SYSTEMATIC CALIBRATION OF DIAMONDOID INDICES AS MATURITY INDICATORS IN PROTEROZOIC ROCKS

A. Leider[1], L. van Maldegem[1,2], B. Nettersheim[1,2], M. Neumann[1,3], J. Meixnerova[4], Y. Hoshino[5], S. Naeher[6], A. Poshibaeva[7], G. Luo[8] and C. Hallmann[1,2]

[1]Max Planck Institute for Biogeochemistry, Jena, Germany, [2]MARUM Center for Marine Environmental Sciences, Bremen, Germany, [3]University of Bremen, Bremen, Germany, [4]University of Washington, Seattle, USA, [5]Georgia Institute of Technology, Atlanta, USA, [6]GNS Science, Lower Hutt, New Zealand, [7]Gubkin State University of Oil and Gas, Moscow, Russia, [8]China University of Geosciences, Wuhan, China

One inevitable challenge for the reliable detection and interpretation of early biological traces in the Precambrian record using lipid biomarkers is to corroborate their unambiguously indigenous origin within the host rock (e.g. Brocks, 2011). Support can derive from investigating consistencies between biomarker occurrence/absence and the thermal history that the rock experienced (e.g. French et al., 2015). But such an assessment may be complicated past the stereochemical equilibrium point of polycyclic terpenoids or when diagnostic compounds are progressively destroyed by cracking at high levels of thermal maturation (e.g. Peters, 1999). In comparison to most other hydrocarbons, diamondoids are highly stable and resistant to both thermal and biological destruction. Diamondoid-based parameters have hence been applied to evaluate the thermal evolution, the extent of cracking, as well as mixing of oils and condensates (e.g. Dahl et al., 1999; Chen et al., 1996), source rock facies (e.g. Wei et al., 2006; Schulz et al., 2001) and the degree of biodegradation (Grice et al., 2000). Since they are often present in appreciable abundances in rocks of upper oil window, or higher maturity, diamondoids ideally lend themselves as a rapid screening tool: the 'quick & dirty' workup of small sample abundances may reveal the thermal maturity and bitumen abundance in a rock, thereby hinting towards its suitability for more comprehensive and clean biomarker studies (NB: many thermally mature old rocks do not yield a sufficient S2 peak during Rock-Eval pyrolysis to use the T_{max} value for the same purpose). But despite the consensus that thermal maturity controls diamondoid ratios at some extend, additional influencing factors exist (e.g. mineralogy) hindering the development of a universal calibration that reliably links them to other, more common thermal maturity schemes such as $\%R_c$ or the stability field of polycyclic terpenoids (e.g. Li et al., 2000; Wei et al., 2006).

We have investigated the abundance of diamondoids and derived indices based on a set of ca. 80 Proterozoic rock samples (ca. 550 to 1000 Ma) from drill cores and outcrops, covering diverse lithologies and depositional settings from eight sedimentary basins with a wide geographical distribution.
Preliminary results show a range of maturity estimates based on methyladamantane and –diamantane indices (MAI, MDI) equivalent to estimated R_c values of 1.1 to >1.9% and which only partially co-vary with abundances of biomarkers. To shed more light on this relationship, results are compared to additional maturity parameters based on Rock-Eval analysis, methylphenanthrene ratios and aromatic steroid based parameters. We will discuss deviations from linear calibrations in terms of age, lithology, depositional facies, biodegradation and evaporation and attempt to provide a correctable universal calibration of diamondoid hydrocarbon abundances and parameters, allowing a reliable estimate of thermal maturity and biomarker preservability on the basis of rapidly analysable diamondoids. This study will hopefully shed more light on some accounts of 'suspicious' biomarker absence in

rocks within a seemingly suitable window of thermal maturation and provide an improved tool for fast determination of bitumen thermal maturity.

Brocks, J.J., 2011. Millimeter-scale concentration gradients of hydrocarbons in Archean shales: Live-oil escape or fingerprint of contamination? Geochimica et Cosmochimica Acta 75, 3196-3213.
Chen, J., Fu, J., Sheng, G., Liu, D., Zhang, J., 1996. Diamondoid hydrocarbon ratios: novel maturity indices for highly mature crude oils. Organic Geochemistry 25, 179-190.
Dahl, J.E., Moldowan, J.M., Peters, K.E., Claypool, G.E., Rooney, M.A., Michael, G.E., Mello, M.R., Kohnen, M.L., 1999. Diamondoid hydrocarbons as indicators of natural oil cracking. Nature 399, 54-57.
French, K.L., Hallmann, C., Hope, J.M., Schoon, P.L., Zumberge, J.A., Hoshino, Y., Peters, C.A., George, S.C., Love, G.D., Brocks, J.J., Buick, R., Summons, R.E., 2015. Reappraisal of hydrocarbon biomarkers in Archean rocks. Proceedings of the National Academy of Sciences 112, 5915-5920.
Grice, K., Alexander, R., Kagi, R.I., 2000. Diamondoid hydrocarbon ratios as indicators of biodegradation in Australian crude oils. Organic Geochemistry 31, 67-73.
Li., J., Philp, P., Mingzhong, C., 2000. Methyl diamantane index (MDI) as a maturity parameter for Lower Palaeozoic carbonate rocks at high maturity and overmaturity. Organic Geochemistry 31, 267-272.
Peters, K., 1999. Biomarker: Assessment of thermal maturity, In: Marshall, C.P., Fairbridge, R.W. (Eds.), Encyclopedia of Geochemistry. Springer Netherlands, pp. 36-39.
Schulz, L.K., Wilhelms, A., Rein, E., Steen, A.S., 2001. Application of diamondoids to distinguish source rock facies. Organic Geochemistry 32, 365-375.
Wei, Z., Michael Moldowan, J., Dahl, J., Goldstein, T.P., Jarvie, D.M., 2006. The catalytic effects of minerals on the formation of diamondoids from kerogen macromolecules. Organic Geochemistry 37, 1421-1436.