

Micro-Raman Spectroscopy of Garnierite Minerals: a Useful Method for Phase Identification

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INTRODUCTION

"Garnierites" are important Ni-ores found in worldwide hydrous silicate-type Ni-laterites. They consist of one or more fine-grained nickel-magnesium phyllosilicates, including serpentine, talc, sepiolite, smectite and chlorite (e.g. Brindley & Maksimovic, 1974; Springer, 1974). They often occur as micron-scale mixtures, so data obtained by conventional techniques for mineral identification and characterisation, such as X-ray diffraction (XRD) and Electron Microprobe (EMP), may not be conclusive.

Several studies on "garnierites", based on XRD, SEM, EMP, thermal and different spectrometric techniques, have been published worldwide. However, to the knowledge of the authors available Raman and mineral databases of micro-Raman spectra lack references of "garnierite" minerals.

Micro-Raman spectroscopy technique represents a reliable method for *in situ* mineral identification. It does not require complex and destructive sample preparation like XRD and TEM, as analysis can be performed directly on standard polished sections or polished thin sections used in optical microscopy (Rinaudo et al., 2003).

Previous results show that Dominican "garnierites" consist of three solid solutions: lizardite-népouite, talc-willemseite (or the hydrated equivalents "kerolite"-pimelite), and sepiolite-falcondoite (e.g. Proenza et al., 2007; Galí et al., 2012). For this reason, "garnierites" have been classified as "serpentine-", "talc-" and sepiolite-falcondoite "garnierites", respectively. In addition, recent data proved the existence of the first Ni-bearing

nontronites reported in the Falcondo Ni-laterite deposit. All these mineral series, which can roughly be recognized optically by different greenish colours, were characterized by means of XRD, Scanning Electron Microscopy (SEM), EMP and Transmission Electron Microscopy (TEM-AEM) (Tauler et al., 2009; Galí et al., 2012; Villanova-de-Benavent et al., 2011a, b). Preliminary data show that talc-like "garnierites" have in general higher Ni contents than serpentine-like "garnierites".

This work is an attempt to identify the different "garnierite" minerals occurring in the Falcondo Ni-laterite deposit by micro-Raman spectroscopy.

METHODS

Four representative samples were selected. According to previous results, these specimens contain: a) Ni-rich serpentine-like "garnierite", b) talc-like "garnierite", c) a mixture of both, and d) falcondoite. Results were obtained with a HORIBA Jobin Yvon LabRam HR 800 dispersive spectrometer, equipped with an Olympus BXFM optical microscope, and using an InGaAs detector cooled at -110°C for the 1064 nm laser line excitation. Non polarized Raman spectra were obtained by applying a 1064 nm laser (beam size around 2 µm) with 10 measurement repetitions for 60 seconds each.

It must be noted that materials containing serpentine minerals present higher fluorescence effects than the others, however these effects were reduced by using the 1064 nm laser.

RESULTS

Micro-Raman spectra of the four samples are shown in Fig. 1.

Ni-rich serpentine samples present bands at 230, 345, 386, 619, 644 and 691 cm⁻¹ (Fig. 1a). The band at 230 is assigned to O-H-O vibrations (Groppo et al., 2006). The 345 and 386 bands are related to bending vibrations of SiO₄ tetrahedra (Rinaudo et al., 2003), whereas the 386 band is attributed to Ni-O vibrations by Frost et al. (2008). Band at 619 is assigned to OH-Mg-OH (Rinaudo et al., 2003) and to Ni-OH vibrations (Frost et al., 2008). Band at 644 corresponds to antisymmetric OH-Mg-OH translation modes (Groppo et al., 2006) and band at 691 is attributed to symmetric Si-O-Si stretching vibrations according to Rinaudo et al. (2003) and Groppo et al. (2006). The peak at 386 is typical for lizardite (Groppo et al., 2006), and the peak at 619 is related to chrysotile (Rinaudo et al., 2003). This is coherent with HRTEM imaging, which revealed the presence of both lizardite and chrysotile in this specimen (Villanova-de-Benavent et al., 2011b).

In the specimen with pimelite (talc-like "garnierite") bands were observed at 188, 362, 385, 640, 675, 735 and 822 cm⁻¹ (Fig. 1b). According to Holtz et al. (1993), 188, 362 and 675 are typical bands for talc, its non-hydrated Mg analogue, whereas 188 and 675 are also related to willemseite, the non-hydrated Ni-talc. (<http://rruff.info/Willemseite>; 2011, march 27). Finally, 822 band is attributed to NiOH deformation by Frost et al. (2008).

In the sample with both Ni-serpentine and talc-like "garnierite" (pimelite), bands at 183, 210, 368 and 680 cm⁻¹ were detected (Fig. 1c). Comparing these results with those obtained previously, 183, 368 and 680 bands may correspond to the pimelite phase, whereas the 210 band is attributed to

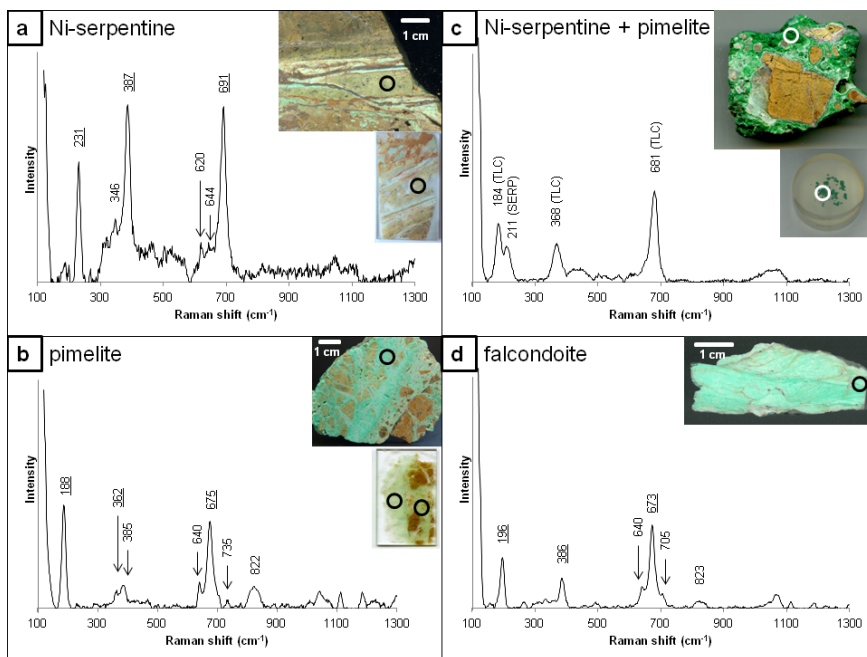


fig 1. Raman spectra of the four samples studied in this paper, including respective specimen, section and thin section photographs: a) Ni-serpentine, b) pimelite, c) sample containing both Ni-serpentine and pimelite (tlc: talc, serp: serpentine), d) falcondoite. The most important bands are underlined.

chrysotile and lizardite by Groppo et al. (2006).

The falcondoite sample shows bands at 196, 386, 640, 673, 705 and 823 cm^{-1} (Fig. 1d). However 386 band may be similar to that of Ni-serpentine, and 640 and 672 bands may be comparable to those of pimelite, the 196 band is characteristic for falcondoite. The 823 band related to NiOH deformation is also present in this spectrum.

CONCLUDING REMARKS

Micro-Raman spectroscopy represents a fast, easy, reliable and non-destructive method for identifying “garnierite” minerals in situ, even when samples are very fine grained and exhibit fine intergrowths and/or are poorly crystalline.

Knowledge of characteristic Raman vibrations of serpentine-like “garnierites” (230, 691 cm^{-1}), talc-like “garnierites” (188, 362 cm^{-1}) and falcondoite (196) are a significant improvement for the mineralogical identification of these minerals. Furthermore sample preparation for micro-Raman spectroscopy is identical to conventional analysis techniques, thus making this method a very useful tool for a fast mineral identification in addition to the usual mineral characterization methods,

such as XRD, SEM-EDS and EMP.

Furthermore, higher Ni content is related to talc-like “garnierites” or pimelite, and this phase can be detected by micro-Raman. Therefore, this technique is a powerful tool which provides efficient results for mineralogical Ni-ore characterisation in Ni-laterite deposits.

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