

Origin and preservation of organic matter in a Pliocene twin-crater

A. Brukner-Wein

Geological Institute of Hungary, Budapest Stefánia 14, H-1143 Hungary

Cs. Sajgó

Laboratory for Geochemical Research, Hungarian Academy of Science, Budapest Budaörsi út 45 H-1112, Hungary

M. Hetényi

Institute of Mineralogy Geochemistry and Petrography, József Attila University, Szeged POB 651 H-6701, Hungary

During the Pliocene as a result of the final basalt volcanism (3–5 millions yrs ago) several maar-type oil shales were deposited in small volcanic craters in Hungary. The depositional environment (current free warm water, abundant nutrient supply) was favourable for accumulation of organic matter. Previous study revealed that the organic matter consists of mainly well preserved fossil colonies of *Botryococcus braunii* algae and the selective preservation of the insoluble macromolecules of outer walls of *Botryococcus braunii* were the main process in the formation of the organic matter (Derenne *et al.* 1997).

Our study was focused on the properties of the organic matter sedimented in a twin-crater including the type and preservation of organic matter and the depositional environment. Though the twin-crater formed the same time (the distance between two crater is 1.5 km) and the organic rich layers deposited on the same basalt tuffit base, the thickness of these layers significantly differ (Várkesző = Vkt → 30 m, Egyházaskesző = Ekt → 6.5 m). The lithology of both sequences studied is uniform. It consists of clayey alginite. Both organic rich sequences can be divided into two sections on the basis of the quantity of soluble organic matter and the Rock-Eval pyrolysis experiment. (Table 1).

This phenomenon can be explained not only the variation of the organic matter input during sedimentation but the variance of depositional environment (redox conditions, sedimentation rate, biological activities).

The type of organic matter is II. according to the Rock-Eval data. Previous simulated thermal maturation study on a Várkesző kerogen showed that the kerogen derived from *Botryococcus braunii* algae and higher plant debris (Hetényi, 1983.). The principal source of the organic matter is the

Botryococcus braunii microalgae but the terrestrial contribution is significant in both crater. The contribution of the higher terrestrial input is supported by the gas chromatographic data of aliphatic fractions. The carbon preference index (CPI) calculated over the n-C₂₂ and n-C₃₂ range shows the dominance of higher n-alkane homologues (CPI = 5–11). The presence of α -phytylcladane peaks derived from the Coniferopsida class of Gymnosperms also corroborates the terrestrial input. On the basis of pyrolysis-gas chromatographic traces, the ratios of aliphatic moieties to aromatic ones are higher in lower sections in both craters and in Várkesző kerogens those are higher, respectively. The relative quantity of n-alk-ene/n-alkane doublets on pyrograms is different in two craters, the C₁₅₊ fraction is considerable more in Vkt samples.

The elemental compositions of kerogens isolated from organic matter in both craters confirm the prevalence of the algal material (H/C = 1.2–1.6). There are some differences between the average data of the H/C and N/C ratios not only between the two craters but within the sections studied in both craters as well (Vkt: H/C → 1.44 and 1.54, N/C → 0.024 and 0.021; Ekt: H/C → 1.31 and 1.43, N/C → 0.019 and 0.022 respectively). There are striking differences in sulphur contents of kerogens between two occurrences. In the case of Vkt the sulphur contents can be attributed to the organic sulphur compounds in kerogens (S/C = 0.002–0.008). In Ekt crater the high sulphur contents of kerogens indicate the presence of considerable amount of pyrite beside the organic sulphur (S/C = 0.054–0.085). The corrected main organic S/C ratio (S/C = 0.027) is higher in this crater indicating different sulphur supply in two craters. The methylthiophene/toluene ratios display contrary trend in twin craters. The ratio represents the relative abundance of organic sulphur.

TABLE 1. Organic geochemical data of pyrolysis experiments and organic geochemical parameters of soluble organic matters

Location and depth (m)	TOC %	T _{max} °C	HI	HC _{pot}	Bitumen %	β %	ΣHC %	ΣNSO %	CPI	o/x	mt/t
VKT											
43-47	7.4	435	475	36.5	0.44	7.4	11.8	88.2	10.8	1.07	0.12
48-71	10.8	422	546	69.0	1.87	19.2	7.2	92.7	9.3	1.75	0.28
Ekt											
34-38	3.4	429	288	11.0	0.18	2.1	10.8	89.2	5.2	0.28	0.26
38-41	10.5	428	494	56.1	0.88	8.3	7.4	92.6	8.8	1.06	0.18

TOC: total organic carbon; HI: mgHC/gTOC; HC_{pot}: kgHC/t rock; bitumen: soluble organic matter; β: bitumen/TOC100; ΣHC = HC_{saturated} + HC_{aromatic}; ΣNSO = resin+asphaltene; CPI: carbon preference index in n-C₂₂ and n-C₃₂ range; o/x: n-oct-1-ene/(m+p)-xylene; mt/t: methylthiophene/toulene

Summarising the above the Type II. kerogens in twin-crater are the products of diverse processes: i) Várkesző kerogens are the mixtures of Type I. and Type III. ones and they preserved relatively well; ii) Egyházaskesző kerogens must have been suffered : biological degradation (relative poverty of C₁₅₊ alkyl moieties in pyrolysis yields) and chemical oxidation during pyrite formation.

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