PCA as a simple tool to characterize the composition of olivine and other oxide minerals from a meteorite sample interrogated by Raman spectroscopy

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Introduction and Objectives

Miniaturised Raman instruments were developed to be deployed on spatial missions to Mars (e.g. NASA’s Mars2020 and ESA’s ExoMars missions) or the Moon (NASA’s Artemis and ESA’s ISRU missions) as they are capable to detect geological substances constituting the rocky surface (inorganic molecules and inorganic molecular ions), which in the case of Mars will provide information on the habitability of the planet [1,2]. Raman spectroscopy was successfully applied to study the presence of mineral phases in a wide variety of space analogue samples. In addition, Raman instruments can detect potential organic carbonaceous molecules, including biological-derivative substances produced by extent or extinct living organisms (often referred to as biomarkers) or thermo-processed carbonaceous molecules, including amorphous carbon materials and kerogens [3]. In preparation for space missions, intended to deploy dedicated instruments developed with constraints such as minimal power budget, mass budget and data budget, documenting the detection capability of miniaturized Raman spectrometers is essential and has been (and still is) conducted on a wide range of terrestrial analogue samples, relevant of various astrobiological scenario [4]. Raman molecular imaging have emerged as a powerful technique to follow the variation of the chemical composition across geological interfaces often found in analogue samples. But Raman imaging implies large sets of spectral data (one spectrum for each x,y coordinate on the exposed surface of the sample interrogated with the Raman instrument) [5]. In the frame of space mission, Raman imaging has been scarcely considered, especially since recording large data sets and transferring these data back on Earth would require energy that is not often permitted by the energy budget of unoccupied missions. Yet, in preparation of future inhabited missions, intended to bring trained astronauts to use these dedicated instruments, and in the frame of the ESA’s PANGAEA training course [6], simple data treatment enabling to reduce the complexity of the data sets (from a few thousands of spectra down to a few spectra) may allow the integration of Raman imaging instruments in future inhabited mission payloads.

In this publication, we will discuss the implementation of principal component analyses (PCA) as a tool to identify underlying molecular signatures in association the microstructures in a sample of the Sericho meteorite. We will demonstrate that PCA can help reducing the data set to a few spectra that contained most of the molecular information in the data set. Raman spectra generated using PCA filter can also provide the composition of the olivine inclusions of the pallasite. We will compare spectral imaging data recorded with benchtop instrument and miniaturized spectrometers developed for space missions.

Methods

In this study a 4 cm^2 section (with a thickness of 2 mm) of the Sericho pallasite was interrogated (Figure 1.A). The 2.8 tons Sericho pallasite was discovered in Kenya near the Sericho city and was recorded as a pallasite in 2017 and the olivine inclusions contain 12.3% of fayalite [7,8]. Raman images were recorded using a benchtop Labram 300 spectrometer (manufactured by Horiba), interfaced with a 532.3 nm DPSS laser (able to irradiate the sample with a power ranging from 40 to 0.4 mW on the samples typically) and a thermoelectrically cooled CCD detector Andor iDus DU401 BRDD. The spectrometer was coupled to an Olympus BX40 microscope equipped with a computerized xy mobile stage enabling to record Raman images with a spatial resolution of 0.5 µm. Data were obtained across the 200-2000 cm^{-1} wavenumber offset range with a spectral resolution of ~3 cm^{-1}. The laser footprint on the sample was ~4 µm in diameter (through an objective Olympus X50, NA 0.50). Raman data were also obtained using a miniaturised a Raman spectrometer developed for space mission at the University of Leicester. PCA analyses were performed using The Unscrambler X (CAMO software).

Results

Olivine (mainly forsterite), goethite, hematite) and chromite were identified from Raman spectra obtained at different microstructures observed at the interface between the olivine inclusions and the iron-nickel. The main constituent of the inclusions being olivine as expected for a pallasite. In addition, carbon was also detected in specific location of the sample, both as disordered carbon and associated diamond carbon. The disordered carbon is likely to be exogenous (either added as a contamination during the slicing of the sample or during the weathering of the sample before it was retrieved), as endogenous organic matter that would have been trapped in the pallasite during its formation would have burnt during the entry of the pallasite in the Earth atmosphere. Yet, the diamond carbon, always found associated with the disordered carbon, may indicate that the trapped carbonaceous material transformed partially under high pressure and temperature during the crash of the pallasite on Earth. PCA was performed on the Raman images (as shown in Figure 1) and enable to resolve six regions of interest with a different geochemistry associated to the presence of olivine, goethite, chromite and hematite. The loadings of the Principal Components enable to visualise the spatial distribution of the minerals at the interface, and the Raman spectra obtained as the mean Raman spectra in these regions of interests enables the identification of the mineral phases. Moreover, based on the Raman spectra obtained for olivine the content of fayalite and forsterite was estimated and was found to vary when the olivine was associated to other minerals at the interface, and even from the edge to the inner part of the inclusions.

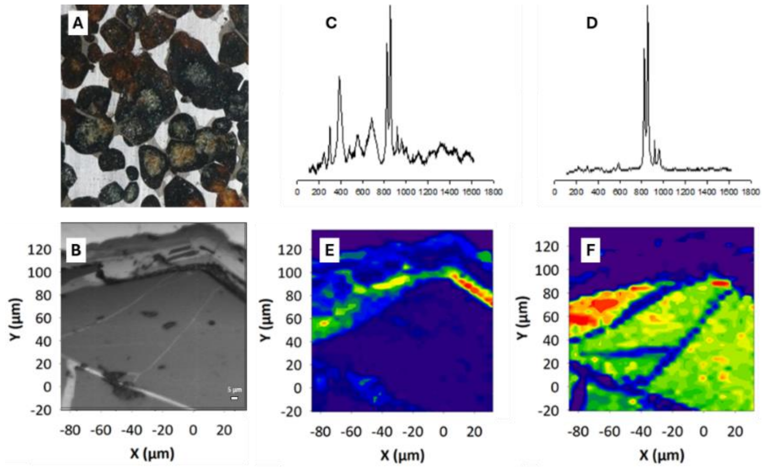

Figure 1. (A) micrography of the olivine inclusions in a sample of the Sericho meteorite. (B) Zoomed micrography on the interface of an olivine inclusion and the iron-nickel alloy, showing various microstructures. (C) Raman spectrum of a mixture of gothite and olivine. (D) Raman spectrum of olivine). (E) Raman image obtained by PCA, showing where the gothite is found in association with olivine). (F) Raman image obtained by PCA, showing the olivine domains.

Conclusions

Principal component analysis (PCA) is indeed an interesting statistical tool to be implemented either to reduce the number of spectra required to identify the main mineral phases present at the interface of the olivine and the iron-nickel alloy of the Sericho pallasite, or to characterise the spatial distribution of these minerals on the interrogated surface of the sample.

Keywords

Raman spectroscopy, PCA, meteorite, imaging, planetary sciences

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