

**QUANTITATIVE DETERMINATION OF GASEOUS PHASES IN FLUID INCLUSIONS BY RAMAN MICROSCOPY.** A. C. Prieto<sup>1</sup>, A. Guedes<sup>2</sup>, A. Dória<sup>2</sup>, F. Noronha<sup>2</sup> and J. Jiménez<sup>1</sup>, <sup>1</sup>GdS Optronlab, Parque Científico UVa, Edificio de I+D, P. de Belén, 1, E-47011 Valladolid, Spain (prieto@fmc.uva.es), <sup>2</sup>Centro de Geologia/ DGAOT, Faculdade de Ciências, Universidade do Porto, P-4169-007 Porto, Portugal.

Due to its non-invasive nature, together with its high lateral resolution, micro-Raman spectroscopy reveals itself as a powerful technique to perform qualitative analysis and to determine the relative molar fractions of the gaseous species present in minerals fluid inclusions. However, the integrated Raman intensity depends, among others, of the concentration of the analyte and of the Raman cross-sections, and these depend on the state variables of the system, therefore, the concentrations of the molecular species present in the gas phase of fluid inclusions determined from Raman spectra are relative quantitative values. From the calculation of the molar concentrations of the gases in the fluid inclusion, and once all phases characterized, it is possible to determine the system state variables (P-V-T-X) in solid-liquid-gas equilibrium.

There are numerous publications concerning the application of micro-Raman spectroscopy to the determination of the composition of fluid and solid inclusions in minerals and processes to obtain molar fractions in COHNS multi-component systems have been also described [1-5]. Micro-Raman qualitative analysis requires the identification of the various constituents of a mixture through the position ( $\bar{\nu}$ , cm<sup>-1</sup>) and the intensities of the fundamental vibration modes of the ionic or molecular group in the Raman spectrum. A collection of the species contained on fluid inclusions and their characteristic vibrational modes are described on Burke [6] and for the relative quantification of gaseous phase of the ionic or molecular species  $i$  present in a fluid inclusion, using the theory of Placzek [7] improved by Dhamelin-court et al.[8], the integrated Raman intensity is  $I_i = I_0 \sigma_i N_i \xi_i$ , where  $I_0$  is the intensity of incident radiation on the sample,  $\sigma_i$ , the Raman scattering cross-section,  $N_i$ , the number of molecules of the species  $i$ ,  $\xi_i$ , the spectral efficiency factor, dependent on the spectrometer, optical instruments and CCD detector. Therefore, the Raman integrated intensity gives information on the number of molecules of a species per unit of volume. The molar fraction  $X_i$  of the species  $i$  is  $X_i = [(I_i / \sigma_i \xi_i)] / \sum [(I_i / \sigma_i \xi_i)]$ .

The present work addresses the determination of the molar fractions percentage on a multi-component system, calculated from the integrated Raman intensity of the bands characteristic of each molecular group. The experimental study has focused on the analyses of CH<sub>4</sub>-CO<sub>2</sub>-N<sub>2</sub> fluid inclusions in cassiterites from the Panasqueira mine (Portugal), previously studied by

microthermometric analyses, and were performed using a microRaman Dilor spectrometers interfaced to an Olympus microscope with 100x objective lens and excitation wavelengths of 488.0 and 514.5 from Ar<sup>+</sup> lasers (Valladolid University) and 632.8 nm from a HeNe laser (Porto University). Spectral decomposition of bands were performed using the program of Dilor LabSpec-Jobin Yvon-Spex, and Raman parameters obtained. Although calibration procedures were already described in the literature, an important controversy is presented to define whether one or both bands of the Fermi resonance (FR) of CO<sub>2</sub>, which should contribute to the calculation of the integrated intensity of CO<sub>2</sub>. Dubessy et al.[3] suggest that the sum of both intensities  $[I(\nu_1) + I(2\nu_2)]$  is constant, although the relative ratio of their areas  $[I(\nu_1):I(2\nu_2)]$  varies with the density and internal pressure. Its pressure dependence and detection limits are reflected in the study of Rosso and Bodnar [9]. Raman intensity studies [10-11] and of the roto-vibrational spectrum [12] of the doublet of the FR of CO<sub>2</sub>, show that, on the equilibrium, the population of states of both vibrational quantum levels  $[\text{CO}_2(10^0_0) \leftrightarrow \text{CO}_2(02^0_0) \pm 102 \text{ cm}^{-1}]$ .

The present work describes the methodology used for the quantification of the different species in the fluid inclusions paying attention to the calibration of measurement spectrometers and to the Fermi resonance of CO<sub>2</sub> vibrations ( $\nu_1-2\nu_2$ ; 1285 -1388 cm<sup>-1</sup>).

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