THERMAL ANALYSIS OF SAPROPELIC ACIDS FROM HOLOCENE AND INTERGLACIAL LAKE DEPOSITS

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## ABSTRACT

Sapropelic acids as well as the whole sapropel of 0 to 8000-year-old Holocene (Lake Lahepera) and interglacial formations at Róngu (50,000 years old) and Kórveküla (300,000 years old) were investigated by thermal methods to elucidate diagenetic changes and those in their depositional conditions.

## INTRODUCTION

Sapropelic organic matter, especially that at a low degree of transformation has been much less studied in comparison with humic organic matter. Using group composition data in cluster analyses it was established that the main differences between sapropels and peats are qualitative ones in their components, sapropelic and humic acids and non-hydrolyzable residue in the first place /I/. This is why we took interest in sapropelic acids as one key compounds of sapropels.

## RESULTS AND DISCUSSION

The origin of sapropels has previously been described /2,3/. Interglacial sapropels differ from much younger Holocene ones by a lower H/C and higher C/N ratio (see the Table), the latter probably reflecting the diagenetic changes in the sapropels under study. The morphology of DTA thermooxidative decomposition profiles of sapropelic acids differs from that of sapropels. The thermooxidative degradation of all sapropelic acids considered is multistep in nature, with two major exothermic events being clearly evident. The DTA maxima of the first exothermic peak are almost the same for all the acids studied and vary in the range 310-320°C. The second peak decreases from  $470^{\circ}$  for the youngest sapropelic acids of Lahepera to  $435-4^{\circ}10^{\circ}$  and  $370-430^{\circ}$  for those of Rongu and the oldest ones of Korvekula, respectively. The first exothermic peak area (H<sub>T</sub>) makes 22-

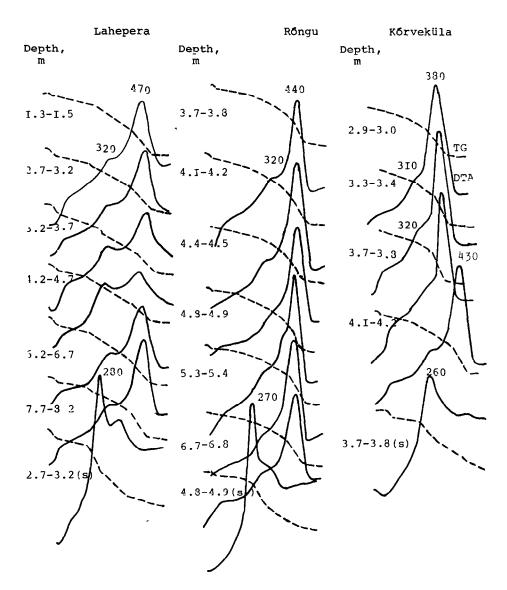


Fig. DTA and TG curves for sapropelic acids and sapropels (s).

Measured simultaneously by Q-derivatograph; sensitivity:

DTA I/5, TG 50 mg; microcrusibles, organic content of samples I3 mg, inert material Al<sub>2</sub>O<sub>3</sub>, heating rate IO<sup>O</sup>/min, air blow 200 ml/min.

Elemental composition of sapropelic acids, DTA and TG data

Table

| of sap- organic mat- ropel, % ter*, %  47.2   | Sapropelic acids |              |         | IO       | DTA and    | ĐĐ                        | data     |            |            |
|---|------------------|--------------|---------|----------|------------|---------------------------|----------|------------|------------|
| of sap- organic mat- ropel, % ter*, % C H N  42.8 56.7 5.5 5.9  29.3 28.8 56.3 5.6 5.4  21.8 40.4 51.7 5.9 5.0  42.7 41.0 56.4 5.3 4.9  20.6 21.4 56.0 5.1 4.5  20.6 33.3 52.8 4.7 2.8  44.0 43.1 52.0 4.6 2.5  29.4 42.5 55.0 4.6 3.0  53.4 44.6 53.3 5.0 3.0  8.1 30.0 55.1 4.6 3.0  21.2 35.2 51.4 4.6 2.9   | 1 comp           | sition, da   | f       | Sapı     | Sapropelic |                           | Sanrobel | pels       |            |
| ropel, % ter*, % C H N  47.2 42.8 56.7 5.5 5.9 29.3 28.8 56.3 5.6 5.4 30.8 29.9 53.0 6.2 5.4 21.8 40.4 51.7 5.9 5.0 42.7 41.0 56.4 5.3 4.9 38.2 42.3 56.0 5.1 4.5 32.6 33.3 56.0 5.1 4.5 32.6 33.3 52.8 4.7 3.0 44.0 43.1 52.0 4.7 2.8 45.8 47.1 46.0 4.2 2.5 29.4 42.5 55.0 4.6 3.0 53.4 44.6 53.3 5.0 3.1 8.1 30.0 55.1 4.6 3.2 20.7 44.6 53.2 21.2 35.2 51.4 4.6 2.9   |                  | <i>y</i> • : |         | ळॅ       | acids      | •                         | 1        |            |            |
| 47.2 42.8 56.7 5.5 5 29.3 28.8 56.3 5.6 5 20.8 29.9 53.0 6.2 5.6 5 21.8 40.4 51.7 5.9 5 42.7 41.0 56.4 5.3 4 44.0 42.3 56.0 5.1 4 52.6 33.3 52.8 4.7 3 44.0 42.5 55.0 4.7 2 45.8 47.1 46.0 4.2 2 53.4 42.5 55.0 4.6 3 20.7 43.0 49.6 4.4 2 21.2 35.2 51.4 4.6 2   | N<br>by          | O H/C        | C/N     | IH<br>WI | I %        | $^{ m I}_{ m H/I}_{ m m}$ | H. 16%   | I III I    | H.         |
| 29.3 28.8 56.3 5.6 5 30.8 29.9 53.0 6.2 5 21.8 40.4 51.7 5.9 5 42.7 41.0 56.4 5.3 4 20.6 21.4 56.0 5.1 4 45.8 47.1 46.0 4.2 2 45.8 47.1 46.0 4.2 2 29.4 42.5 55.0 4.6 3 20.7 42.5 55.0 4.6 3 20.7 43.0 49.6 4.4 2 21.2 35.2 51.4 4.6 2  | .5 5.9 3I        | .9 I.I5      | II.2    | 27       | 39         | , h I                     | 72 6     | о н        | 6          |
| 30.8 21.8 40.4 51.7 5.9 53.8 40.4 51.7 5.9 58.2 42.7 42.3 56.0 5.1 4 52.6 53.3 52.6 53.3 52.8 4.7 52.0 4.7 45.8 47.1 46.0 4.2 29.4 42.5 55.0 4.6 53.3 50.0 55.1 46.0 55.1 46.0 55.1 50.0 55.1 46.0 55.1 65.0 55.0 65.0 55.0 65.0 55.0 65.0 55.0 65.0 55.0 65.0 55.0 65.0 6  | .6 5.4 32        | 9I.I 7.      | I2.2    | 22       | Iη         | 1.9                       | 9 29     | .I 69      | Ι·         |
| 21.8  | .2               | 04°I 4       | 11.5    | 34       | 45         | I.3                       | 76 7     | 70 0:9     | , 6<br>, 7 |
| 42.7 41.0 56.4 5.3 4  28.2 42.3 56.0 5.1 4  20.6 21.4 56.0 5.0 3  32.6 33.3 52.8 4.7 3  44.0 43.1 52.0 4.7 2  45.8 47.1 46.0 4.2 2  29.4 42.5 55.0 4.6 3  8.1 30.0 55.1 4.6 3  21.2 35.2 51.4 4.6 2   | .9 5.0 37        | .4 I.37      | I2.I    | †<br>†   | 50         | I.I n                     | not de   | determine  | ne         |
| 38.2 42.3 56.0 5.1 H 20.6 21.4 56.0 5.0 3 32.6 33.3 52.8 4.7 3 44.0 43.1 52.0 4.7 2 45.8 47.1 46.0 4.2 2 29.4 42.5 55.0 4.6 3 53.4 44.6 53.3 5.0 3 8.1 30.0 55.1 4.6 3 21.2 35.2 51.4 4.6 2   | .3 4.9 33        | .4 I.I2      | 13.6    | 28       | 43         | H.5                       | 77 7     | 7I 0.9     | , 6        |
| 20.6 21.4 56.0 5.0 3 32.6 33.3 52.8 4.7 3 44.0 43.1 52.0 4.7 2 29.4 42.5 55.0 4.6 3 53.4 44.6 53.3 5.0 3 8.1 30.0 55.1 4.6 3 20.7 43.0 49.6 4.4 2 21.2 35.2 51.4 4.6 2  | .т ц.            | 4 I.09       | 1 d . 4 | 56       | 33         | I.3 n(                    | not de   | determined | ned        |
| 32.6 33.3 52.8 4.7 3 44.0 43.1 52.0 4.7 2 29.4 42.5 55.0 4.6 3 53.4 44.6 53.3 5.0 3 6.0 3 6.0 7 2 6.0 | .0 3.            | 4 I.08       | 18.0    | 27       | 33         | I.2 n                     | not de   | determined | ned 1      |
| 44.0 43.I 52.0 4.7 2 29.4 42.5 55.0 4.6 3 53.4 44.6 53.3 5.0 3 8.I 30.0 55.I 4.6 3 20.7 43.0 49.6 4.4 2 21.2 35.2 51.4 4.6 2  | .7 3.0 39        | 90.1 3.      | 20.3    | 21       | 31         | I.5 (                     | 9 99     | 68 I.      | 0.         |
| 45.8 47.1 46.0 4.2 2 29.4 42.5 55.0 4.6 3 53.4 44.6 53.3 5.0 3 8.1 30.0 55.1 4.6 3 20.7 43.0 49.6 4.4 2 21.2 35.2 51.4 4.6 2  | .7 2.            | 5 I.08       | 21.9    | 20       | 38         | 1.9                       | 9 99     | 62 0.      | 6.         |
| 29.4 42.5 55.0 4.6 5<br>53.4 44.6 53.3 5.0 3<br>8.I 30.0 55.I 4.6 3<br>20.7 43.0 49.6 4.4 2<br>21.2 35.2 51.4 4.6 2   | .2 2.            | II. I        | 2I.I    | 22       | 35         | 1.6                       | 65 6     | .I 99      | 0.         |
| 8.I 30.0 55.I 4.6 5.<br>20.7 43.0 49.6 4.4 2.<br>21.2 35.2 51.4 4.6 2.  | .6 3             | TC.I 4       | 21.9    | бĦ       | 97         | 7. I                      | 65 5     | 57 0.      | 6          |
| 8.I 30.0 55.I 4.6 3.<br>20.7 43.0 49.6 4.4 2.<br>21.2 35.2 51.4 4.6 2.  | .0 3.1 3S        | 90'I 2'      | 70.4    | 12       | 64         | ) ó. I                    | 67 5     | 58 0       | (Jr        |
| 20.7 43.0 49.6 4.4 2.<br>21.2 35.2 51.4 4.6 2.  | .6 3.            | 00'I I       | 20.I    | 21       | 39         | 1.9                       | 9 26     | 68 0.      | 8          |
| 21.2 35.2 51.4 4.6 2.   | .4 2.6 43        | .4 I.06      | 22.0    | 28       | 33         | 6.I                       | 92 7     | 0 0        | œ          |
|   | .6 2.9 4I.       | 1.06         | 20.8    | 59       | 33         | I.2                       | 90 7     | 2 0.       | , ω        |
| 8.8 24.5 52.7 4.6   | 6 3.             | 70.I 7       | 20.6    | 54       | 33         | T.4                       | 77 8     | 5 0.       | 9,         |

\* Obtained after successive separation of bitumen A, hot and boiling water soluble and easy-hydrolyzable matter and bitumen C /4/.

44% of the whole area (H) while the magnitude of the first thermo-oxidative event ( $\rm m_I$ ) is 33-50% of the whole weight loss (m) for the Lahepera sapropelic acids. These values are considerably lower for interglacial sapropelic acids as well as for the initial sapropels (see the Table). The first exothermic event may be due to the burning of hydrogen-rich compounds and liberation of oxygen-containing functional groups of sapropelic acids. The second event is believed to be the burning of the non-volatile compounds formed during the first thermooxidative event and of those of the original organic matter. Higher  $\rm m_I/H_I$  ratios in the first exothermic event differentiate sapropelic acids from sapropels, indicating that it is the loss of functional groups rather than burning that is significant in preparing sapropelic acids for the second exothermic event.

Variations and tendencies in elemental composition and thermal analysis data are considered to be due to intergration of two kinds of changes, viz. those in depositional conditions during sapropel formation and diagenetic ones occurring in sapropels later.

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