

# Raman Spectroscopy, Unveiling the Secrets of Limestone

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## Key Words

DXR Raman Microscope, Calcite, Dolomite, Limestone, Mineral, Raman Spectroscopy, Rock Formation

## Introduction

Raman spectroscopy provides a technique for rapid identification of carbonate minerals and provides additional relevant information that facilitates interpretation of these rocks. Raman spectroscopy is especially advantageous, as it can be performed on unpolished sawn surfaces of rocks and hence minimal sample preparation is required to perform an analysis. This application note identifies calcite, dolomite, aragonite and organic carbon in various samples.

Carbonates provide a wealth of information about sedimentary environments and ancient climates, as well as being important in the formation of oil reservoirs; however, interpreting the textures in a rock sample can be challenging. These interpretations are important for a number of reasons. The rock record allows us to investigate the relationship between ocean currents, seawater chemistry and global warming and cooling, thus informing predictions about what the climate might do in the future. Similarly, many limestones are a snapshot of ancient ecosystems and allow us to investigate how the remarkable array of modern life may have arisen. The high solubility of carbonate minerals in water means that these rocks often undergo complex alteration, known as diagenesis, after their initial formation. Interpreting the extent of diagenesis can be crucial for distinguishing information about the time of sediment deposition from secondary processes, and the chronology of diagenesis controls whether the rock could contain oil. For example, a rock in which the pores between grains are sealed at an early stage by a carbonate cement may be less effective as a reservoir than a highly porous limestone. However, a non-porous limestone could act as the seal on a reservoir, but only if the cement sealing the pore space grew early on, before the oil escaped.



Carbonate minerals such as calcite, dolomite and aragonite have similar optical properties and distinguishing them is often difficult. Optical techniques also require the preparation of thin sections which is time-consuming and consequently expensive. Methods such as X-ray diffraction lack spatial resolution (in most cases being restricted to examination of crushed rock or single crystals extracted from a sample) and electron microscopy techniques require polished and carbon-coated surfaces that may not be possible on the material provided (e.g. traditional covered thin sections). Moreover, calcite and aragonite cannot be distinguished by compositional data.

## Experimental

The samples were prepared by standard petrological techniques (sawing, grinding with SiC and diamond suspension). Raman spectra and maps were obtained using a Thermo Scientific™ DXR™ Raman microscope. A 532 nm laser, providing between 5 and 9 mW at the sample surface, was used to obtain all spectra. Reflected and transmitted light optics were used to select and photograph analysis regions. The spectral acquisition times and distance between analysis locations were 2 s and 20  $\mu\text{m}$ , 2 s and 10  $\mu\text{m}$  and 12.5 s and 1.5  $\mu\text{m}$  for the Strimbes Limestone, the oolitic limestone and the coral samples, respectively. The oolitic limestone sample fluoresced strongly and a photo bleaching period of 5 s was used prior to the acquisition of each spectrum.

## Results and Discussion

### *Dolomite and Calcite in the Strimbes Limestone (Jurassic, Greece)*

The eroded surface of this limestone has striking concentric circular textures, as shown in Figure 1. In order to understand how these textures formed, a Raman map of a thin section was collected to assess the correlation between the visually-observed textures and the mineralogy. As Figure 2a shows, the sample has alternating areas of coarse and fine grains. Typical Raman spectra of these two regions are shown in Figure 2b. Comparison to a spectral library identifies the coarse-grained material as calcite and the fine-grained material as dolomite. By processing the map to show the ratio of dolomite to calcite, as identified by their characteristic peaks at 1098 and 1086  $\text{cm}^{-1}$  respectively, it is clear that the mineralogical difference between the layers is consistent and not limited to one or two spots, as illustrated by Figure 2c.

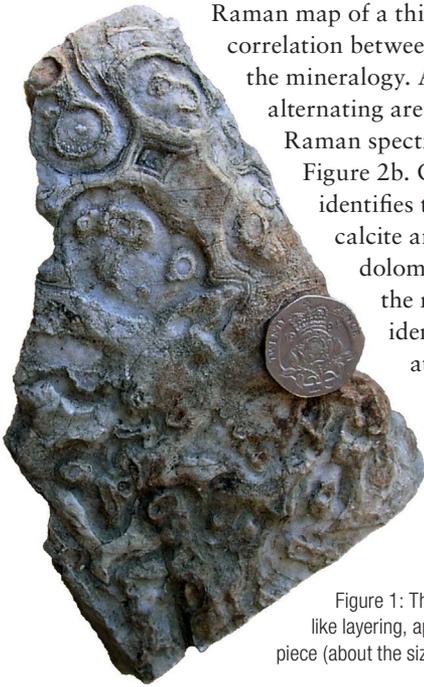


Figure 1: The hand specimen illustrated, with its stromatolite-like layering, appears in thin section. The coin is a British 20p piece (about the size of an American nickel).

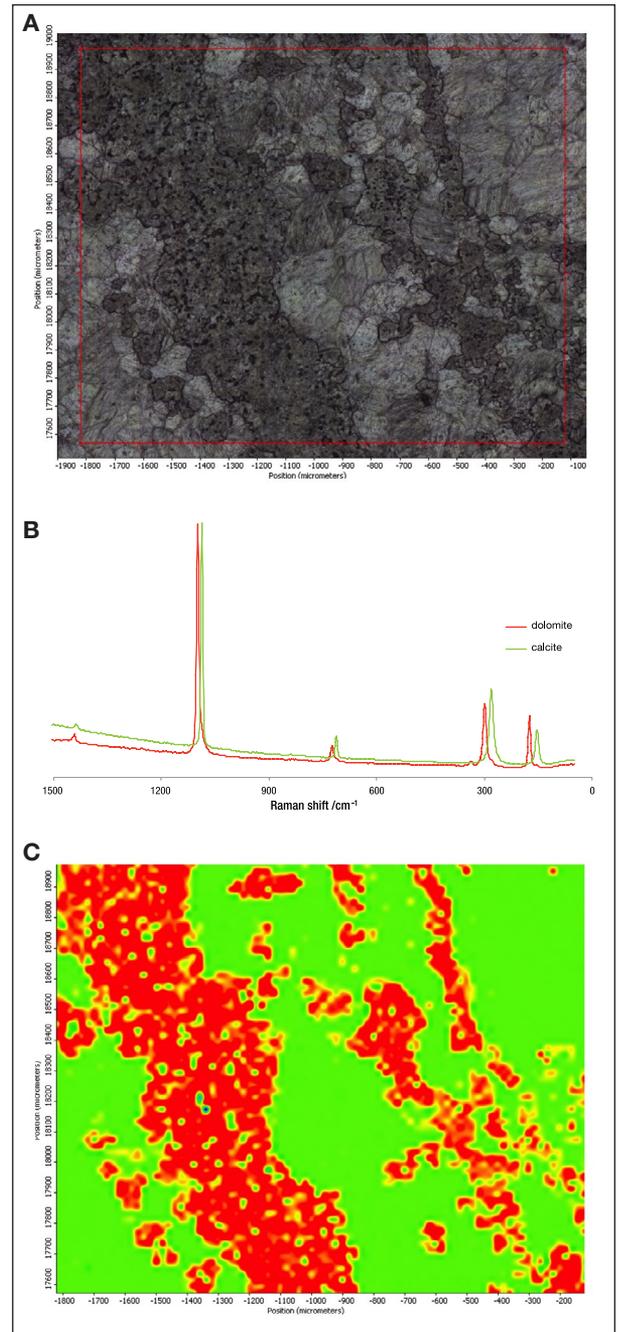


Figure 2: a) A thin section of the hand specimen, illustrating the alternating coarse- and fine-grained carbonate layers. b) Raman spectra of dolomite and calcite in the Strimbes Limestone, showing the differences in peak positions that allow the distribution of the phases to be mapped. c) The Raman map showing the specimen to be composed of calcite (green) and dolomite (red).

### ***Cementation and Organic Material in an Oolitic Limestone (Carboniferous, Wales)***

This sample is a Viséan (Carboniferous) limestone from south Wales (UK). This limestone is principally composed of ooids, carbonate spheres that usually form in tropical beach environments, illustrated by the cross section shown in Figure 3a. The mineralogy of ooids is usually either calcite or aragonite, which correspond to climatic greenhouse and icehouse conditions: being able to distinguish the two is important in interpreting the environmental significance of a particular rock formation. Raman spectroscopy is the only practical non-destructive way to distinguish the two minerals. A Raman map of the polished surface shows calcite to be the only carbonate mineral present, however, there are two interesting features of the map that provide further information. First, peaks at  $\sim 1350$  and  $1600\text{ cm}^{-1}$ , shown in the spectrum in Figure 3b, indicate the presence of amorphous krogen-like carbon. This is likely to derive from the

breakdown of biological material. Raman spectroscopy is the only technique that could have detected the amorphous carbon and distinguished it from graphite, which could be sedimentary in origin. The organic carbon is absent from the core of one ooid and from the cement between the grains, as shown in Figure 3c, indicating changes in the availability of biological material during the formation of the rock. The second interesting insight Raman spectroscopy provides is that the fluorescence of the sample varies within the ooids and between regions of the cement, and allows multiple phases of ooid growth and cementation to be identified, which is depicted in Figure 3d, e. Although the exact cause of the fluorescence is not known, the ability to distinguish multiple cementation events is still useful in determining the history of the rock. This works on the same principle as cathodoluminescence imaging.

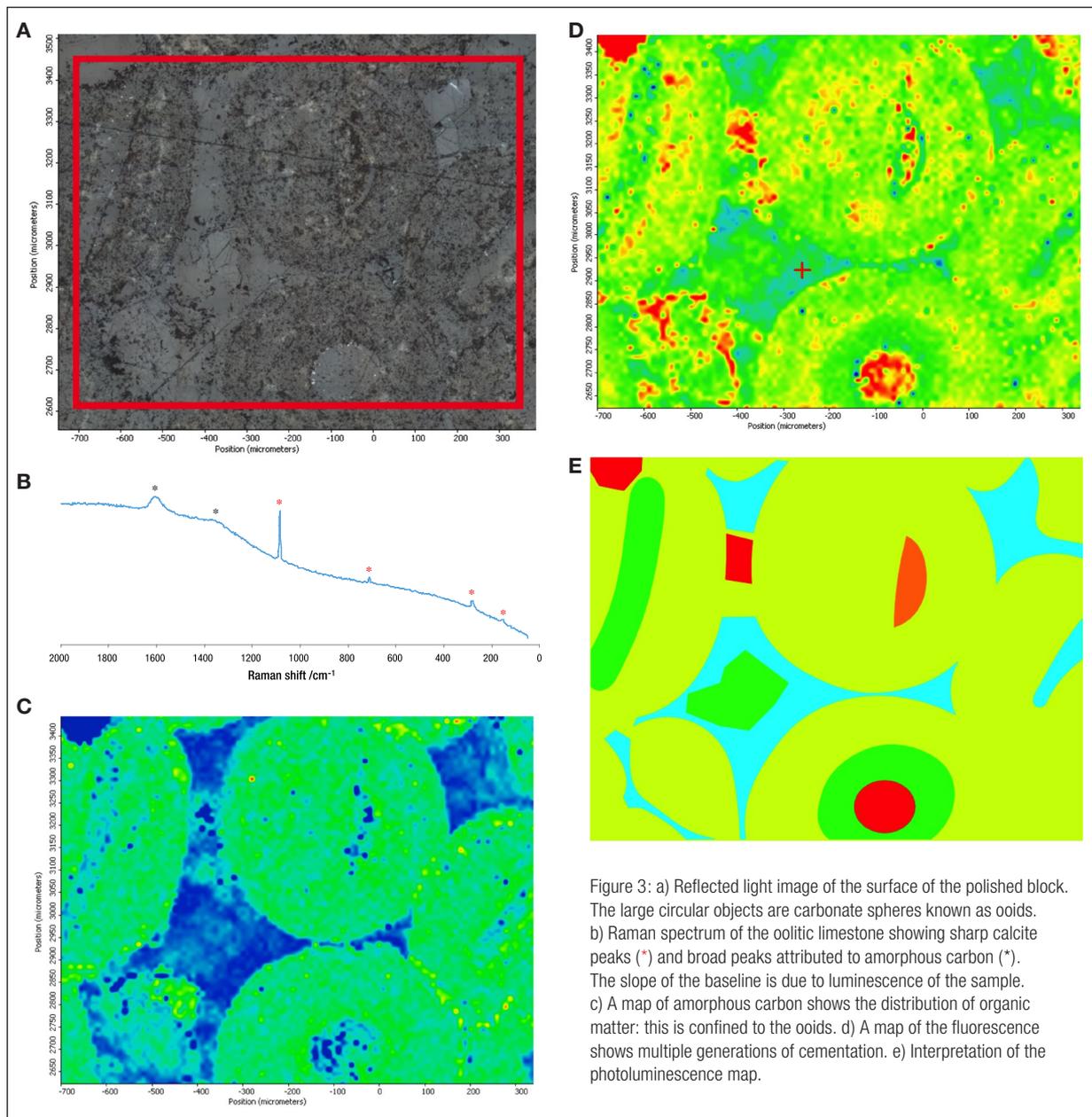


Figure 3: a) Reflected light image of the surface of the polished block. The large circular objects are carbonate spheres known as ooids. b) Raman spectrum of the oolitic limestone showing sharp calcite peaks (\*) and broad peaks attributed to amorphous carbon (\*). The slope of the baseline is due to luminescence of the sample. c) A map of amorphous carbon shows the distribution of organic matter: this is confined to the ooids. d) A map of the fluorescence shows multiple generations of cementation. e) Interpretation of the photoluminescence map.

### Fossil Material

Aragonite and calcite are both present in this coral sample, Figure 4, which is being used to determine the seawater chemistry at the time the coral was alive. Screening the sample to exclude later unrelated carbonates was essential. Many hard components of organisms are formed from either calcite or aragonite (or both), and Raman spectroscopy is the easiest and most convenient method of distinguishing the two minerals. An additional challenge that precluded the use of alternate techniques was that the sample was covered with a cover-slip. The confocal capabilities of the DXR Raman microscope allowed the sample to be analyzed with minimal contribution from the surrounding glass and mounting glue.

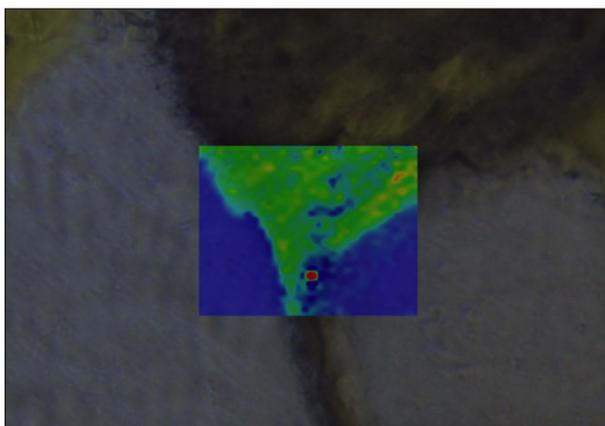


Figure 4: Transmitted light image of the sample overlain with a map of the intensity of a characteristic Raman peak of aragonite. The coral skeleton is aragonitic (green in Raman map), whereas the later cement infilling of the coral zoids is calcite (blue in Raman map). Mapped area 50 × 40 microns.

### Conclusions

Raman spectroscopy is a powerful technique that can be used to analyze many varieties of rock and mineral samples. With the information obtained from Raman spectroscopy, geologist and mineralogist can learn about material composition as well as infer information about the environment local to the sample at the time of its formation. Raman spectroscopy is advantageous because it is relatively easy to obtain spectra from just about any sample conformation, even under a glass coverslip and mounting glue. Raman spectroscopy has been shown in this application note to provide insights into the formation of carbonate-containing materials with ease.

### Acknowledgements

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