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Raman Application Note
Geology 01

Raman Spectroscopy for Geological Materials Analysis

Introduction

Natural rocks composing the Earth are complex. They consist of an aggregate of one or more minerals. Each mineral can be defined by its chemical composition and its crystalline structure and sometimes can also contain fluid inclusions. Geologists need a powerful characterization technique to get detailed information on the rock formation history. Raman spectroscopy is extremely information-rich (chemical identification, characterization of molecular structures, effects of bonding, environment and stress on a sample). With its non-destructive properties and high spatial resolution (< 1 µm), it is thus a tool of choice for geological studies.

Raman Spectroscopy specificities

- The Raman effect is highly sensitive to even slight differences in chemical structures. Even if not all vibrations are observable with Raman spectroscopy (depending on the symmetry of the molecule or crystal), sufficient information can be obtained to discriminate different structural groups or phases related to the same mineral class, like silicates or carbonates.
- Sometimes a high spectral resolution is needed to resolve closely spaced peaks. This is the case when specific pressure and temperature conditions are applied to a mineral using for example a diamond anvil cell (DAC) to recreate what can happen deep in the earth. Indeed spectral discrimination will be the key factor to detect small peak shifts induced by high pressure and temperature conditions.
- Systems offering multiple laser excitations can efficiently counter the possible fluorescence of geological samples. Coupled to confocal microscopy, Raman spectroscopy provides information with high spatial resolution (< 1 µm).
- On-site analysis can also be undertaken with mobile units possibly by using remote sampling accessories.
- Raman spectral libraries are also a great help for easy identification of minerals, relying on supplier's libraries [1] or on databases created by the end-user.

Chemical selectivity

a- Silicate minerals

The silicate minerals, often designated simply by the term "silicates", represent the most important class of rocks forming the crust and mantle of the Earth. A silicate is a compound whose skeleton is essentially composed of silicon and oxygen tetrahedra and with additional elements such as aluminum (aluminosilicates), magnesium, iron, calcium, potassium, etc. They are classified based on the mode in which the silicate groups coalesce. The Raman spectra of the different classes of silicate minerals provide rapid identification of the particular class. Figure 1 indicates some of the arrangements of fused tetrahedra that are possible.

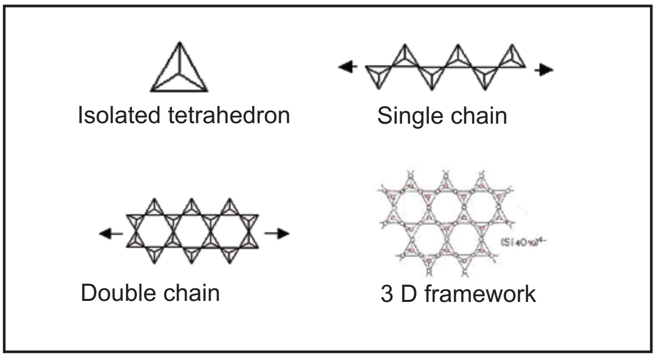

Figure 1: Different tetrahedral arrangements

Olivine is one of the most common minerals of the igneous rocks type (formed by magma). It belongs to the nesosilicates (or orthosilicates) subclass characterized by an isolated tetrahedra $[SiO4]^{4-}$. Its Raman spectrum shows intense stretching modes in the 800-1000 cm^{-1} region and bending modes between 300 and 650 cm^{-1}. (Figure 2)

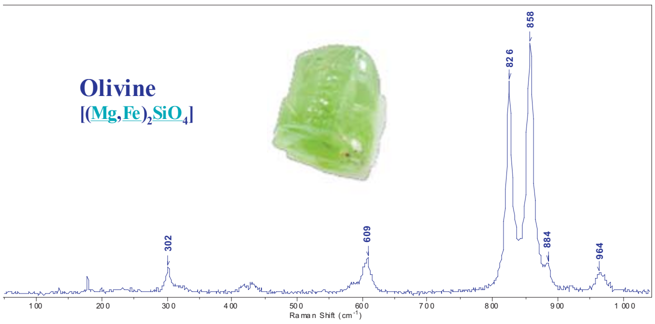

Figure 2: Raman spectrum of olivine

The term inosilicates is used for chain silicates. They are divided in two groups: pyroxenes and amphiboles. Pyroxenes contain single chains of SiO_4 groups. Like jadeite, their spectra present an intense Raman band between 650 and 700 cm^{-1} [2]. In contrast to the single chain structure of pyroxenes, amphiboles contain double chains of tetrahedra. One representative amphibole mineral is actinolite and its variety nephrite. Both jadeite and nephrite are recognized as the gemstone jade (Figure 3).

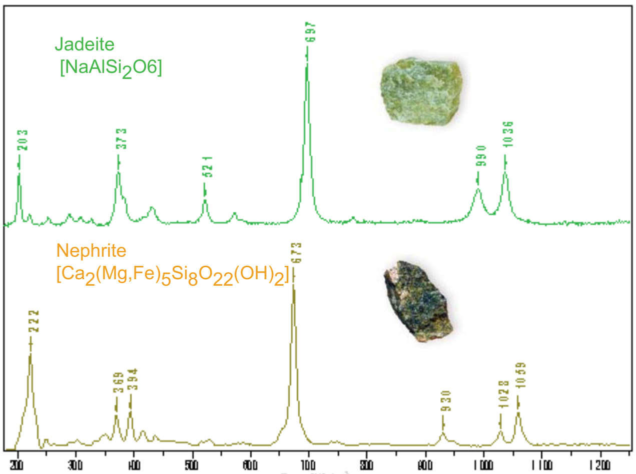

Figure 3: Nephrite and jadeite Raman spectra

Feldspars and zeolites belong to the tectosilicates groups, also known as three-dimensional framework silicates. Feldspars can have three end-membered elements: potassium (orthoclase), sodium (albite) and calcium (anorthite). A variation in peak positions, especially for the peaks near 500 and 280 cm^{-1} can be used to discriminate between them.

Because of their porous properties, zeolites are rarely pure and numerous types of zeolite frameworks exist. A natrolite spectrum is given for example (Figure 4). The most intense band at 532 cm^{-1} corresponds to the breathing mode of the four-membered alumino-silicate ring [3].

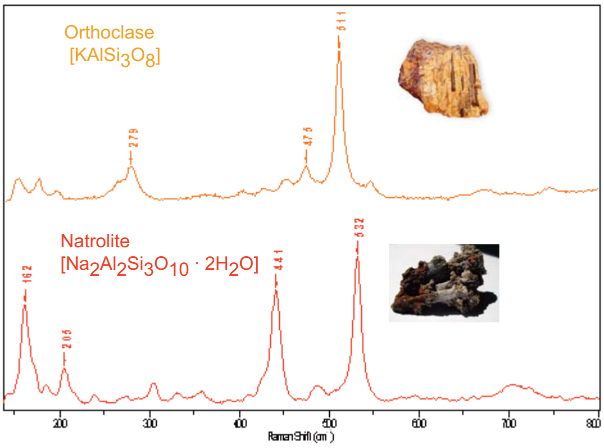

Figure 4: Natrolite and orthoclase Raman spectra

b- Carbonates

Like silicates, carbonates are minerals that are present in abundance on the surface of the Earth. They are characterized by the presence of a carbonate ion CO_3^{2-} and Raman spectra are slightly different depending on the divalent cation (Ca^{2+}, Fe^{2+}, etc) coordinated to the carbonate ion. Frequency shifts can be observed in two spectral areas:

- between 120 and 450 cm^{-1}– this region indicates crystallographic structures
- between 1080 and 1100 cm^{-1} – this band is specific to the carbonate ion CO_3^{2-}

A test sample containing different species of carbonates has been fully imaged using the DuoScan option in macro-mapping mode. Average spectra in pixels of 200 μm^2 have been collected on a surface of about 1 cm^2 in less than an hour. The low frequency region has been studied and six different species have been easily detected. Their distribution and associated spectra are given in the figure 5a.

Another map in traditional point-by-point mode has been carried out on a small area containing only two dolomite crystals. The high spectral resolution of the LabRAM HR has enabled detection of the small frequency shift existing between the two carbonates, the green one having traces of Fe (Figure 5b).

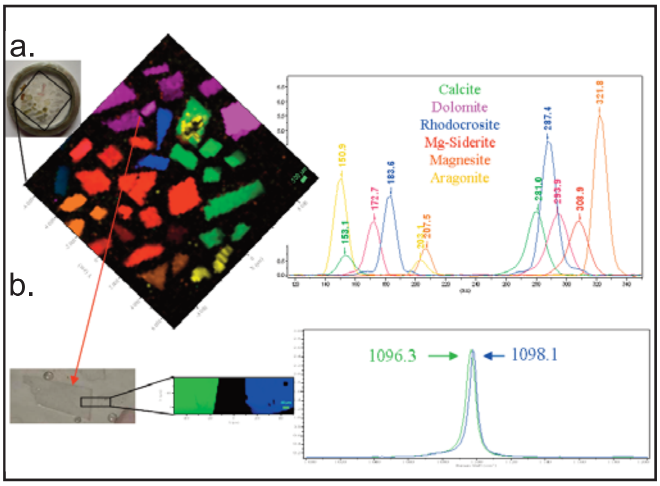

Figure 5: a- Raman imaging of different types of carbonates crystals using the DuoSan option and their associated spectra
b- High spectral resolution map of two dolomite crystals based on the small spectral shift existing between the two crystals spectra.

Silicate and carbonate classes contain numerous species, each of them having characteristic Raman bands. Raman spectroscopy is thus an ideal technique to quickly identify them.

Fluid inclusions and confocality

Minerals often contain fluids or solids which have been trapped during the formation of the crystal and thus can provide information about the conditions existing during the mineraliziation (composition, temperature, pressure…). Liquid or gas bubbles are called fluid inclusions. Their size ranges from less than a micrometer to several hundred micrometers in diameter. A Raman system coupled to a confocal microscope is required to obtain high spatial resolution and to analyse inclusions located below the surface without destruction.

a- Principle of confocality

In a confocal microscope, an adjustable pinhole is optically conjugated to the sample. Thus, all out-of-focus radiations can be rejected from the collected Raman signal. For example, if the pinhole is closed enough, a small embedded inclusion signal is efficiently discriminated from the matrix signal. The figure 6 illustrates this principle. In confocal mode, the signal of the matrix is less visible than in the non-confocal mode.

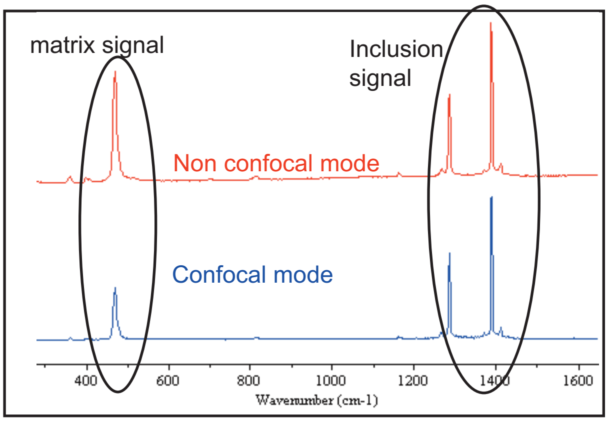

Figure 6: Comparaison of the confocal and non confocal mode for the analysis of a fluid inclusion

b- Point measurements

Raman analysis of a 20 µm fluid inclusion embedded in a quartz matrix was carried out on the LabRAM HR. The inclusion is a two phase system, where the gas phase consisting of a mixture of CO_2 (1285 cm^{-1} and 1388 cm^{-1}), CH_4 (2914 cm^{-1}), N_2 (2331 cm^{-1}) and H_2S (2611 cm^{-1}) in enclosed in the liquid phase (3200-3700 cm^{-1}) (Figure 7)

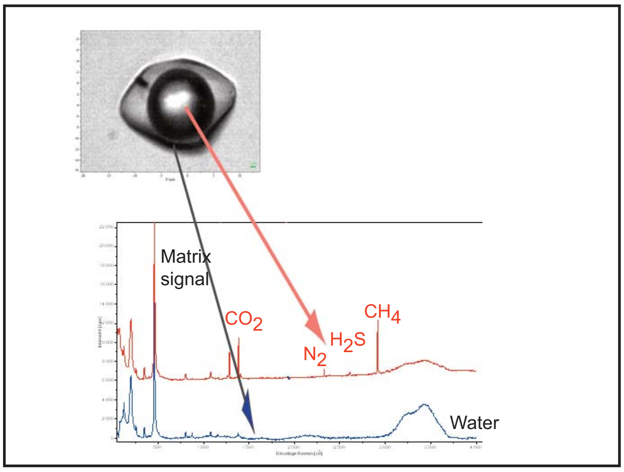

Figure 7: Raman spectra obtained in different areas of the fluid inclusion

c- Imaging

The high spatial resolution of the system, better than 1 µm, enables one to image the components of the fluid inclusion presentes in the example above and so highlight the distribution of the different phases (Figure 8).

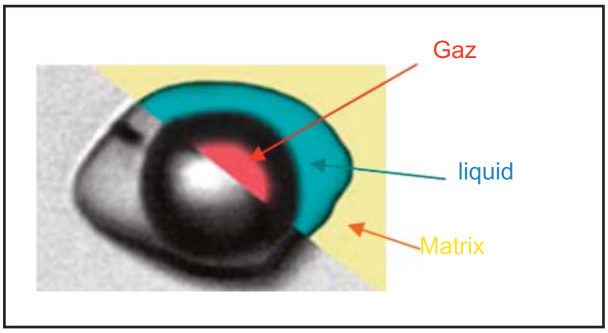

Figure 8: Raman image of a fluid inclusion

d- Use of a corrected objective

Fluid inclusions are embedded in a transparent or semi-transparent matrix with an index of refraction higher than 1.4. For matrix having an index of refraction close of this glass, the use of a dry objective with cover slip correction can be a solution to minimize the degradation of the lateral and axial resolutions implied by the drastic change of the index. [4]

A test was performed on a CO_2 bubble embedded 100 µm deep in a quartz matrix (Figure 9).

The Raman peaks of the CO_2 (1285 and 1388 cm^{-1}) are much stronger when using the corrected objective because the corrections provide better collection efficiency and focus on the entrance slit of the spectrograph.

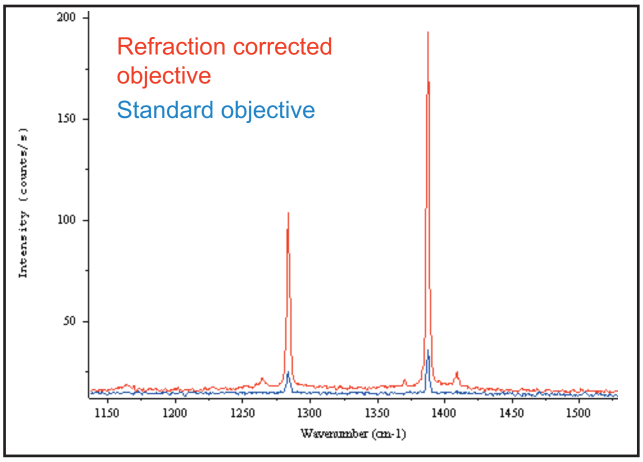

Figure 9: Comparison between standard and corrected objectives on a 100µm deep CO_2 inclusion

Because of their size and location in minerals, fluid inclusions can be hard to analyze. With its high spatial resolution, Raman spectroscopy is very useful to determine the composition of the embedded fluids. Imaging of fluid inclusions is also possible and the use of corrected objective can help to obtain higher signals.

Conclusion

Raman spectroscopy is a practical exploration tool to study geological materials. This technique is a rapid and reliable way to confirm, for example, that a geological sample is really a jade gemstone, or that its composition is dolomite. Chemical information can be obtained without any extraction procedure or sample preparation. Thus, the analysis can be achieved in situ and if necessary directly at the geological site. Raman imaging is also useful to study heterogeneous samples provided by the various fields of application of Earth Science: mineralogy, gemmology, petrology, geoarcheology, paleontology, planetology or volcanology. By the mean of this vibrational technique, the complex history of the Earth can be better understood.

References

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