

## MOLECULAR CHARACTERIZATION OF DOM EXTRACTED FROM COALS IDENTIFIED BY FT-ICR MS

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Water soluble organic compounds released from coals over both geological and human time scales are a complex molecular mixture, which can reflect the variation in coal organic matter source, the effect of coalification as well as post-depositional oxidation during weathering or industrial processing. It has been previously proposed that the loss of oxygenated compounds from coals can feed the deep biosphere (Vu et al., 2013).

Here we present new insights into oxygen containing compounds that are extractable in aqueous solution from five New Zealand coals. The coal samples cover a time period from Eocene to middle Pleistocene. Three of them were taken from different depth of DEBITS-1 well in Waikato Basin. Samples C1 and C2 above the unconformity of the well were two lignites with  $R_o = 0.29\%$ . C3 below the unconformity of the well was a sub-bituminous coal with  $R_o = 0.39\%$ . Other two samples C4 and C5 are two outcrops taken from Waikato Basin and West Coast Basin with  $R_o$  value of  $0.45\%$  and  $0.52\%$ , respectively (Zhu et al., 2017). From the n-alkanes distribution and the predominant compound within them of the solvent extracts, it can be speculated that the two lignites are derived from a deciduous flora while the three bituminous coals might originate from grass and moss vegetation.

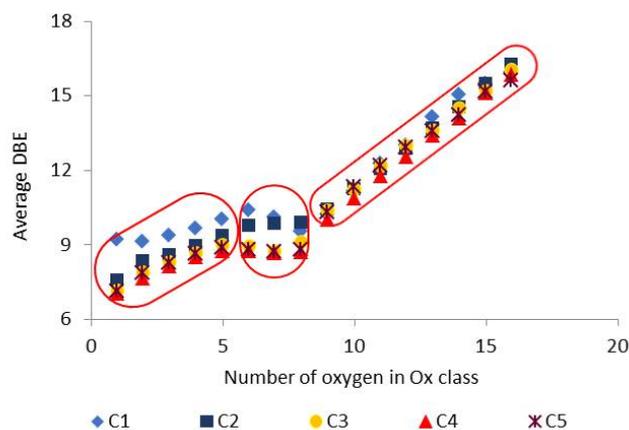
High resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) combined with electrospray ionization (ESI) run in negative ion mode was applied to solid phase extracts (SPE) of the water extracts of the coal samples for dissolved organic matter (DOM) characterization. DOM composition were described in terms of elemental class, compound class and DBE distribution as well as the variation of average DBE and average carbon number to elucidate differences in molecular composition of DOM.

The oxygen containing compound class ( $O_x$ ) dominates the coal extracts and counts for more than 77.8% of total monoisotopic ion abundance (TMIA) followed by  $O_xN_y$  classes with 6.7% to 12.8% TMIA in the DOM. The two lignite extracts show quite similar distribution of oxygen classes. The intensities of  $O_1$  to  $O_8$  classes increase with increasing number of oxygen atoms and then decrease for higher oxygen numbers. The intensities of oxygen classes of the three bituminous coal extracts first increase up to  $O_8$  and then strongly decrease in  $O_9$ - $O_{11}$  classes.

A monomodal distribution of double bond equivalents (DBE) can be observed in all the oxygen classes for the five coal extracts. In the  $O_1$ - $O_8$  classes, compounds with 7 to 9 DBEs are the most abundant species, while compounds with 9 to 16 DBEs have maximum intensity in the  $O_9$ - $O_{16}$  classes. The DBE distributions are nearly similar for the lignite extracts on the one hand and the bituminous coal extracts on the other hand. A broader range in DBE distribution by extension to higher DBE values can be observed for the DOM of the two lignite extracts.

The overall DBE distribution of a selected compound class can be described by its intensity-weighted average DBE. The changes of average DBE in each oxygen class with the number of oxygen atoms can be used to assess the contribution of oxygen atoms to average DBE in

an average molecule (Fig. 1). The slight increase of average DBE with increasing number of oxygen atoms in O<sub>1</sub>-O<sub>5</sub> classes indicate that most of the oxygen atoms are bound with  $\sigma$ -bonds in hydroxyl groups. In O<sub>6</sub>-O<sub>8</sub> classes, the constant value of average DBE is influenced by four prominent peaks with extremely high intensities. In O<sub>9</sub>-O<sub>16</sub> classes, the average DBE shows a linear increase with increasing number of oxygen atoms with a high slope, which indicate that more oxygen atoms are bound with  $\pi$ -bonds in carboxyl or carbonyl groups.



**Figure 1** Average DBE of each O<sub>1</sub>-O<sub>16</sub> class is plotted against the respective oxygen number. The plots can be divided into three groups, O<sub>1</sub>-O<sub>5</sub>, O<sub>6</sub>-O<sub>8</sub> and O<sub>9</sub>-O<sub>16</sub> as indicated by the elliptical frames.

For O<sub>1</sub>-O<sub>5</sub> classes, the average molecular core structure can be speculated by combining the variation of average DBE and average carbon number of the oxygen classes. The average molecular core structures of the three bituminous coals appear to be quite similar and different from the lignite extracts. The possible average molecular core structure of the five samples might consist of two benzene rings. In O<sub>9</sub>-O<sub>16</sub> classes, it can be calculated that more carbon atoms and less oxygen atoms are required to form a double bond for the lignite extracts than for the bituminous coals.

This study demonstrates that DBE, average DBE and average carbon number distribution obtained by high resolution mass spectrometry can be used to elucidate and compare the oxygen containing molecular structures of DOM in coal extracts and probably other water samples. For the coal extracts it was shown that the organofacies of the coals has significant influence on the DOM composition.

## References:

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