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A RaMM study of thermal maturity of dispersed organic matter in marine source rocks

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A B S T R A C T

The Raman Maturity Method (RaMM) is a non-graphical technique for thermal maturity determination based on the multi-linear regression analysis of parameters derived from carbon Raman spectra of humic macerals. It is calibrated against vitrinite reflectance with a suite of Australian mostly Permian coals. In a previous communication an equation to cover the range 0.4–1.2% equivalent vitrinite reflectance was derived. In this report we extend the range with a second equation for the range 1.0–2.5%, and validate its use by testing a series of Australian Permian and German Carboniferous coals. The special features of the technique are that it is equally applicable to vitrinite and inertinite, it corrects internally for the suppression of vitrinite reflectance effect, grains as small as 5 μm are suitable, and it does not require well depth information to be available.

The technique has been applied to two wells, Cape Range-2 and Dampier-1, from the rift margin of the North West Shelf of Australia. Both wells intersect large thicknesses of fine-grained marine Jurassic and Cretaceous sediments including the major source rock formation of the Carnarvon Basin. There are no terrestrial sediments for control. There is good agreement between RaMM and VR results for VR > 1.2% for Cape Range-2. However within the oil window in both wells RaMM results indicate the vitrinites in many of the samples have reflectance suppression to such a degree that the VR results would be misleading or useless for maturity modeling. It is likely that this problem, which is well documented for marine influenced coals, to some degree affects organic matter in marine source rocks worldwide.

1. Introduction

In Wilkins et al. (2014) the proposition was examined that carbon Raman spectra of any mixture of individual inertinite and vitrinite macerals, may be deconvoluted to provide a set of parameters that can be processed by multi-linear regression to provide equivalent vitrinite reflectance (EqVR) data. The method, called RaMM, was calibrated on a reference suite of mainly Australian Permian coals and tested on a suite of Australian Permian and Ruhr Carboniferous coals. The time required for a determination is approximately the same as vitrinite reflectance (VR), allowing the possibility that the method could be applied in a routine fashion to determine thermal maturity of dispersed organic matter (DOM) in clastic sequences, especially those that do not contain intervals of coaly strata.

Raman spectroscopy has been found to be a valuable tool for the study of DOM (Pasteris and Wopenka, 1991; Hu et al., 1993; Beyssac et al., 2002; Guedes et al., 2005; Rahl et al., 2005; Marshall et al., 2007; Kwiecinska et al., 2010; Romero-Sarmiento et al., 2014 and references therein), however most of these applications have been on low to high grade metamorphic rocks in which there tends to be a convergence in the optical properties of different macerals from what is normally observed in the zone of catagenesis (Smith and Cook, 1980). Raman studies have been reported on collotelinite, fusinite and macrinite in a rank sequence of coals (Guedes et al., 2010), and of artificially matured semifusinites and fusinites of coking coals (Morga, 2011). Two extensive recent studies (Mendonça Filho et al., 2010; Hackley et al., 2015) have commented on the difficulty of obtaining VR results of good reproducibility from marine sedimentary rocks. Samples lean in organic matter (total organic carbon <1%), and/or of higher maturity (>1.5% VR) present a particular challenge. Hackley et al. (2015) noted that the identification of indigenous vitrinite in DOM remains a major problem.

A particular advantage of the RaMM technique is that it can be applied to DOM for which the identification of vitrinite is equivocal, that is, it works to overcome the element of subjectivity resulting from the uneven level of skill, or bias, among different petrographers. Another apparent advantage of this approach is a solution to the vitrinite reflectance suppression problem, which in some cases, may seriously affect the outcome of maturation modeling. Whether RaMM achieves these aims remains to be proved.

In the present study, we apply RaMM to thermal maturity determinations on a suite of samples from two wells from the North West Shelf

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of Western Australia. The wells were chosen because they are extensively cored, avoiding the risk that results could be compromised by cavings or other contaminants. Both wells intersect large thicknesses of marine sediments, and many of the available samples either are lean in organic matter, or have a level of thermal maturity well beyond the oil window, thereby providing challenging material to test the new technique. RaMM offers a new approach for pursuing solutions to problems of thermal maturity modeling in North West Shelf basins (Swift et al., 1988; Wilkins et al., 1994; Kaiko and Tingate, 1996; He and Middleton, 2002; He et al., 2002).

2. Materials

The two wells are situated in the northern Carnarvon Basin of Western Australia (Fig. 1). The off-shore Dampier-1 well is located in the Dampier Sub-basin. Core samples, mounted in epoxy blocks in 1998 were cut back 2 mm and repolished to expose fresh grains for microscopic examination. Although samples are rather old, the fine grained matrix of the claystones and siltstones should have been effective in protecting the organic matter from oxidation (Wilkins et al., 1998). The integrity of the organic matter in carbonate samples with higher porosity from the upper levels of Dampier-1, is less certain.

The second well, on-shore Cape Range-2, is located in the Exmouth Sub-basin. At the time of sampling, not long after first received in 1976 at the then Commonwealth Scientific and Industrial Research Organization (CSIRO) Division of Mineralogy laboratory in North Ryde, blocks were cut and mounted in epoxy resin for petrographic examination. At about the same time, some of the core samples were finely crushed and the organic matter concentrated by froth flotation. The details of the treatment are not available, but as the flotations were carried out in a large coal preparation facility, the possibility of coal dust contamination has to be borne in mind. The organic matter concentrates were also preserved in epoxy blocks. All of the blocks were cut back and re-polished to expose fresh surfaces for microscopic examination. Unfortunately, limited systematic organic geochemical data are available on material from these two old wells.

The coal samples used to extend the calibrated range of RaMM were from a suite of medium and low volatile coking coals prepared and measured for VR at the BHP Research Laboratory, Newcastle, supplemented by some semi-anthracite coals from deep boreholes in the Bowen Basin, Queensland. Chemical analyses were not available for these coals. Australian Permian and Ruhr Carboniferous validation coals were obtained from the University of Newcastle, Australia, courtesy of Prof. Claus Diessel. All coal samples were measured for mean random telovitrinite reflectance following Australian Standards 2486–1989, 1989 except the Ruhr Basin coals, on which measurements were made in water immersion medium and subsequently transformed to equivalent reflectance in oil (with $r^2 = 0.992$). Details are given in Diessel and Wolff-Fischer (1987).

3. Methods

3.1. RaMM calibration and testing

The calibration of RaMM over the oil window (VR = 0.4–1.2%) has been fully described in Wilkins et al. (2014) and those wishing to employ the method should refer to that paper. In the present report, we extend the calibration to VR = 2.5% in recognition of current interest

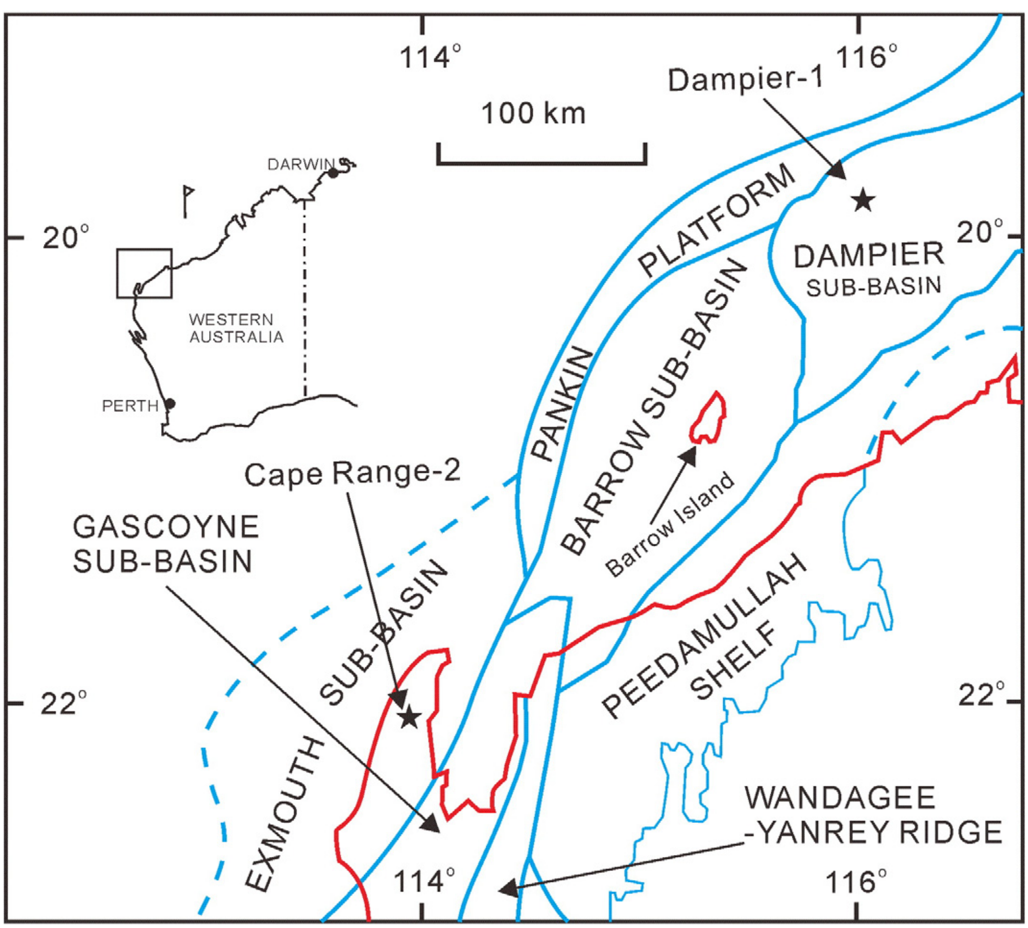

Fig. 1. Map showing structural units of the northern Carnarvon Basin, Western Australia and the location of the on-shore Cape Range-2 well in the Exmouth Sub-basin, and the off-shore well Dampier-1 in the Dampier Sub-basin. Boundaries to structural units after Hocking (1988).