

VARIATION OF ROCK-EVAL DATA AS A FUNCTION OF HEATING RATE

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INTRODUCTION

Rock-Eval (RE) pyrolysis has been widely used by petroleum industry and by geosciences for decades. It provides information about the amount, type and maturity of the organic matter and the petroleum potential of rocks. Although this technique was originally designed for studying the mature organic matter from source rocks, recent work showed that it could be applied also for evaluating the amount and properties of immature organic matter from Recent sediments (Sanei et al. 2005) and soils (Di Giovanni et al. 1998). In addition to the basic information that is given by the bulk RE data, mathematical deconvolution of the pyrograms allows one to follow the evolution of the humification process. It can also be used to quantify the relative contribution of the thermally labile and resistant biomolecules and that of humic substances in organic matter in soils (Disnar et al. 2003, Hetényi et al. 2005) and in wetlands (Hetényi et al. 2006).

Some modification of the standard RE method, used for mature kerogen, is needed when it is applied to immature organic matter present in soil and recent sediments. Limitations of the method include the influence of pollution by drilling fluid and natural impregnation of hydrocarbons, as well as the mineral matrix effect (e.g. Larter 1984, Espitalié et al. 1986, Wilhelms et al., Dembicki 1992, Hetényi 1995). In contrast, the dependence of the bulk data on the analytical conditions has been less investigated (Espitalié et al. 1985). Probably this is because during the last three decades RE was mainly used as a standard method in petroleum exploration and the measurements were performed under standard analytical conditions practically in all laboratories. The publication concerning the analytical conditions highlighted, first of all, the importance of the amount and preparation of sample (Espitalié et al. 1985). The role of the heating rate, however, has been only marginally examined (Bordenave et al. 1993).

In a previous work we have studied a wide range of the experimental RE-conditions to select the most suitable ones for estimating the proportion of the components with different thermal stability in immature organic matter both by mathematical and experimental methods (Hetényi et al. 2005). These results demonstrated that the heating rate influenced not only the T_{max} value, as it has already been reported (Bordenave et al. 1993), but also the other RE data.

Here we present RE data measured at two different heating rates in series of experiments performed on (i)

immature organic matter isolated from oil shale (ii) peaty gley soil organic matter (iii) in the presence and absence of minerals (calcite or montmorillonite). Furthermore, composition of the organic matter, namely the relative contribution of the labile and resistant biopolymers and geopolymers, was assessed by mathematical deconvolution of RE pyrograms.

EXPERIMENTS

RE pyrolyses were performed on kerogen isolated from Pula oil shale (West Hungary) and on refractory, non-hydrolysable, macromolecular organic matter (ROM) isolated from a slightly acid peaty gley soil from East Hungary. Isolation protocols and geochemical features of whole samples have been previously reported (Hetényi et al. 1995; Hetényi et al. 2006). Bulk RE data were measured and pyrograms were recorded by a Delsi Oil Show Analyzer using standard heating conditions: heating at 180 °C for 4 min, followed by programmed pyrolysis at 25 °C/min (or at 5 °C/min), to 600 °C under He flow and oxidation at 600 °C under an oxygen flow. Relative contributions of major classes of organic constituents (referred to as F1, F2, F3, F4) were calculated by mathematical deconvolution of S2 peaks (Sebag et al. 2005). Biological constituents are composed of a small amount of thermally labile biomacromolecules (F1) such as fresh plant material and rather resistant biopolymers (F2) such as lignin and cellulose. F3 represents the immature geomacromolecules (humic substances in sensu lato) and F4 represents refractory organic fractions such as mature geomacromolecules, naturally stable biological components, weathered fossil OM and black carbon.

RESULTS AND DISCUSSION

Bulk Rock-Eval data

Bulk RE data measured on kerogen isolated from oil shale and on ROM isolated from a peaty gley soil, in the absence and presence of minerals, are summarized in Table 1.

The temperature of the peak of hydrocarbon production varied with the heating rate for both of the studied immature organic matter. Independently of the origin and maturity of OM, higher T_{max} values were recorded at rapid heating. Using a heating rate of 25 °C/min, T_{max} values were found to be around 430 and 410 °C for kerogen and ROM, respectively. Using a heating rate of 5 °C/min, however, T_{max} values were detected at 410 and 386 °C (Table 1). This observation is consistent with the somewhat higher differences (435 and 390 °C) obtained

Table 1. Rock-Eval data measured at different heating rates.

Sample	Heating rate	S1	S2	Tmax	HI	TOC	TOCre	TOCi
	°C/min	mg/grock	mg/grock	°C	mg/gTOC	%	%	%
K	25	1.20	307.20	429	873	35.16	25.60	9.56
K+calc	25	1.02	159.20	430	908	17.53	13.30	4.23
K+mont	25	0.27	170.80	429	1020	16.74	14.20	2.54
K	5	1.50	474.80	398	1105	42.94	39.53	3.41
K+calc	5	0.90	238.40	401	1000	23.83	19.87	3.96
K+mont	5	0.15	235.80	402	989	23.84	19.58	4.26
ROM	25	0.55	75.25	410	147	51.13	6.29	44.84
ROM+calc	25	0.42	37.75	411	146	25.73	3.16	22.57
ROM+mont	25	0.25	33.65	410	169	19.85	2.81	17.04
ROM	5	0.35	84.75	386	542	15.63	7.06	8.57
ROM+calc	5	0.20	40.82	386	634	6.43	3.40	3.03
ROM+mont	5	0.22	37.65	384	155	24.15	3.14	21.01

K: kerogen isolated from Pula oil shale, ROM: organic matter isolated from a marsh soil, calc: calcite, mont: montmorillonite (Wyoming), TOCre: reactive carbon, TOCi: inert carbon

by Bordenave et al. (1993) for rocks containing OM the thermal maturity of which corresponded to the oil window. It is noted that the presence of minerals did not modify the values of this maturity parameter (Table 1).

Contrary to the temperature of the highest hydrocarbon production (Tmax), the influence of heating rate on the amount of hydrocarbonaceous compounds formed during pyrolysis appeared to change with the nature of the source biomass. In agreement with S2 values measured on recent lacustrine sediments (Sanei et al. 2005), the present results suggested that rapid thermal alteration (25 °C/min) is insufficient for complete destruction of liptinite-rich immature well-preserved type I kerogen in oil shale deposited in a small maar-type lake. About two-thirds of pyrolysis products were monitored at 25 °C/min heating rate comparing with the results obtained at 5 °C/min heating rate. The necessity of a longer thermal residence time or slower heating rate for complete destruction of the immature liptinitic macerals has been corroborated by organic petrography performed on a recent lacustrine sediment (Sanei et al. 2005). Their experiments demonstrated the presence of fluorescing liptinites after release of S2-compounds. These findings were due to the fact that RE method was designed for rock samples that had

previously undergone natural thermal diagenetic changes. The increase of the heating rate, however, reduced only with 11 % of the amount of hydrocarbons formed from immature plant-derived OM occurring in the studied peaty gley soil (Table 1). Consequently, considering the measurement reproducibility, which is ± 10 % for S1 and S2 peaks, the minor difference (11 %) between the S1+S2 values measured at the two different heating rates allows one to use the

rapid heating rate to evaluate the hydrocarbon potential of immature plant-derived OM.

The present experiments revealed that the yield of OM cracking (S2 value) was not modified essentially by the presence of calcite and only a little by the presence of montmorillonite. (It is noted that for the interpretation of the RE data, summarized in Table 1, it is important to take into consideration that mixtures of OM and minerals contained only half of the OM

Table 2. Proportion of biopolymers and geopolymers.

Sample	Heating rate	F1	F2	F3	F4	R
	°C/min	%	%	%	%	
K	25	2.2	43.5	36.2	18.1	0.05
K+calc	25	2.0	40.1	38.5	19.4	0.05
K+mont	25	1.6	39.5	40.6	18.3	0.04
K	5	1.5	35.0	42.6	20.9	0.04
K+calc	5	3.1	32.8	40.5	23.6	0.09
K+mont	5	3.0	34.3	42.3	20.4	0.09
ROM	25	16.7	28.8	44.5	10.0	0.58
ROM+calc	25	21.3	30.9	38.5	9.3	0.69
ROM+mont	25	10.6	30.5	49.6	9.3	0.35
ROM	5	21.6	37.7	32.1	8.6	0.57
ROM+calc	5	22.3	37.4	28.4	12.0	0.60
ROM+mont	5	17.8	40.5	32.2	9.6	0.44

F1: labile bio-macromolecules, F2: resistant bio-macromolecules, F3: immature geo-macromolecules, F4: refractory organic fraction, R = F1/F2

compared with kerogen and ROM samples in the absence of minerals).

Our experiments provided evidence that heating rate controlled TOC values and the effect strikingly depended on the nature of the source biomass. The differences between TOC values monitored at the two different heating rates were 18 % for kerogen and 69 % for ROM. Furthermore, while the lower heating rate resulted in higher TOC values for kerogen, it resulted in an essential drop in TOC content measured for ROM. TOC content recorded by Rock-Eval pyrolysis is defined as the sum of pyrolysed organic carbon content and organic residue content. Pyrolysed organic carbon, representing the part of OM which generates hydrocarbons, is calculated by Rock-Eval micro-processor from the sum of S1 and S2 and it is termed as reactive organic carbon (TOC_{re}). Consequently, differences as a function of heating rate observed for TOC_{re} are determined by differences occurring in the amount of pyrolysis products. The proportions of reactive TOC measured at rapid heating rate (73 and 12 %) correspond to the widely accepted transformation ratios of kerogen type I and III. Pyrolysis of immature organic matter has shown that 70-80 % of type I kerogen and only 10-25 % of type III are transformed into hydrocarbons (e. g. Tissot and Welte 1984, Bordenave et al. 1993).

In contrast with the RE data detected during pyrolysis, the sample residence time during the oxidation phase exerted a considerable influence on the measured organic carbon content of the inert kerogen (TOC_i in Table 1) which produces no hydrocarbons. The bigger portion of the carbon dioxide formed from the inert carbon appeared to be lost during the long residence time in the oxidation module. That is the sample is processed in the oxidation module while the next one is processed in the pyrolysis module. Furthermore, the presence of minerals has also modified the measured values of inert carbon. The latter effect is also especially conspicuous in the case of ROM.

The results detailed above display the importance of the heating rate applied during RE pyrolysis and suggest to perform these measurements using the standard heating rate (25 °C/min).

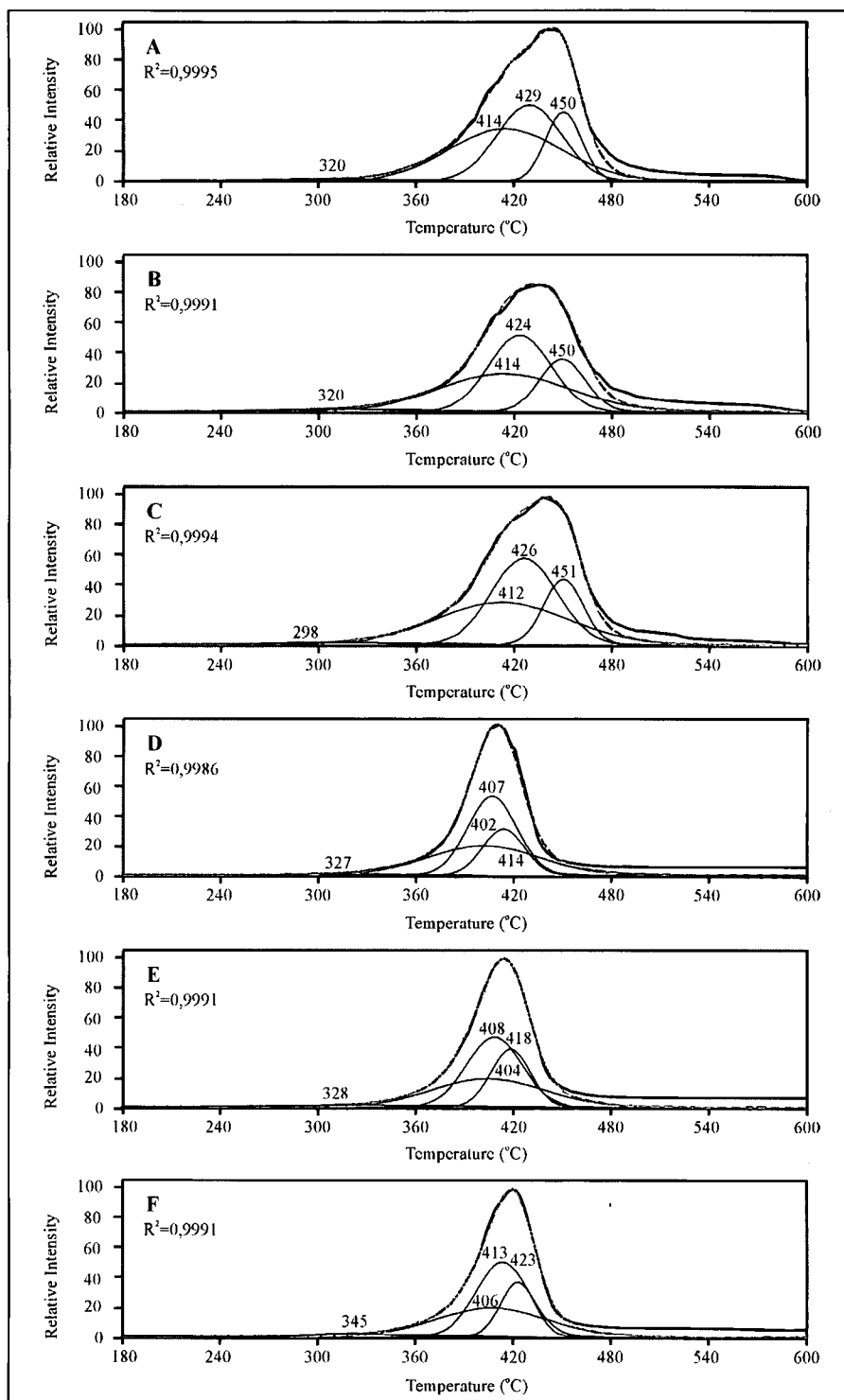


Fig. 1. Mathematical deconvolution of pyrograms monitored on (A) ROM in the absence of minerals and a mixture (1:1) of (B) ROM and calcite, (C) ROM and montmorillonite at 25 °C/min heating rate, as well as on (D) ROM in the absence of minerals and a mixture (1:1) of (E) ROM and calcite, (F) ROM and montmorillonite at 5 °C/min heating rate. Refractory, non-hydrolysable organic matter (ROM) was isolated from a slightly acid peaty gley soil from East Hungary.

Organic matter composition

The contribution of bio-macromolecules (the sum of F1 and F2 in Table 2, determined at heating rate of 25 °C/min), exceeding 40 % both in

kerogen (45.7 %) and ROM (45.5 %), revealed organic matter corresponding to the diagenesis stage. Nevertheless, strikingly different ratios of the labile and resistant biological constituents

(R-values in Table 2) reveal very immature OM in ROM and OM at the end of the diagenesis stage in the studied kerogen. These findings are in agreement with organic maturity indicated by Tmax values (Table 1), which reflect the early and the late diagenesis for ROM and for kerogen, respectively.

The twice higher proportion of the refractory organic matter constituted the fraction of geomacromolecules (F3+F4 in Table 2) in the ROM (about 4/1) compared with kerogen (about 2/1). The highly refractory ROM fraction contained a relatively high abundance of black carbon (BC) as it was displayed by mathematical deconvolution of its RE pyrogram (Fig. 1) and as it had previously been evidenced both by isolation of BC and by its electron microscopy observation (Hetényi et al. 2006). BC is a collective term for residues of incomplete combustion of organic materials and it exhibits a high resistance to diagenetic degradation (Schmidt et al. 2001, Poirier et al. 2001). Notwithstanding that this carbon form is widely distributed over the entire surface of the earth and play a major role as a sink in the global C cycle via burial in marine sediments (Vandenbroucke and Largeau 2007), there is no standard, generally accepted technique to identify and quantify BC and the results are in poor agreement among the alternative protocols (Schmidt et al. 2001). However, recent publications have shown that high Tmax values (higher than 460 °C) might be caused by the presence of BC. The good correlation determined between the yield of isolation and the abundance of BC calculated by the integration the pyrogram revealed that Rock-Eval pyrolysis could be applied for the estimation of BC contribution (Hetényi et al. 2006). The peaks with Tmax values between 458 °C and 515 °C (Fig. 1) suggested the presence of BC in the studied ROM sample. Mathematical deconvolution of pyrograms containing peaks with Tmax values lower than 460 °C (Fig. 2) displayed that there was no BC contribution to the type I kerogen.

Although the heating rate did not influence the S2 value essentially (Table 1), it exerted a considerable influence on the organic composition

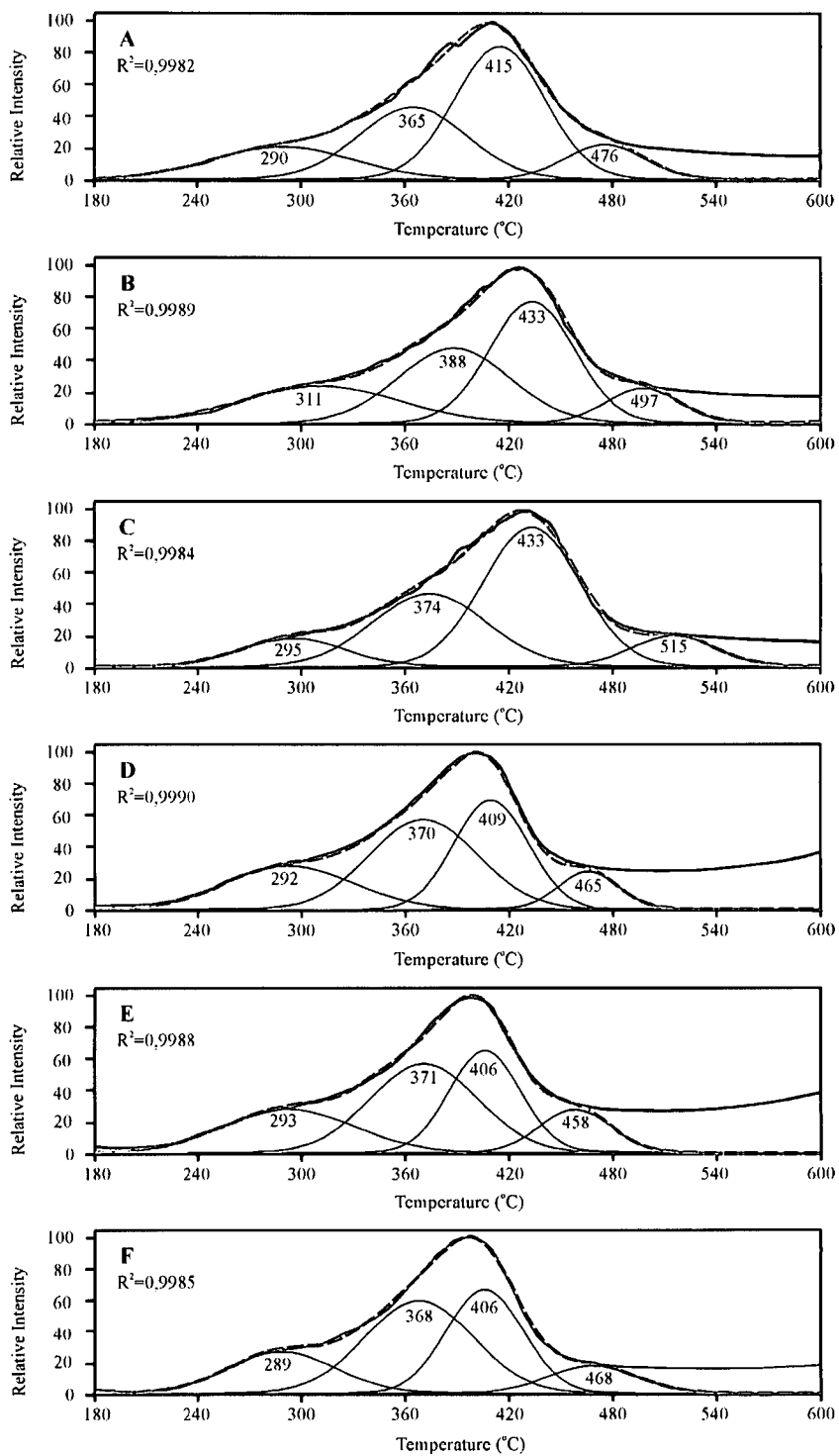


Fig. 2. Mathematical deconvolution of pyrograms monitored on (A) kerogen in the absence of minerals and a mixture (1:1) of (B) kerogen and calcite, (C) kerogen and montmorillonite at 25 °C/min heating rate, as well as on (D) kerogen in the absence of minerals and a mixture (1:1) of (E) kerogen and calcite, (F) kerogen and montmorillonite at 5 °C/min heating rate. Type I kerogen was isolated from Pula oil shale (West Hungary).

calculated by mathematical deconvolution of S2-peak monitored on ROM (Table 2). A significantly lower proportion of biomacromolecules and a slightly lower ratio of the highly

refractory components within geomacromolecules were detected during slow pyrolysis than during rapid pyrolysis. Nevertheless, changes were not observed in the ratio of labile and

refractory biomacromolecules as a function of heating rate in the absence of minerals. The presence of minerals modified the ROM composition calculated from mathematical deconvolution of pyrograms monitored at different heating rates. The results presented here suggested that the effect of minerals was less significant during slow pyrolysis.

Bulk RE data, detailed above, showed that the heating rate significantly controlled the total amount of pyrolysis products formed from a lipid-derived type I kerogen. Furthermore, a series of pyrolyses carried out on sedimentary rock samples (Hetényi et al. 2005) have already demonstrated that mathematical deconvolution of RE pyrograms, which could effectively be used for quantifying the major classes of organic constituents in soils, was not a reliable tool for the estimation of thermally labile and refractory components in type II kerogen. The present results revealed that differences occurring in source biomass, formation pathways and chemical structure of type I and III kerogens could be recognized not only in the shape of the S2 peaks but also in the effect of heating rate comparison (Fig. 2). The latter influenced mainly the proportion of the moderately resistant components and only slightly the proportion of the refractory constituents. The small contribution of the most labile components (F1 in Table 2) appeared to be negligible. Although the above method could not be applied reliably for quantifying the labile and resistant biopolymers and geopolymers in type I kerogen, it provided further evidence about the homogeneity of this Botryococcus-derived kerogen. Botryococcus-origin and homogeneity of the studied kerogen have already been reported: Palynological examinations clearly showed the overwhelming contribution of fossil colonies of Botryococcus algae (Kedves 1983), excellent preservation of which was directly evidenced by Scanning and Transmission Electron Microscopy observations (Derenne et al. 1997). Stepwise oxidation results exhibited the high degree of polymerization and homogeneity of the kerogen (Hetényi and Sirokmán 1978). Our results, namely the narrow S2-peak, monitored at 5 °C/min, and the hardly different Tmax values, obtained by its mathematical deconvolution, (Fig. 2) reflected very homogeneous character of the studied type I kerogen confirming the results of previous studies.

CONCLUSIONS

Overall, the above results showed that the heating rate modified RE data measured on lipid-derived and plant-derived OM to different degree. Independently of the nature and maturity of organic matter, standard RE conditions - namely heating rate of 25 °C/min - proved to be more suitable for determination of bulk RE data. The results presented here suggested that thermal residence time exerted an especially significant influence on measuring of the inert organic carbon content, which constitutes the major part of the plant-derived OM and only a minor part of the lipid-derived OM. The heating period influenced the pyrolysis yields, obtained from reactive OM, insignificantly in the case of plant-derived OM and significantly in the case of lipid-derived OM. The relative contributions of the labile and resistant biopolymers and geopolymers calculated by mathematical deconvolution of RE pyrograms, monitored on ROM fraction, varied moderately with heating rate. Rapid

heating displayed a more advanced stage of humification process and a more intense mineral matrix effect relative to slow heating. The method, which was developed for evaluating the composition of soil organic matter, has not proved to be an effective tool for evaluating the proportion of organic components of different thermal stability in a lipid-derived, very homogeneous kerogen.

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