AUTOMATED CURVE-FITTING OF RAMAN SPECTRA BY AN ITERATIVE, RANDOMIZED APPROACH APPLIED TO CARBONACEOUS MATTER AND MINERALS. N. K. Lünsdorf and J. O. Lünsdorf, 1Department of Sedimentology & Environmental Geology, Georg-August-University Göttingen, Germany, e-mail: keno.luensdorf@geo.uni-goettingen.de, 2R&D Division Energy, OFFIS Oldenburg, Germany

This software is intended to reduce the so called operator bias during spectral curve-fitting [1] in Raman spectroscopy of carbonaceous matter (RSCM). It is designed to work with large datasets and it can be used to fit nearly any mineral Raman spectrum.

RSCM allows to estimate the maximum metamorphic temperature of a rock containing CM and is frequently used in geosciences. It is based on the progressive transformation of CM to graphite during regional or contact metamorphism [2-4]. This structural transformation is recorded in the Raman spectrum and is quantified by curve-fitting. After preprocessing (denoising, baseline extraction, etc.) a set of functions (Lorentzian, Gaussian, Voigt, etc.) is used to model the spectrum and a ratio, based on the functions parameters (center, intensity, fwhm, area), is calculated to quantify the spectrum [3-6]. However, curve-fitting is often performed manually and especially baseline extraction is prone to subjectivity which reduces the comparability of results [1]. Together with an increasing amount of measurements (hyperspectral maps, solid statistics, etc.) there is a strong need for automated spectral evaluation.

Here we present a software package which is designed to fit Raman spectra of carbonaceous material, but can also be used to fit any other Raman spectrum (Fig. 1). A model, which is the sum of a series of Lorentzian or Voigt functions, is fitted to the data by randomly changing the functions parameters. The process is iterative, as in each iteration a new baseline or signal function is added to the model and after the parameters have been modified, it is checked if the sum of squared residuals (SSR) has been reduced. The modification of function parameters is controlled by constraints, i.e. maximum and minimum intensities or widths. In this way baseline functions and signal functions can be modeled separately but still influence each other. The software continues to insert functions and to modify parameters until the SSR cannot be reduced further with the set of constraints. No preprocessing of the spectra is needed and after the fitting is complete the functions parameters can be used to form user defined parameter ratios. Because the software is based on random numbers and automated, spectra with overlapping Raman bands can be routinely evaluated multiple times to assess the ambiguity of the spectrum and the curve-fitting process (Fig. 1).

In case of RSCM two new parameter ratios were found, which correlate very well with maturity and metamorphic degree of CM; the so called Raman Area and Raman Intensity Ratio (RAR and RIR, respectively). RAR is the sum of areas of all functions divided by the area of the most intense function in the D-band. RIR is similar to RAR, but uses the intensity values instead of areas. These ratios are sensitive for the maturity range of ca. 1 – 8 % Vr and for lower greenschist facies to upper amphibolite facies conditions (Fig. 2). RAR and RIR show a distinct minimum which is marked by a break in the width-distance ratio. Thus,
Fig. 2: The correlation of the Raman Area Ratio (RAR) and the Raman Intensity Ratio (RIR). The samples are sorted by increasing degree of diagenesis and metamorphism. Representative spectra of the transformation path of amorphous CM to graphite are shown. The black lines estimate the data trend and serve as a guide for the eyes. The width-distance ratio can be used to decide on which side of the minimum RAR or RIR is located (Fig. 2). This enables the software to automatically determine if the CM spectrum indicates a high or low temperature value. To the left of the minimum, the RAR and RIR show an exponential correlation with vitrinite reflectance and to the right RAR and RIR correlate linearly with increasing degree of metamorphism. A correlation with metamorphic temperature is in progress.

This software provides a versatile tool for handling spectral data and it is able to automatically evaluate large datasets while simultaneously eliminating the subjectivity of the curve-fitting process. Because of the versatility it is likely that the software could also be used in infrared, luminescence or X-ray spectroscopy.

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