The statistical equivalence of the CO_2 Raman densimeter equations

REMIGI S.[1], MANCINI T.[2], FERRANDO S.[3], FREZZOTTI M. L.[1]

[1]Department of Earth and Environmental Sciences, University of Milano Bicocca, Piazza della Scienza 4, 20126, Milano, Italy (s.remigi@campus.unimib.it; maria.frezzotti@unimib.it)

[2]Department of Economic, Social and Political Sciences, University of Southampton, University Road, *SO17 1BJ, Southampton, United Kindom* (T.Mancini@soton.ac.uk)

[3]Department of Earth Sciences, University of Torino, Via Valperga Caluso 35, 10125, Torino, Italy (simona.ferrando@unito.it)

Raman spectroscopy allows measuring the density of CO_2 fluid inclusions. Several Raman densimeter equations have been proposed to relate the distance of the main CO_2 peaks (Δ; in cm^{-1}) to fluid density. Although a specific Δ should correspond to a single density value, calculated CO_2 densities may vary depending on the selected equation. In particular, at equal Δs, Raman densimeter equations define two groups of density values differing up to 0.09 g/cm^3. The reason behind this bimodal distribution of density values has not yet fully explored, and thus, a general application of published equations is not recommended. We have investigated the influence of the analytical setup on the calculation of Raman densimeter equations to statistically evaluate to what extent the difference in calculated CO_2 densities may influence the reliability of data derived by empirical equations. This has also been accomplished by the calculation of a new equation by adopting a "standard" analytical set up (Kawakami et al. 2003; Yamamoto and Kagi 2006). Further, we have compared existing Raman densimeter equations using R statistical software. For this step, we calculated the 0.95 confidence intervals for each equation after the application of an advanced statistic algorithm, allowing the study of non-normal distribution regressions such as the Δ-d relations (Efron, 1979).

Present results confirms that the spectral resolution is the main parameter infkuencing the Δs measurement in Raman spectra. Also, we probed that relative peak positions can be measured with a higher accuracy using fitting algorithms. The statistical treatment of data further shows that densimeters based on Δs in Raman spectra acquired with the same spectral resolution are statistically equivalent: they calculate CO_2 densities that are comparable at the 0.95 of confidence.

[1] Kawakami et al., (2003). *Appl. Spectrosc.* **57**, 1333-1339; [2] Yamamoto and Kagi, (2006). *Eur. J. Mineral.* **20**, 529-535; [3]Efron B (1979). *Ann. Stat.* **7**, 1-26.