

**The contribution of Near Infrared Spectroscopy for the characterization of calcite-rich rocks**

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**Introduction**

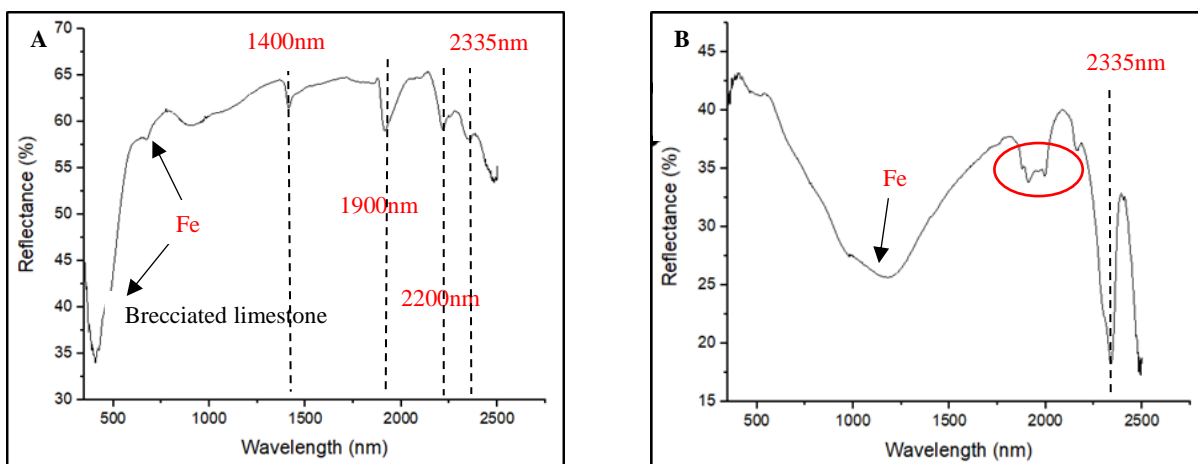
The subject addressed in the present contribution is related to the application of Near Infrared Spectroscopy on calcite-rich rocks for mineralogical identification. Calcite is an abundant mineral in many geological environments. Depending on their CaCO<sub>3</sub> and MgCO<sub>3</sub> content carboniferous sedimentary rocks are differentiated into limestones, dolomites and the in-between categories. In addition, calcite is frequently the main cementing substance between the siliceous grains of sandstones, which are clastic sedimentary rocks, composed mostly of quartz, feldspars, clay minerals and also include fragments of breccias and conglomerates. Furthermore, calcite is the main constituent of marbles, which are crystalline rocks used as structural stones according to their quality. The use of NIR spectroscopy is an easy and straightforward method that can determine the mineralogical composition of carbonate rocks. The aim of the present work is to compare the spectral signatures of Near Infrared region for different lithotypes, with a semi-quantitative mineralogical determination and their petrographic study. For this reason, limestones, marbles and calcitic sandstones were used to determine how the participation of other minerals influence the spectral features obtained.

**Materials and methods**

The samples analyzed were collected from Astypalaia (AST7, AST9A2, AST10, AST12, AST25, AST26) and Kos Island (PPY3, PKR1, PKR5, KF4) in the Aegean Sea, Greece. The two islands have completely different lithologies. The geologic structure of Astypalaia Island comprises both Alpine and post-Alpine formations (Marnelis & Bonneau, 1977; Marnelis, 1986). Due to extended deformation mechanism, Astypalaia Island can be divided in two areas, with the eastern part consisting of Santonian-Maastrichtian limestones, and the central and western part of the Island mainly consisting of flysch deposits. On the other hand, Kos Island geological structure, consists of a range of lithologies that cover the main tree categories of rock types (magmatic, metamorphic and sedimentary) (Drinia et al. 2010, Soder et al., 2016, Kalt et al., 1998). For the petrographic analysis, thin sections were prepared and studied using polarized microscope (Zeiss AxioScope A.1) in order to determine the mineralogical composition of each sample and their textural characteristics. Furthermore, through X-Ray Powder Diffraction analysis (BRUKER D8 Advance) the mineralogy of the samples was verified, and a semi-quantification was performed. The Near Infrared spectra were acquired on the smooth and clean surface hand specimens with a SM-3500 Spectral Evolution portable spectrometer. Furthermore, the Cathodoluminescence method (Reliotron III Cathodoluminescence system attached on a Leitz Wetzlar Orthoplan Microscope), provided us more information about the mineralogy of the sample, that was not perceptible through normal observation, during the petrographic analysis. The methods discussed above were applied at the Research Laboratory of Minerals and Rocks, Department of Geology, University of Patras.

**Results and Conclusions**

The calcitic sandstones are rocks rich in siliceous grains of quartz and feldspars cemented together with micritic calcite. Their mineralogical composition is supplemented by clay minerals, which give the samples a yellowish color. The micro-brecciated limestone is rich in metallic and siliceous minerals and has channel-like porous. The spectra have small, sharp absorption features ~1400nm and a shoulder-like feature at 2200 nm which represent the presence of clay minerals in the sample.



**Figure 1. A) Representative spectrum from brecciated limestone (sample AST12), B) Representative spectrum from a marble (sample PKR5)**

Also, the ~1900 nm absorption feature is deep and rounded and indicate unbound water in the structure of the samples (figure 1A). The characteristic absorption feature of calcite at ~2340nm is small and not distinctive for the sample and could be confused with absorption features of clay minerals. An important role for the shape of the spectrum plays the presence of metallic minerals which characterizes the reflectance of the spectrum. The fossiliferous micritic limestone is a non-cohesive formation with visible microscopically porosity, with channels-like porous and consists of micritic calcite and bioclasts and endoclasts in a small percentage. The spectrum is characterized by the major absorption feature of calcite in ~2340nm but also by the ~1400 and ~1900 nm rounded features which indicates the presence of water. The marbles are coarse-grained samples with the typical granoblastic texture, comprising calcite and minor wollastonite, diopside and hedenbergite. The spectra are characterized by the major absorption feature of calcite at ~2340nm (figure 1B), by the characteristic doublet feature at ~1.890 and ~2000 nm (see red circle in figure 1B) and by a broad absorption feature at ~1100nm.

According to the above study, the following conclusions were drawn:

- Calcite, when present in small proportions, is difficult to be identified and usually present similar absorption features with chlorites and mica.
- Quartz and feldspars are featureless in the Near Infrared region, however their percentage contributes to the overall reflectance of the sample
- The percentage of clay minerals in the sample strongly influence the absorption features of the sample and may subdue the absorption features of calcite, when is present in small amounts.
- When dolomite is present in small amounts in the mineralogy of the lithotype, it cannot be discriminated from calcite. However, when dolomite dominates, the absorption features are shifted to smaller wavelengths.
- A possible difference among marbles and limestones could be the presence or absence of broad absorption features at ~1400 and ~1900 nm. However, in the case of well crystalized limestones, this argument might not be representative.
- The reflectance variations of the spectra caused by the grain size of the minerals does not affect the position of the absorption features.
- Absorption features at the visible range of the electromagnetic spectrum are caused by the presence of ferrous minerals.
- The broad absorption feature at ~1100nm is caused by the presence of ferrous iron either substituting  $\text{Ca}^{2+}$  in calcite, or due to the presence of ferrous minerals like diopside on hedenbergite, in the case of marbles.
- The spectra of these lithologies even though address to a specific mineral, the calcite, do not add any information for the conditions of formation of these rocks, or for their crystallinity.

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