

VARIATIONS IN THE COMPOSITION OF STERANES AND  
TRITERPANES IN OIL SHALES OF DIFFERENT  
ORIGINS AND STAGES OF MATURITY

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ABSTRACT

Sterane and triterpane stereochemistry as quantitatively analysed by computerized capillary gas chromatography - mass spectrometry is mainly used for oil-oil and oil-source rock correlation. These saturated tetra- and pentacyclic hydrocarbons are rather easily detectable because of their specific mass spectrometric fragmentation patterns. The following examples demonstrate the applicability of sterane and triterpane stereochemistry to comparative organic geochemical investigation of oil shales of different origins and stage of maturity.

1. INTRODUCTION

Oil shales deposited in Upper Permian desalinated shallow sea (Tutonchana, USSR), Upper Jurassic epicontinental sea of normal salinity (Sysola, USSR) and in Paleogene fresh water basin (Krasava, Bulgaria) have been investigated. The X-ray diffraction method was used to examine the mineral composition of oil shales. In the Tutonchana shale calcite predominates (50%), while in the Kra-

sava one analcite (60%) and in the Sysola shale clay minerals (75%) are prevailing. The organic content of oil shales differs: 63.3, 27.9 and 30.2% respectively.

## 2. EXPERIMENTAL

Soluble organic matter was isolated from the powdered oil shales by Soxhlet extraction using chloroform. After saponification of the extract with a 5% KOH solution in methanol diethyl ether and water were added and neutral products extracted with diethyl ether. The aqueous phase was acidified with HCl and acidic products were extracted with diethyl ether. The neutral compounds were separated by thin-layer chromatography on silica gel L 40/100 $\mu$  with hexane:diethyl ether as eluent. The Hewlett Packard C-GC-MS system consisting of a 5940 A gas chromatograph, 5985 A mass spectrometer and HP 1000 computer was used to examine TLC fractions and fatty acids. Experimental conditions were: 10m x 0.25mm OV-101 and Silar 5 CP WCOT columns with temperature programming, electron energy 70 eV. He as a carrier gas was used. Computer reconstruction of mass fragmentograms was carried out by key mass spectral ions with  $m/z$  191 (triterpanes),  $m/z$  217 (regular steranes),  $m/z$  231 (4-methylsteranes), and molecular ions. The mass spectra of individual stereoisomers were studied.

## 3. DISCUSSION

The composition of n-alkanes and fatty acids of extracts (Fig. 1) show the predominance of procaryotic water organisms as a biological precursor of the organic matter of all three oil shales. For the lipids of these organisms fatty acids  $C_{16}$  and  $C_{18}$  are the most typical. In the Krassava shale organic matter the terrigenous material (long-chain fatty acids and n-alkanes) is more abundant than in the other oil shales. The carbon preference index is highest for Sysola n-alkanes (1.61) and decreases to 1.22 for

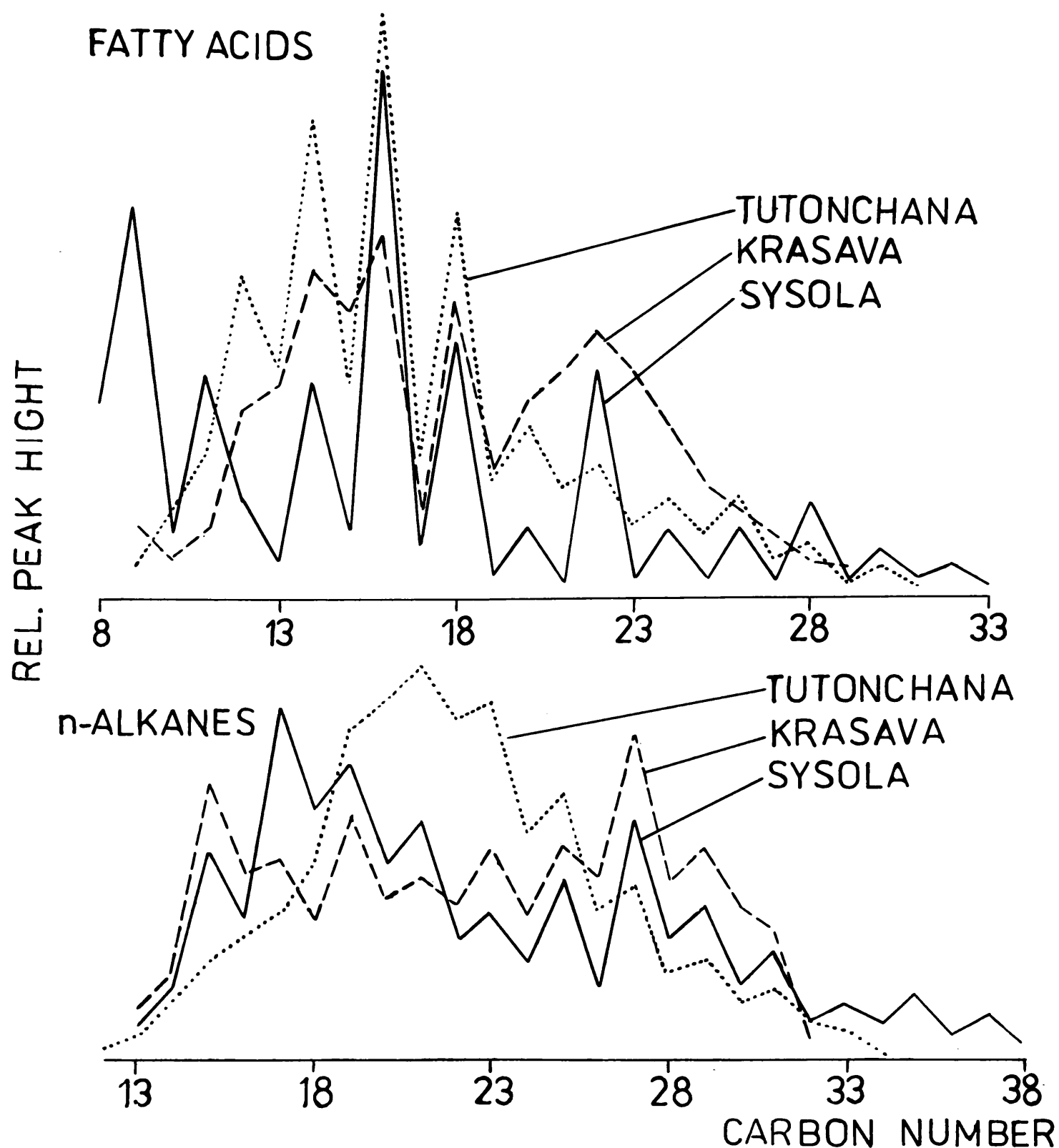


Fig. 1. Distribution diagrams for fatty acids and n-alkanes in oil shales extracts.

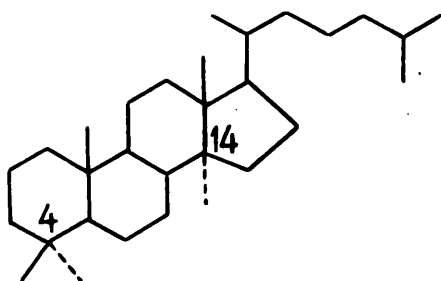
Tutonchana ones (Krasava 1.40). The distribution of n-alkanes of Sysola and Krasava oil shales with the strong predominance of odd homologues is typical for the immature and low-mature organic matter. In the Tutonchana oil shale the predominance disappears in a low-molecular range (to  $C_{21}$ ) and n-alkanes distribution is typical for the

organic matter of moderate maturity.

The oil shales under study differ in the content and distribution of steranes and triterpanes with the same molecular mass, the latter differing in the distribution of stereoisomers (Figs. 2 and 3). In the Krasava shale steranes and triterpanes make up 15% of aliphatic hydrocarbon fraction, in the Sysola one 3%.

The distribution of stereoisomers of triterpanes seems to be the most useful for the comparison of the maturation of oil shales organic matter. So, biogenic  $17\beta\text{H}$ ,  $21\beta\text{H}$ -hopanes are absent in the more mature Tutonchana shale and are preserved in the other shales (Fig. 2). In the Krasava and Sysola shales the biohopanes/geohopanes ratio ( $17\beta\text{H}, 21\beta\text{H}/17\alpha\text{H}, 21\beta\text{H}$ ) is 0.15 and 0.78 respectively. Like biohopanes, moretanes disappear gradually with increasing degree of maturity. The moretanes/hopanes ratio ( $17\beta\text{H}, 21\alpha\text{H}/17\alpha\text{H}, 21\beta\text{H}$ ) decreases from 0.82 in the Sysola oil shale to 0.49 in the Tutonchana shale (Krasava 0.67). In the more mature oil shales 20S-epimers of hopanes begin to predominate over the biogenic 20R-epimers (Tutonchana shale, Fig. 2). The  $17\alpha\text{H}, 18\alpha\text{H}, 21\beta\text{H}$ -28,30-bisnorhopane (BNH) in sediments is suggested to be the indicator of the low redox potential of paleoenvironment. It is almost absent in the Tutonchana shale and is perceptible in the others.

The origin of triterpanes is attributed to bacteria and partly to primitive terrestrial plants, while compounds with a steroidal skeleton are synthesized by all living organisms and, in principle, by the same pathway. The precursor of steroidal skeleton is the squalene formed from acetic acid during stepwise fermentative biosynthesis. The first tetracyclic product of squalene cyclization is lanosterene  $\text{C}_{30}$  with the lanostane skeleton:



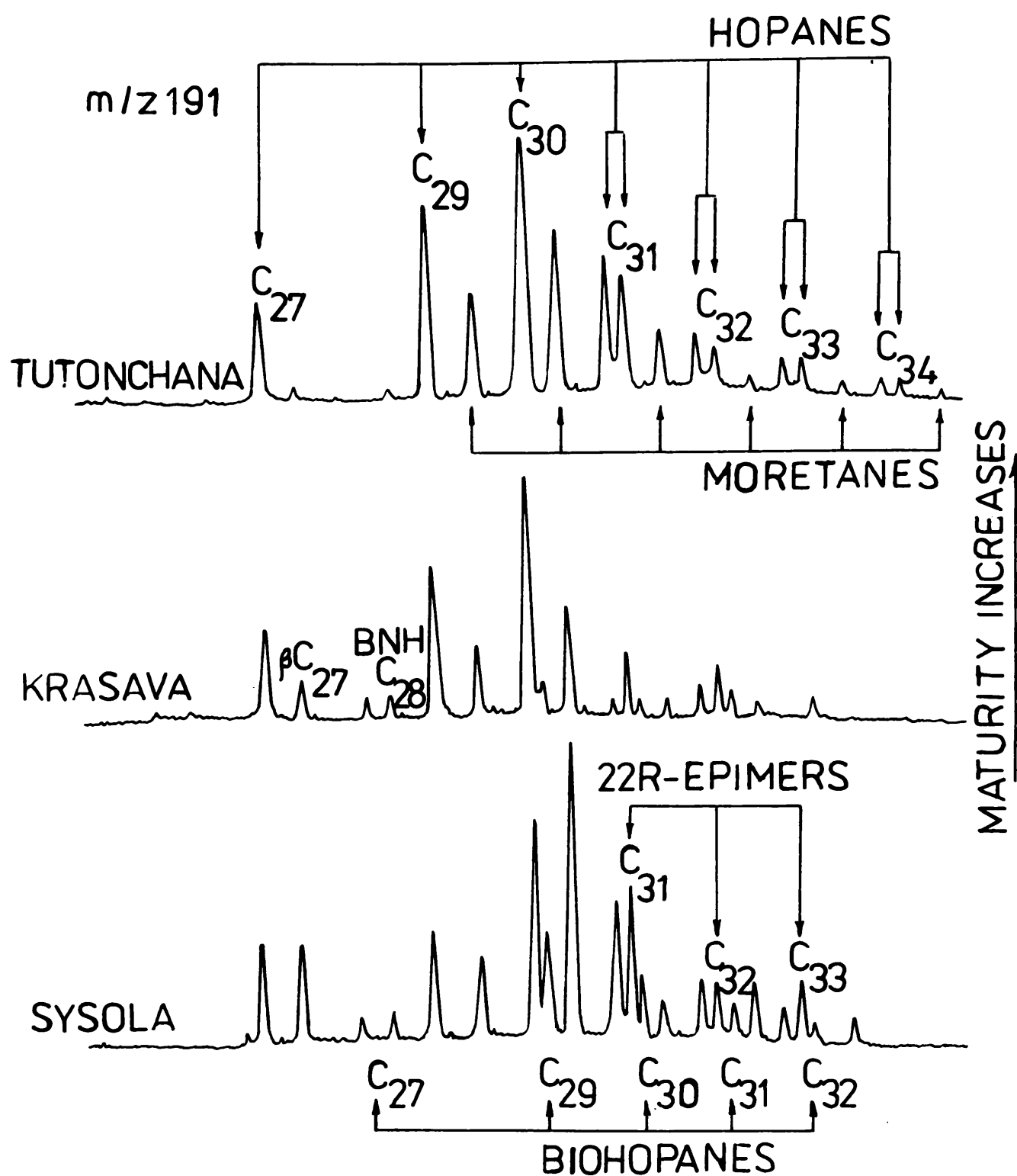


Fig. 2. Mass fragmentograms of m/z 191 ion, characteristic of triterpanes.

In animals and higher plants lanosterene is transformed to other sterenes (C<sub>27</sub>, C<sub>29</sub>) by subsequent removal of methyl groups from C-14 and C-4 atoms. Unlike other organisms, microorganisms are able to produce sterene derivatives with methyl groups in the 4-position. So, in bacteria the synthesis of sterols is blocked at the formation of 4,4-dimethyl- or 4-methylsterols, 4-desmethylsterols being not formed.

m/z 217

m/z 231

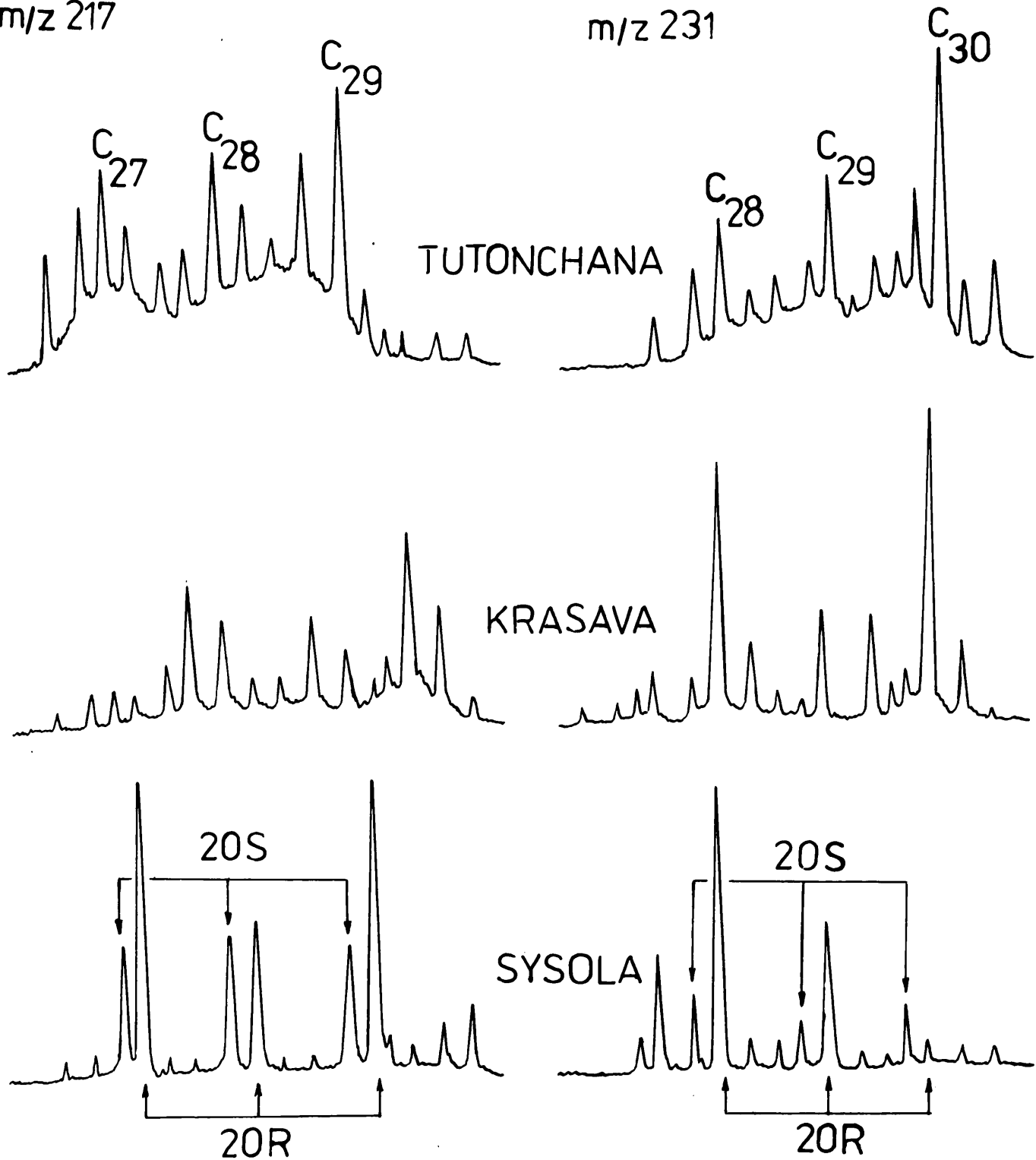


Fig. 3. Mass fragmentograms of m/z 217 ion, characteristic of regular steranes and m/z 231, a significant ion of 4-methylsteranes.

Except regular steranes, in the oil shales investigated 4-methyl- and 4,4-dimethylsteranes of bacterial origin were identified (the latter in the Krasava shale). In the Krasava shale methylsteranes prevail over the regular steranes indicative of a very strong bacterial alteration of organic matter in diagenesis. As for the Krasava oil shale genesis, the stratified (meromictic) lake concept may be

postulated, as well as to the Green River shale genesis. Both the oil shales are similar in the mineral and organic composition. In meromictic lakes extensive bacterial alteration of organic matter takes place not only in the sediment but also during the transition of organic matter particles through chemocline and monimolimnion zones.

The contribution of aquagenous ( $5\alpha$ - $C_{27}, C_{28}$ -steranes) and terrigenous ( $5\alpha$ - $C_{29}$ -steranes) bioproduction to the organic matter of Sysola oil shale is especially clear (Fig. 3). For the other shales, the picture is complicated due to the high concentration of  $14\beta$ H-steranes (*iso*-steranes) and rearrange  $10\alpha$ H,  $13\beta$ H,  $17\alpha$ H-steranes (diasteranes) (in Fig. 3 are not marked). In the Tutonchana shale diasteranes are absent despite the higher degree of maturity of its organic matter. The role of the thermal stress in the diasteranes formation is not so important as catalytic effect of clay minerals. Indeed, the Tutonchana oil shale mineral matter is predominantly carbonate.

Together with usefulness of sterane composition for oil shale organic matter-biological precursors correlation sterane stereochemistry is important for oil shales maturity comparisons, too. The value of the  $(20S+20R)$ -*iso*-steranes/ $20R$ - $5\alpha$ -steranes ratio (maturity index) is due to epimerization of C-14 atom requiring more strict conditions than epimerization of a chiral centre C-20. In Sysola oil shale the maturity index is near 0.0 and increases to 1.08 in the Tutonchana shale (Krasava 0.35).

#### 4. CONCLUSIONS

The relationships elucidated between the stereochemical peculiarities of steranes and triterpanes in oil shales, on the one hand, and biological precursors of organic matter, paleoenvironment, mineral composition of shales and its thermal history on the other hand, give evidence of a geochemical significance of these relict hydrocarbons in investigating the structure and genesis of oil shales.