

NEW QUANTITATIVE MODEL TO DETERMINE FAYALITE-FORSTERITE CONTENT IN OLIVINE MINERALS BY RAMAN SPECTROSCOPY. I. Torre-Fdez, P. Ruiz-Galende, J. Aramendia, L. Gomez-Nubla, K. Castro, G. Arana, J. M. Madariaga, Department of Analytical Chemistry, University of the Basque Country (UPV/EHU), Barrio Sarriena s/n, 48940 Leioa, Spain (imanol.torre@ehu.eus).

Introduction: As has been recently discovered, there exists a correlation between olivine and carbonate signatures in some sedimentary areas in Mars, such as in Jezero Crater in the region of Nili Fossae, where the rover of the upcoming Mars 2020 mission will land. Specifically, the carbonate occurrences are associated with the Fe-rich olivines [1]. These carbonate minerals, along with the clay minerals present in the crater, are essential in the understanding of the formation of the Jezero Crater delta and the possible water channels that transported the sediments. The fact that they are associated with olivines depending on their forsterite-fayalite composition ($\text{Mg}_2\text{SiO}_4\text{-Fe}_2\text{SiO}_4$ ratio) makes the study and characterization of these silicates more meaningful, as they can help in the research of the carbonate minerals.

In this regard, Raman spectroscopy has been found to be a successful tool not only to observe olivine as a mineral phase present in a sample, but also to characterize the forsterite-fayalite content present in it [2, 3]. In this sense, Raman spectroscopy can become a reliable tool in both the identification and cationic quantification of olivines, which would lead to the finding of the carbonate and clay deposits too. However, the already existing models provide results with an inaccuracy higher than $\pm 10\text{-}15\%$, which can lead to misinterpretation of those results (such as spotting carbonates and clay areas). The aim of this work is to create a new calibration model for the quantification of forsterite-fayalite content in olivines, improving the already existing ones, so that it can be used to characterize olivines more accurately.

From the 36 Raman active vibrational modes that olivine has, the ones present in the region between $700\text{-}1100\text{ cm}^{-1}$ are assigned to the internal stretching vibrational modes of the ionic group SiO_4 [3]. It is in this region where the main bands of olivine are observed, appearing always as a doublet of varying relative intensities. The doublet also has shifts in the position of both bands wavelength. Depending on the amount of Mg and Fe present in the crystal structure of the analyzed sample, the bands appear in the range of $815\text{-}825\text{ cm}^{-1}$ (for the band that we call RB1, symmetric stretching for the Si-O bond) and $839\text{-}856\text{ cm}^{-1}$ (for RB2, asymmetric stretching for the Si-O bond). As they are the main bands and also have shifts depending on the concentration of Mg and Fe, they are the ones used for the quantification model.

Data acquisition: Measurements of olivines were carried out using a Renishaw inVia Raman micro-spectrometer (Renishaw, UK) equipped with 532, 633 and 785 nm excitation lasers. The mean spectral resolution of the instrument is around 1 cm^{-1} . It was coupled to a microscope, where an objective of 50x was used for the spectral acquisition. In order to guarantee the accuracy of the spectra, a daily calibration of the instrument was performed using a silicon chip and its 520.5 cm^{-1} band as a reference. The spectral acquisition conditions were optimized depending on the analyzed sample, although the usual parameters were 5 accumulations and 5 seconds of integration time. The laser power was modulated so that the sample received always less than 20 mW in order to avoid thermodecomposition and chemical or mineralogical transformations.

In the absence of some olivine samples of particular forsterite-fayalite ratios, Raman spectroscopic data of olivines from literature was used to complete missing information of specific compositions or to increase the experimentally obtained one [3-9].

In addition, a certified olivine standard ($\text{Fo}_{89.5\pm 1.8}\text{Fa}_{10.5\pm 0.5}$), characterized by X-Ray Powder Diffraction (XRD) and Electron Micro Probe Analysis (EPMA) was used in order to test the robustness of the calibration models. It was then analyzed with the inVia system, acquiring the spectra of 10 different grains of the sample and obtaining the average spectrum of them.

Results and Discussion: In Figure 1 it is observed the forsterite content (Fo_x) of the different olivine samples plotted against the RB1 and RB2 Raman bands wavelength position, respectively. In both cases an exponential regression curve was calculated and plotted. Red error bands of $\pm 1\text{ cm}^{-1}$ are plotted as well, and none of the experimental points are outside of that range.

In the case of RB1, it is observed how the experimental data clearly fit into an exponential regression curve with the equation shown in Figure 1 ($r^2=0.9720$), which is a very good result for a mineral quantification model using Raman spectroscopy. However, several points appear in the $\pm 5\text{-}10\%$ range of the regression residuals (Figure 2), which is undesirable for a good model. When the standard olivine was quantified using this model, a composition of $\text{Fo}_{92\pm 5}\text{Fa}_{8\pm 1}$ was obtained, having a 3 % of deviation from the certified value.

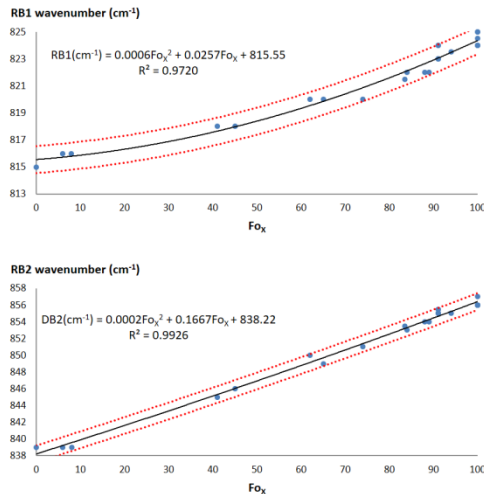


Figure 1. Calibration models for the determination of forsterite content in olivines using RB1 and RB2.

In the case of RB2, the experimental data fit both into a linear and an exponential regression curve almost perfectly. However, the exponential model (Figure 1) has better regression quality parameters than the linear model (r^2 , σ of the slope, σ of the origin ordinate and the regression residuals). Regarding the regression residuals for the model (Figure 2), it is observed how none of the points are outside the $\pm 5\%$ threshold. In addition, the concentration of forsterite obtained from the analyzed standard olivine was $\text{Fo}_{91\pm4}\text{Fa}_{9\pm1}$, having only a 2 % of deviation from the certified value.

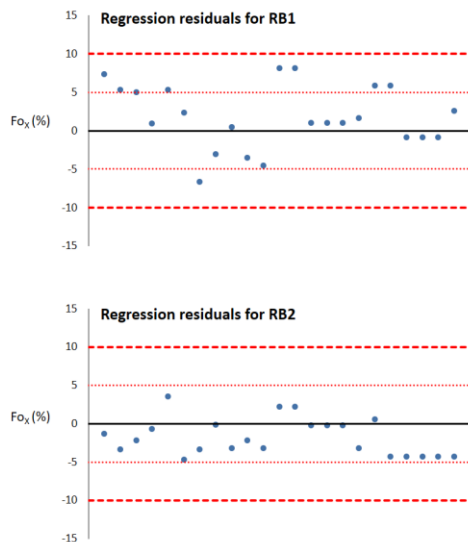


Figure 2. Regression residuals for the calibration models of RB1 and RB2.

Taking these results into account, both calibration models are adequate to quantify the forsterite-fayalite composition of olivines by means of Raman spectroscopy, as they provide accurate results, tested with the

certified olivine standard, and have a very good fit with the experimental results. Between both, the RB2 model is superior than the RB1, as it has a slightly better r^2 , lower values in the regression residuals and provides more accurate results.

The models found in the literature to quantify the forsterite-fayalite ratio by Raman spectroscopy provide an accuracy of $\pm 10\text{--}15\%$ [2, 3]. With the models proposed in this work, accuracies in the range of $\pm 2\text{--}3\%$ can be achieved, being a significant improvement with regard to the already existing ones.

Conclusions: The identification of olivines, especially Fe-rich olivines, can facilitate the finding of carbonate and clay occurrences, such as in Jezero Crater, which are critical for the study of the past presence of water on the planet. We propose Raman spectroscopy as a tool to identify these Fe-rich olivines, as this technique is sensitive to the forsterite-fayalite ratio variations in olivines. Due to this fact, it is crucial to have a high accuracy method to detect Fe-rich olivines, as they would be an important target in Martian missions. In consequence, we propose the two developed accurate quantitative models to obtain the forsterite-fayalite content of olivine using Raman spectroscopy assuring less than 3% of error.

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References: [1] Brown A. J. et al. (2018) *LPS IL*, Abstract #2083. [2] Mouri T. and Enami M. (2008) *J. Miner. Petrol. Sci.*, 103, 100-104. [3] Kuebler K. E. et al. (2006) *Geochim. Cosmochim. Ac.*, 70, 6201-6222. [4] Servoin J. L. and Piriou B. (1973) *Phys. Status Solidi*, B55, 677-686. [5] Besson J. M. et al. (1982) *J. Geophys. Res.*, 87, 10773-10775. [6] Guyot F. et al. (1986) *Phys. Chem. Minerals*, 13, 91-95. [7] Chopelas A. (1991) *Am. Mineral.*, 76, 1101-1109. [8] Kolesov B. A. and Tanskaya J. V. (1996) *Mater. Res. Bull.*, 31, 1035-1044. [9] Kolesov B. A. and Geiger C. A. (2004) *Phys. Chem. Minerals*, 31, 142-154.