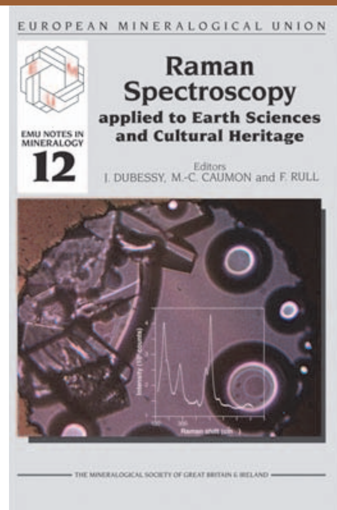
RAMAN SPECTROSCOPY APPLIED TO EARTH SCIENCES AND CULTURAL HERITAGE[1]



Raman spectroscopy is a highly flexible tool that can be applied to the analysis of fluids and solids, including minerals and glasses. In recent years the application of Raman spectroscopy in Earth science and cultural heritage studies has seen enormous growth. Early on, Raman was mostly a qualitative to semiquantitative technique used to test for the presence or absence of particular molecular species, and the large majority of early studies in the Earth sciences were related to the analysis of fluid inclusions using the MOLE Raman microprobe. Today, Raman is a quantitative tool that not only identifies which species are present but also the amounts. The increased use of Raman spectroscopy can be related to major improvements in instrumentation that have occurred over the past few decades. Early designs included photomultiplier (PMT) detectors that required scanning over the range of wavenumbers of interest. Modern instruments employ charge-coupled device (CCD) detectors that allow analyses, which previously took tens of minutes to sometimes hours, to be completed in seconds. Today, with modern fast computers, Raman data can be collected and processed in essentially real time.

Recognizing the growing interest and number of applications in Raman spectroscopy in the Earth sciences and the documentation of historical artifacts, the European Mineralogical Union (EMU) held a workshop on Raman spectroscopy at the University of Lorraine (France) following the Geo-Raman X meeting in Nancy in June 2012. Lectures presented at the workshop have been published as EMU Notes in Mineralogy 12 – *Raman Spectroscopy Applied to Earth Sciences and Cultural Heritage*, edited by Jean Dubessy, Marie-Camille Caumon, and Fernando Rull.

The book consists of 14 chapters and is organized in a manner such that it will be useful to both the newcomer to Raman spectroscopy as well as the experienced practitioner. The first chapter summarizes the theoretical basis for the Raman effect and describes in some detail the types of molecular vibrations that are Raman active. This introductory chapter also describes briefly other less commonly employed aspects of Raman spectroscopy, including resonance Raman, coherent anti-Stokes Raman (CARS), and surface-enhanced Raman spectroscopy (SERS). This introductory chapter introduces the novice to the theoretical basis for Raman spectroscopy, yet is written such that the reader need not be an expert in quantum physics or crystal chemistry to understand the basic concepts.

One chapter is devoted to Raman instrumentation, a topic often overlooked in similar contributions. The chapter provides detailed descriptions of the complete Raman system, including the advantages and disadvantages of different excitation (laser) sources, the design of the spectrometer and gratings, as well as the various types of detectors available. This is a clear and well-written overview of Raman instrumentation, and I would strongly encourage any students (or other beginners) entering the Raman arena to read this chapter before starting any study involving Raman analysis.

Raman spectroscopy is especially well suited for analysis at elevated *P–T* conditions, and several chapters describe various types of cells that can be accommodated by the Raman sample stage for this purpose. Chapters by Chou and by Schmidt and Chou describe various cell designs used to study fluid phase equilibria in situ at elevated *P–T* conditions. These chapters describe the application of these cells to determine the solubility of methane and methane hydrate in water using fused-silica capillaries, as well as speciation and solubility studies for a wide range of chemical systems of geologic interest at deep-crust to upper-mantle conditions using a hydrothermal diamond anvil cell. Other chapters describe the application of Raman spectroscopy to determine speciation in silicate melts.

Until relatively recently our understanding of the mineralogy of the Earth's mantle has been based mostly on interpretations of geophysical data. Today, it is possible to examine phase transitions of mantle minerals in situ at mantle *P–T* conditions using Raman spectroscopy combined with diamond anvil cells. The chapter by Reynard, Montagnac, and Cardon provides a thorough overview of the methodology for collecting data at mantle *P–T* conditions, as well as methods to extract thermodynamic data from the Raman spectra.

An area in which Raman has proven to be especially important in recent years has been the characterization of carbon and carbonaceous (graphitic) materials in both natural and synthetic samples. Raman analysis is well suited to determine the degree of crystallinity of graphitic carbon, and this information can be used to approximate the maximum temperature that the sample has experienced. Beyssac and Lazzeri summarize the theoretical basis and application of Raman in studies of graphitic carbon.

Raman spectroscopy is now used routinely to characterize valuable gemstones, owing to its diagnostic capabilities and the fact that it is a nondestructive technique. Raman has been used to identify solid and fluid inclusions in gems, and these features in turn sometimes identify the provenance of a stone. The presence and nature of inclusions has also been used to prove that a gemstone is a natural and not a synthetic material. Many gemstones occur in a wide variety of colors, with some colors being less common and, therefore, more valuable than others. As such, some less scrupulous dealers attempt to artificially color the stones using a variety of organic coloring agents. The presence of these artificial coloring agents is easily revealed by Raman spectroscopy. These and many other applications of Raman spectroscopy in gemmology are summarized by Fritsch and others.

Perhaps the most recent application of Raman spectroscopy has been to characterize historical (cultural) artifacts, including ancient manuscripts, jewelry, paintings, and other artwork, as summarized in the chapter by Vandenabeele. Raman analysis has been used to infer sources of materials used in pigments and to better understand the nature of the degradation of paints. The need to conduct some analyses in situ (such as the analysis of the ceiling of the Antwerp Cathedral) has led to the development of portable Raman systems (see also the discussion of miniaturization of Raman microprobes in the chapter on geobiology and astrobiology by Daniel and Edwards).

In summary, *Raman Spectroscopy Applied to Earth Sciences and Cultural Heritage* is an outstanding contribution that should be included in the personal library of anyone interested in Raman. The book includes chapters that introduce the basics of Raman spectroscopy and discusses specific applications in detail. As such, it is ideally suited for use as a textbook in a graduate course in Raman spectroscopy or analytical techniques, and it will serve well as a reference material for the Raman spectroscopist. Perhaps the only shortcoming of the book is that there is no chapter devoted specifically to Raman mapping—a tool that is proving to be valuable for understanding the nature of heterogeneities in samples. In spite of this, I highly recommend this book and commend the editors and authors on a job very well done.

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1 Dubessy J, Caumon M-C, Rull F (2012) Raman Spectroscopy Applied to Earth Sciences and Cultural Heritage. EMU Notes in Mineralogy 12, European Mineralogical Union, ISBN 978-0-903056-34-2, XV + 438 pp, £40 (institution), £25 (individuals)