Madejova, and Faïza Bergaya. (2017) Elsevier, pp. 620, $175 hardcover and eBook, ISBN: 9780081003596 (eBook); ISBN: 9780081003558 (Hardcover).

More than 40 years from its publication, *The Infrared Spectra of Minerals* edited by Victor Colin Farmer (Mineralogical Society Monograph 4, London, 539 pp., 1974) is still a popular reference book for infrared (IR) studies aiming to identify mineral species and to derive information concerning their structure, composition, and reactions in the environment. While most of Farmer's works are a benchmark in the field of clay and soil sciences, *Infrared and Raman Spectroscopies of Clay Minerals* aims to update the state-of-the-art in IR and Raman methods applied to the study of clay minerals.

Infrared and Raman Spectroscopies of Clay Minerals contains 14 chapters with figures in black and white. Although each chapter in this book is written by several contributors, the authors follow a similar outline and writing style, with each topic clearly introduced and well-articulated throughout. The chapters are also arranged to provide references to the other chapters in which specific topics are overlapped or covered in more detail. However, each chapter may also be read entirely independently from the others. A complete list of references is provided at the end of the book allowing readers to seek further reading material on specific applications of vibrational spectroscopies to clay minerals, accompanied by a useful alphabetical index of topics.

Infrared and Raman Spectroscopies of Clay Minerals is conceived to be a continuity of Farmer's book, credit to Farmer's career and his scientific contributions is given in the general introduction (Chapter 1). The next three chapters provide a comprehensive overview on the theoretical basis of IR and Raman spectroscopy written for those with a background in solid-state physics (Chapter 2), the advancement of vibrational spectroscopy instrumentation and guidance on the most suitable sampling methods for collecting high-quality spectra (Chapter 3), and the description of spectral processing (Chapter 4). The information presented in these chapters is clear and well-illustrated.

The in-depth discussion on the advantages and limitations in modern IR and Raman techniques applied to clay studies is particularly significant. Specifically, the progress achieved in instrumentation [i.e., the advent of fiber optic probes, high-resolution detectors, and portable Fourier transform infrared (FTIR) spectrometers] are clearly outlined. The discussion of practical aspects related to the most suitable methods of sample preparation (Chapter 3) and different data manipulation approaches (Chapter 4) to obtain straightforward information from IR and Raman spectra are particularly eye-catching. Given the structural complexities of clay minerals (i.e., site occupancy, isomorphic substitution, order-disorder, structural water, exchanged cations, interstratification, etc.), these chapters are a fundamental learning tool for researchers and professionals.



The following chapters offer extensive overviews and exhaustive interpretations of characteristic vibration bands in IR spectra as diagnostic for natural and synthetic clay minerals. Chapters 5, 7, 8, and 9 are a valuable resource for the correct assignment of IR bands, offering scientists an unprecedented capability to study the clay mineral family. The meticulous review and interpretation of IR spectral changes of hydroxyl (OH) groups (i.e., frequency shifts, band intensity and width) in Chapter 5 is of special interest in the attempt to unambiguously identify structural features of a specific clay mineral and explain dehydration and dehydroxylation processes or cation exchange properties.

Smectites are the most widely studied of the 2:1 clay minerals. The interpretation of IR spectra is particularly challenging due to the octahedral occupancy and cations relation to their nearest neighbors through shared OH bonds. The discussion on the effects on the OH IR band shifts owing to the crystal chemistry of smectites is given in Chapter 5 and it continues in Chapter 7.

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Chapter 7 outlines the methods supporting the interpretation of near infrared (NIR) and mid-infrared (MIR) spectra of smectites and the various approaches to quantify octahedral occupancy from IR spectra.

Chapter 8, which reviews the interpretation of IR spectra of synthetic clay minerals, provides insight on how clay minerals nucleate and grow. Moreover, this chapter highlights how clay mineral synthesis is essential to understand the physical and chemical conditions for clay minerals to form in natural environments or on extra-terrestrial materials. Further explanations about clay minerals-water interactions can be found in Chapter 9. This chapter underlines how IR studies provide key insights about the role of isomorphous heterovalent cation substitution occurring in the interlayer in directing clay mineral-H_2O interactions.

A significant portion of the book extensively covers the experimental discoveries achieved using IR spectroscopies on the different families of clay minerals and it is clear that several "unknowns" still exist in the interpretation of Raman spectra. However, Chapter 6 elucidates the major experimental advances achieved in the last decades using Raman spectroscopy and the valuable contribution of multivariate and chemometric methods to make more accurate assignment of vibrational bands.

The second part of the book focuses on the applications of the vibration spectroscopies to clay science. The authors present comprehensive reviews on case studies of interest to clay scientists using a clear, systematic approach and provide helpful additional interpretations on existing data.

Chapters 10 and 11 contain particularly interesting extensive discussions of organoclay interlayer properties and structure. The general overview on the structural features of organoclays in Chapter 10 provides the reader with a good introduction to these materials.

Although organoclays have several important practical applications (e.g., carriers of drugs, components of clay-polymer nanocomposites), the case studies reported are mostly related to areas of interest in public health and environmental protection. The last part of Chapter 10 is devoted to the investigation of organoclays as important adsorbents of organic pollutants in water to understand the mechanisms that govern the interaction between the organoclay and the pollutants in aqueous systems. Specifically, the chapter provides a complete yet concise introduction on structural information obtained using FTIR spectroscopy and X-ray diffraction.

The exhaustive interpretation of the experimental and theoretical advances of the application of Raman and IR spectroscopies on modified clays reported in Chapter 11 provides insights on the mechanisms by with various organic complexes interact with clay minerals. The attention to details is truly impressive. The deep discussion of the data related to the intercalation of kaolinite with organic molecules is accompanied by tables that summarize the observed FTIR and Raman bands for kaolinite intercalated with hydrazine, urea, formamide, and acetamite. The tables are a useful reference for researchers who are becoming acquainted with modified clays. The discussion on organoclays is intermitted by Chapter 12 in which a scrupulous overview of pillared smectites, materials mostly studied for their catalytic and adsorption properties, is provided.

Further discussion on the band shifts related to the OH-modes in near-infrared (NIR) spectra upon structural changes of organoclays induced by mechano-chemical treatments can be found in the second half of Chapter 13. The first part of Chapter 13 discusses the variation of band position in near-infrared spectra of smectite due to mechanical (e.g., dry grinding) and acid treatments. The crystal-chemical changes induced by mechano-chemical treatments discussed in this chapter are of particular interest in different fields of application ranging from Earth and environmental sciences to the synthesis of advanced materials. The multiple examples reviewed in this chapter clearly evidence the great potentialities of NIR spectroscopy in clay and organoclays studies.

An innovative addition in the volume is a chapter (Chapter 14) devoted to the characterization of clay minerals in planetary materials (i.e., meteorites, comets, and asteroids) and martian soils. The presence of clay minerals on Mars underwent a debate in the 70's–90's. As specified in the introduction of Chapter 14, it was not until 2004 that the discovery of clay minerals on Mars was confirmed using a visible/near-infrared (VNIR) imaging spectrometer on Mars Express mission. This chapter reviews data from laboratory studies to support the remote identification of clay minerals in extra-terrestrial materials using VNIR and mid-IR spectroscopies. The discussion of data is corroborated with several figures from relevant publications. Nevertheless, a loss of information and details from the black and white figures in the printed book is inevitable. Specific studies of spectral remote sensing applied to clay minerals found in Earth materials and terrestrial environments are supportive to better comprehend the occurrence of clay minerals in analogous materials and locations on Mars. Challenges in remote sensing for clay mineral characterization on Earth and Mars are discussed, assisting scientists to advance in this fascinating field of research.

Overall, the major contribution of this book is to have, at hand and in one place, the experimental and theoretical IR and Raman spectroscopic data collected over several decades, aiding scientists to get an accurate IR and Raman band assignment of natural, synthetic, and modified clay minerals.

Infrared and Raman Spectroscopies of Clay Minerals, Volume 8, Developments in Clay Science represents a valuable update of Farmer's book making this volume an essential reference for leading researchers and graduate students involved in studies in geoscience, soil science, environmental science or closely related fields, as well as professionals involved in the many industries where clays are widely used.

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