

RAMAN SPECTROSCOPY AS A MEASURE OF THERMAL MATURATION IN IRISH COAL AND SHALE SAMPLES



A. Rooney¹, J. Watkins², G. Clayton³, R. Goodhue³

¹School of Physics, Dublin Institute of Technology, Kevin Street, Dublin 8

²Department of Physics, Carleton University, Ottawa, Ontario, Canada

³Department of Geology, Trinity College, University of Dublin, Dublin 2

Corresponding author: abigail.rooney@dit.ie

INTRODUCTION

Raman spectroscopy uses the inelastic scattering of monochromatic light to chemically fingerprint a material. Recent work on the Raman spectra of coal samples has led to the derivation of thermal maturation indices which correlate to vitrinite reflectance (VR) (Liu *et al.*, 2013). This technique is mainly applicable to carbonised samples of solid organics that are thermally mature to overmature with respect to hydrocarbons.

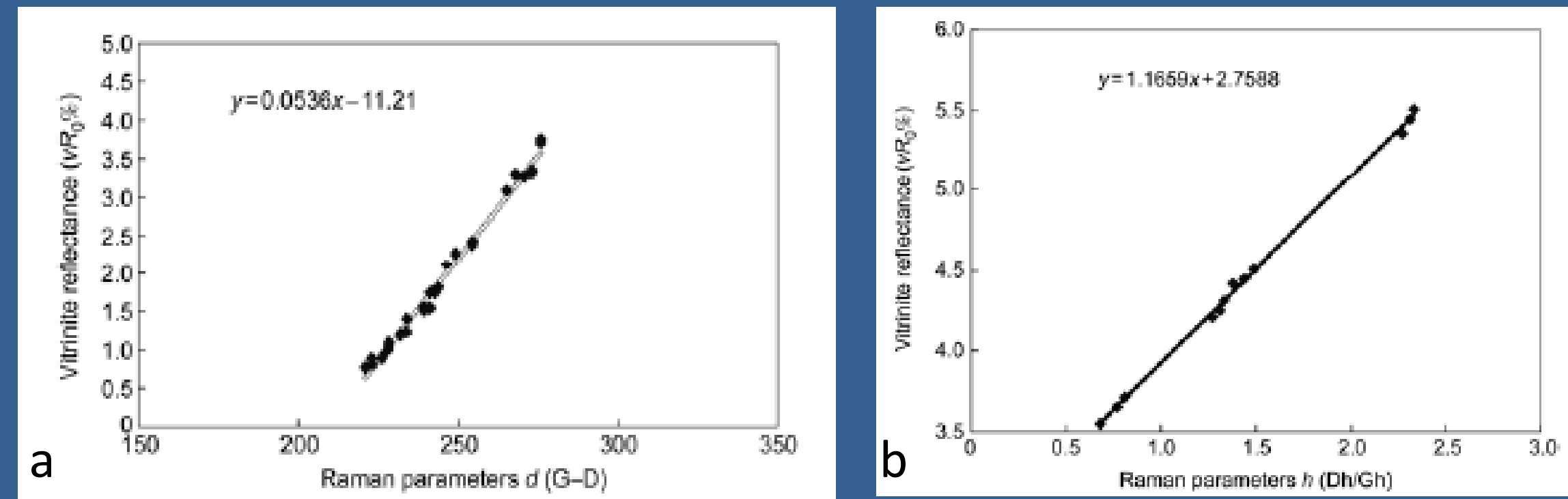


Figure 1. Raman parameters (a. interpeak distance, b. peak height ratio between the D and G peaks) shown against vitrinite reflectance values, as published by Liu *et al.* (2013).

Two indices were proposed by Liu *et al.* (2013), the first utilising the change in the interpeak distance between the “G” (C-C stretching in graphitic materials) and “D” (measure of disorder) peaks (G-D). This index was proposed to measure mature to highly mature samples. The second index utilises the change in peak height ratio (D/G) to determine the equivalent vitrinite reflectance value for overmature samples.

MATERIALS AND METHODS

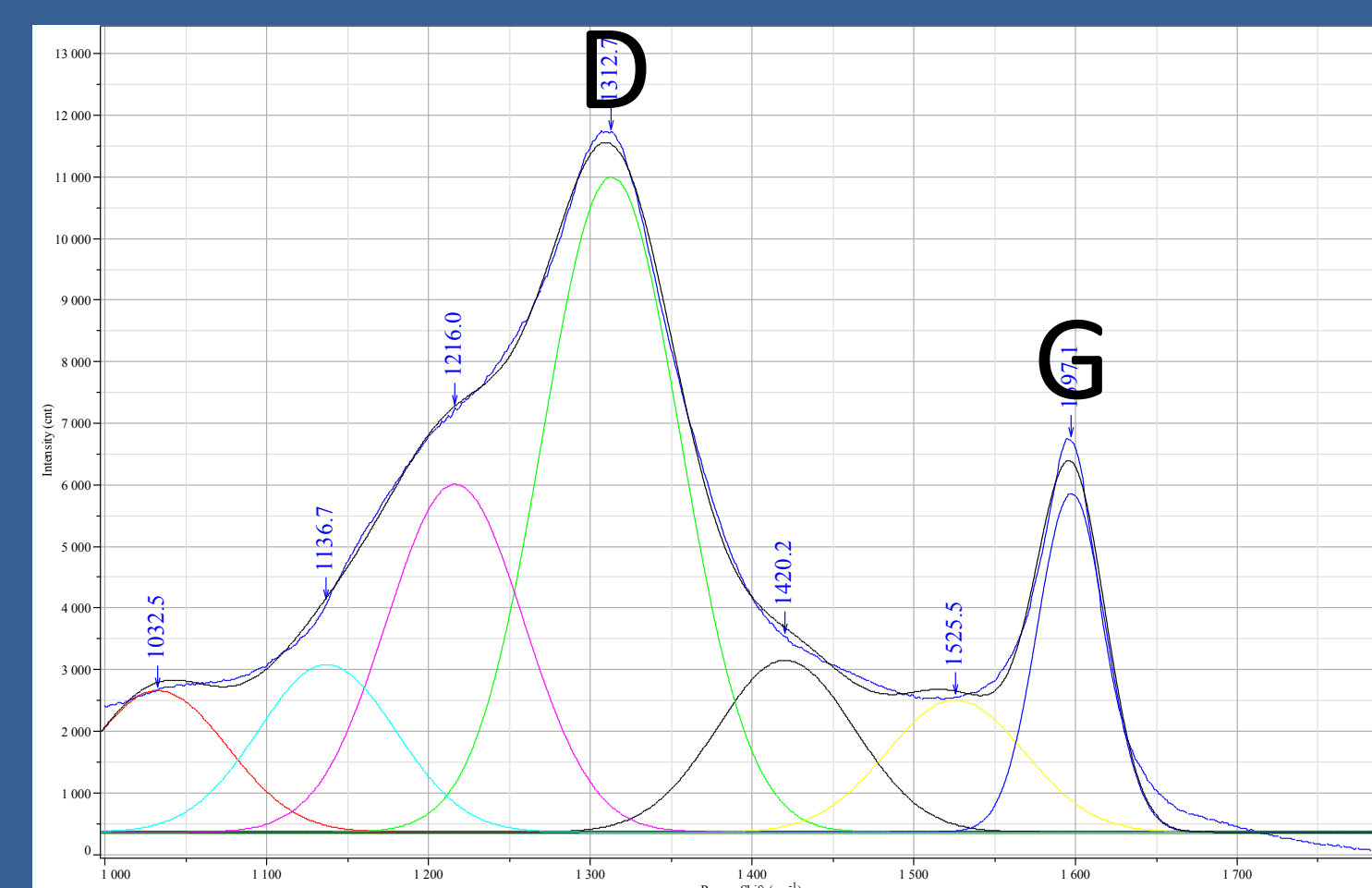
- Seven Irish coal and shale samples were analysed for this study.
- A portion of each sample was crushed, set into a vitrinite block and polished.
- Raman analyses were carried out using an Horiba Jobin Yvon LabRAM HR 800 Dual Microscope. Two laser wavelengths were chosen: 532 nm, 785 nm for comparison. Objectives ranged between x50 – x100. A 1 % or 10 % laser filter was used to reduce sample burning.
- Vitrinite reflectance values were obtained by standard methods with a Leitz Ortholux H-MPV reflectance microscope, calibrated with standards of known reflectivity.

PROBLEMS

Peak fitting

The shape of the ‘D’ peak is often irregular, and can be resolved into sub-peaks as shown below, further complicating the correlation with VR.

Figure 2. Raman spectrum of Liscannor VR block

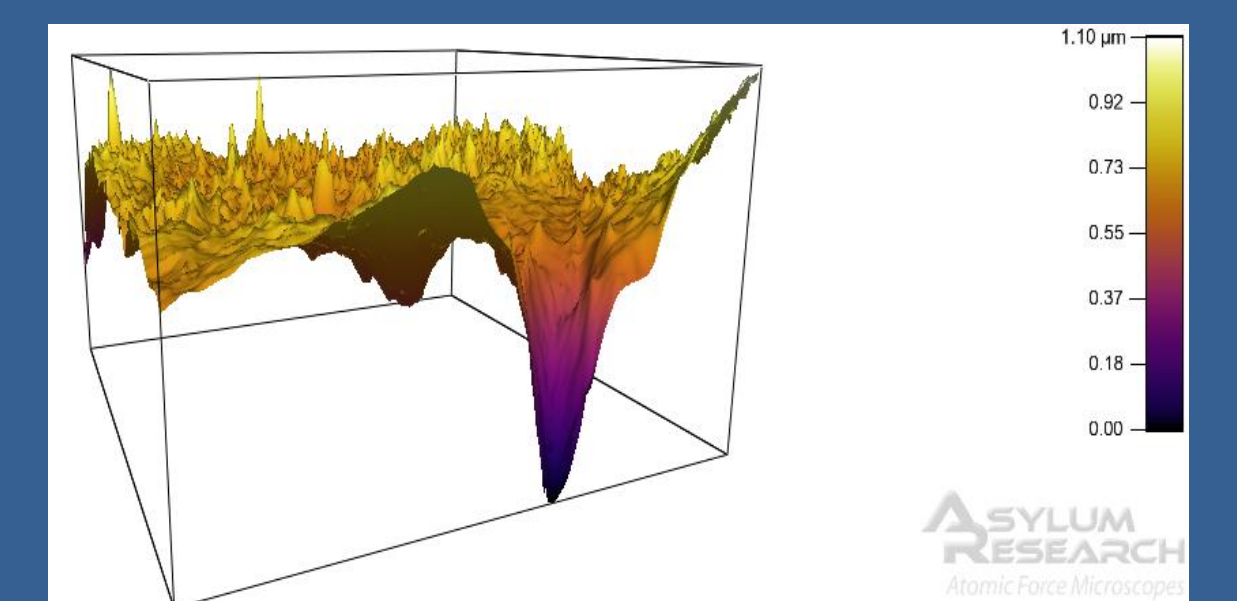


“Non-Destructive”

Raman spectroscopy is not always “non-destructive”. Burning can occur when the laser power is too high, possibly producing misleading results.



Figure 3. Reflected light microscope (x100) and atomic force microscopy images of sample burning caused by Raman laser (785 nm) set at 50 %.



RESULTS

Consistent Raman reflectance measurements (based on Liu *et al.*, 2013) were recorded between different rock orientations and preparation methods (figures 4 & 5). However, the proposed correlation by Liu *et al.* (2013) does not show similar consistency to the measured VR values for the Irish samples.

VR equivalent values using Raman spectroscopy (R_{mcR_0} %):

3.58 % 3.49 % 3.50 %

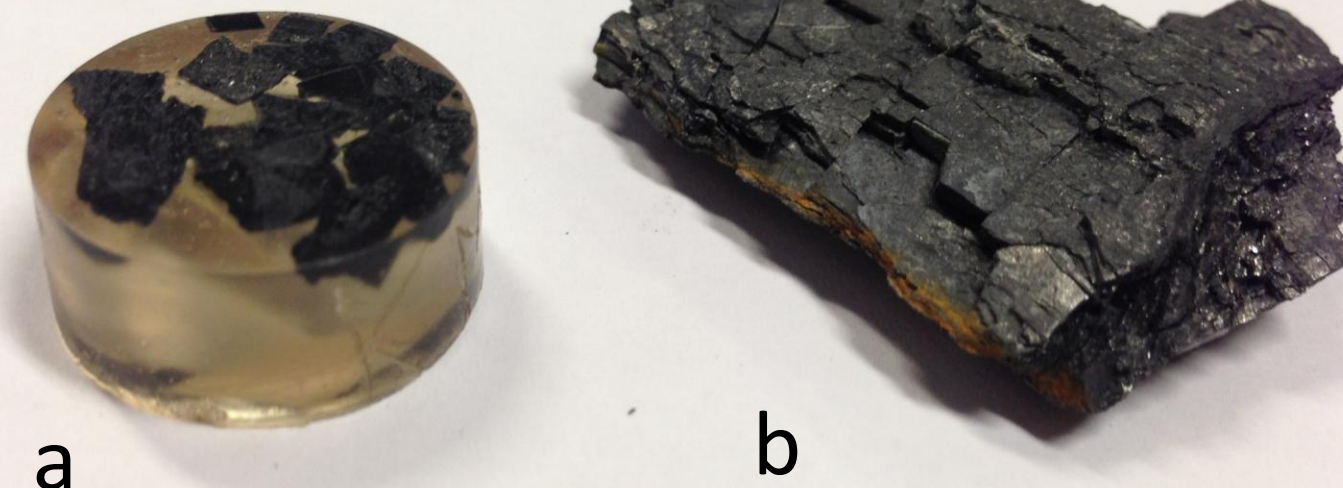


Actual VR value: 4.54 %

Figure 4. Raman reflectance measurements taken from three different orientations: a) // bedding, b) perpendicular to bedding // strike, c) perpendicular to bedding // dip

VR equivalent values using Raman spectroscopy (R_{mcR_0} %):

4.33 % 4.35 %



Actual VR value: 5.37 %

Figure 5. Raman reflectance values taken from the same sample: (a) polished VR block, (b) basic rock sample.

There is a noticeable offset between the two laser lines (figure 6), where the samples analysed on the 785 nm laser line show slightly stronger correlation to VR than the samples analysed on the 532 nm laser.

Samples of lower maturity often have high fluorescence. This leads to increased background noise in the Raman spectrum. The longer wavelength, 785 nm, also helps to reduce this problem.

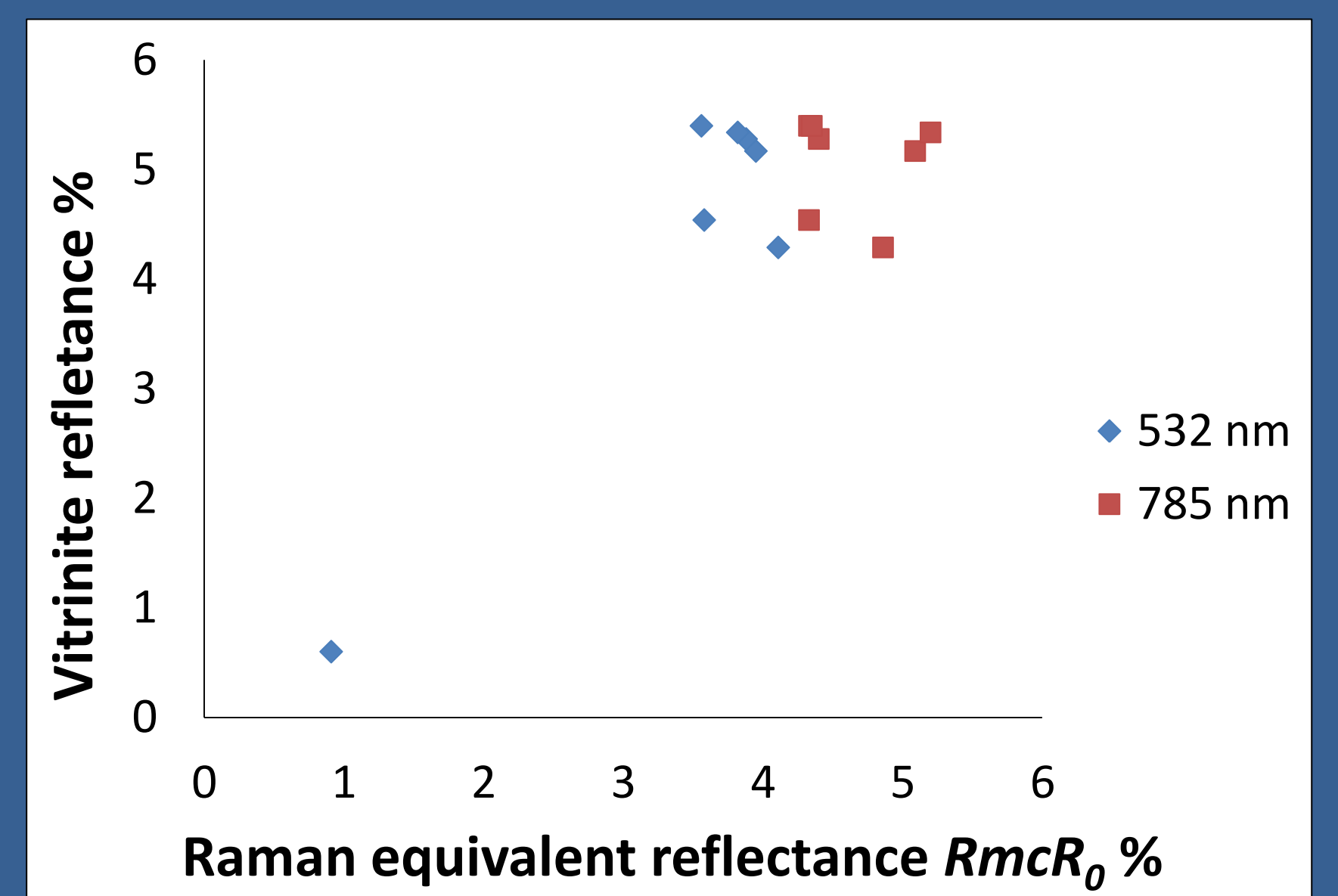


Figure 6. Raman reflectance values (Liu *et al.*, 2012) v. vitrinite reflectance values, of Irish coal and shale samples.

CONCLUSIONS

- The Raman – VR correlation proposed by Liu *et al.* (2013) does not appear to show similar consistency for the Irish samples.
- The offset between the two laser wavelengths should be taken into consideration for future correlations.
- Further work is required to improve the correlation between Raman spectroscopic measurements and vitrinite reflectance measurements.

REFERENCES & ACKNOWLEDGEMENTS

Liu D., Xiao X., Tian H., Min Y., Zhou Q., Cheng P. and Shen, J. (2013). Sample maturation calculated using Raman spectroscopic parameters for solid organics: Methodology and geological applications. *Chinese Science Bulletin*, 58(11), 1285-1298.

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