

# LITIKUM

A Kőkor Kerekasztal folyóirata  
Journal of the Lithic Research Roundtable  
3. évfolyam • Volume 3 • 2015





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Zsolt Mester, György Lengyel, Viola T. Dobosi,  
Attila Király



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
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The multifaceted biface - Bifacial technology in Prehistory  
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## Analysis of Organic Compounds: Applications in Archaeology and Earth Science

Oliwia Grafka<sup>1</sup>, Dagmara H. Werra<sup>2</sup>, Rafał Siuda<sup>1</sup>

**Abstract** Analysis of molecular composition of organic matter in lithics can determine correlations between organic matter and rock source. The paper presents the possibilities and limitations of using this method in Earth Sciences and Archaeology.

**Kivonat** **Szerves alkotóelemek vizsgálata: régészeti és földtudományi alkalmazások**  
A kőzetekben található szerves anyagok molekuláris összetétele árulkodó lehet a kőzet eredetének helyét illetően. E cikkben bemutatjuk ezen elemző módszer felhasználásának lehetőségeit és korlátait a földtudományokban és a régészetben.

**Keywords** *Flint, Analyses of molecular composition of organic compounds, Archaeology, Earth science*

**Kulcsszavak** *kova, szerves alkotóelemek molekuláris összetételének analízise, régészet, földtudomány*

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### 1. Introduction

The majority of tools used by prehistoric communities were made of stone, a material that provided implements with sharp and durable edges. The most suitable type of stone needed to be hard and with a homogeneous structure, for instance obsidian (volcanic glass). But deposits of obsidian were not easy to come by, so early communities turned their attention towards flint, another high-quality raw material commonly occurring in Europe, which became the prime material for tool production in prehistoric times.

When studying prehistoric flint, one of the most interesting issues to be examined is the connection between deposits exploited at the time and the tools recorded at archaeological sites. By following the spread and distribution of particular raw materials we can study the spreading of prehistoric communities, their mobility and mutual contacts, as well as the size and quality of exchange networks.

At the same time, those features which caused siliceous rocks to be highly prized by ancient communities also mean that it is extremely difficult to link a deposit to concrete artefacts found at an archaeological site. That is why researchers try to describe the diagnostic features of siliceous rocks using various petrographic and geochemical methods (e.g. Sieveking et al. 1972; Sieveking, Hart 1986; Sieveking, Newcomer 1987; Schild, Sulgostowska 1997; Allard et al. 2008; Přichystal 2009, 2013; in Poland: Schild 1971; Lech 1980; Michniak 1980; Budziszewski, Michniak 1989; Kamińska-Szymczak, Szymczak 2002; Krajcarz, Krajcarz 2009).

One of the new methods recently introduced to archaeology is analysis of the molecular composition of organic compounds in flint. The method is commonly used in geology and serves to determine the source of the organic matter and its degree of transformation, both thermal and resulting from secondary processes such as its later oxidation or decomposition by microorganisms. It is also applied for correlation between liquid hydrocarbons (crude oil) and

the source rock from which the hydrocarbon originates. The method's success in the case of hydrocarbons, encouraged archaeologists to try it out on flint, in order to connect the flint used to produce tools to the deposit from which it was extracted. The determined organic matter comes from transformation of the mainly soft tissue of organisms that died and were deposited at the bottom of a body of water. The organic compounds of which the organisms were built underwent a series of geochemical transformations, providing hydrocarbons which could be extracted and determined analytically (e.g. Peters et al. 2005; Killops, Killops 2005).

## 2. Description of the method

The preparation of the sample is time consuming. The first stage entails selecting a piece of rock of appropriate weight. In the case of flint, which has a low organic carbon content, this means about 300 g. The flint is then washed in running water and cleaned mechanically (using an iron brush) to remove all impurities. Finally, the material must be cleaned further, using an organic solvent such as acetone or methanol, in order to remove any contamination by petroleum compounds (very common in the environment today). Also, the rock sample cannot be weathered. The next stage involves grinding the sample to a powder (c. 20  $\mu\text{m}$  in diameter). The powder is placed in cellulose thimbles and undergoes extraction with organic solvents (in our case: dichloromethane and methanol in a ratio of 97:3).

The extraction process, in a Soxhlet extractor lasts about 72 hours for a single sample. The obtained extract is then separated, for instance using a modified chromatography column (Bastow et al. 2007), into three principal fractions: aliphatic, aromatic and polar.

During further stages only the aliphatic and aromatic fractions are used. These are analyzed in a gas chromatograph coupled with a mass spectrometer (GC-MS, in the case of the below mentioned grant a Perkin Elmer Clarus 500). This is done to identify determinable organic compounds. The analysis is carried out using a capillary column (Elite - 5MS 30 x 0.25 mm, diameter 0.25  $\mu\text{m}$ ), where the carrier gas is helium.

For the aliphatic fraction in the gas chromatograph (GC) the following programme is used for the oven: initial temperature of 40 °C is held for one minute and then rises by 20 °C/min to 120 °C. The temperature then rises by 3 °C/min to 300 °C. The final temperature is held for 30 minutes. The complete programme time is 95 minutes.

For the aromatic fraction the following GC programme was used: initial temperature of 40 °C held for 2 min. In the next phase the temperature increased by 10 °C/min to 120 °C and then 4 °C/min until reaching 300 °C. The final temperature was held for 35 min. Complete time of analysis was 90 min. The mass spectrometer worked in the weight range 45–550 Da.

## 3. Applications in Archaeology and Earth Science

Analysis of the molecular composition of organic matter has been successfully used in geology since the 1960s.

In order to identify the source of the organic matter dispersed in rocks and the transformations it underwent due to temperature changes (being driven deep into the earth), or weathering of rocks, the common approach is to interpret the distribution of whole groups of organic compounds or the presence of single hydrocarbons, so-called biomarkers. For instance, it is thought that when compounds with an odd number of carbon atoms in the molecule dominate among *n*-alkanes with long hydrocarbon chains ( $n\text{-C}_{25}$ – $n\text{-C}_{31}$ ) it would suggest the input of land plants in the organic matter, but this feature gradually disappears with the increased degree of thermal transformation of rocks (e.g. Killops, Killops 2005; Peters et al. 2005).

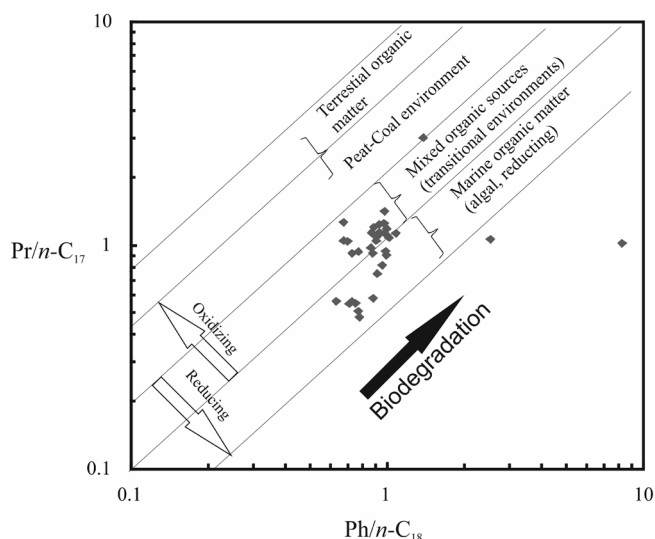
Biomarkers are organic compounds present in extractable organic matter which indisputably indicate a connection with biological precursors, in spite of the changes they were subject to during, among other things, diagenesis. Owing to the diversity of compounds, biomarkers can often be linked to a concrete group of plants, animals or bacteria from which they originate. Biomarkers are very useful in following the 'geohistory' of oil, its origin and maturation. Complex molecules such as 4 and 5 ring cyclic isoprenoids, i.e. steranes and hopanes, provide the most information.

For instance diterpenoids, cyclic isoprenoids composed of four isoprene units, come from compounds identified in resins of vascular plants, especially resins of conifers. Examples of compounds from this group are norpimarane, labdane, fichtelite, pimarane, isopimarane, abietane or the kaurene group.

A high concentration of fichtelite in the extracted organic matter, together with the presence of abietanes, is considered to indicate the presence in the extract of organic matter originating from the pine family (*Pinaceae*), while extracts containing phenol derivatives of abietanes are thought to indicate a predominance of the cypress family (*Cupressaceae*). In turn, derivatives of, among others,  $\beta$ -amiryn,  $\alpha$ -amiryn, friedelin and lupeol are considered biomarkers of angiosperms (Fabiańska 2007).

Geology uses not only individual biomarkers but also diagrams which take into account the relative concentration of concrete hydrocarbons, also biomarkers. Calculation parameters and diagrams proposed by Marynowski et al. (2000), worked well when the authors analyzed organic matter from the Devonian carbonate rocks of the Holy Cross (Świętokrzyskie) Mountains, as well as from Sylurian siliceous rocks (hornstones, shales and cherts) from the Bardzkie Mountains (Sudetes). One example of such an interpretation is presented in Fig. 1 (Grafka 2013).

The presence and relationship between relative concentrations of organic compounds provides information about



**Figure 1.** Diagram showing relationship between content of linear isoprenoids of pristane (Pr) and phytane (Ph) and  $n$ -alkanes with 17 ( $n$ -C<sub>17</sub>) and 18 ( $n$ -C<sub>18</sub>) carbon atoms in chain. From this we can surmise that the organic matter from outcrops of Early Palaeozoic rocks in Żdanów (Bardzkie Mts.) is of marine origin, mainly algae and was deposited in an oxygen-poor environment (Grafka 2013). //

**1. ábra.** A prisztán (Pr) és fitán (Ph) lineáris izoprenoid tartalom, valamint a 17 ( $n$ -C<sub>17</sub>) és 18 ( $n$ -C<sub>18</sub>) atomos szénláncú  $n$ -alkán tartalom közötti összefüggést mutató diagram. Ez alapján feltételezhető, hogy Żdanów (Bardzkie-hg.) korai paleozoikumából származó kőzeteinek szerves összetevői tengeri eredetűek, főleg algák, melyek oxigénszegény környezetben rakódtak le (Grafka 2013).

the environmental conditions in which the sediments were deposited. Geologists are very interested in rocks which were formed when a body of water suffered oxygen depletion or in euxinic conditions. A well-documented event of this kind in the Late Devonian formations from the Holy Cross Mountains has been described by Marynowski and Filipiak (2007) and Marynowski et al. (2010), and by others elsewhere, for instance in the USA the Devonian–Carboniferous black shale (Brown, Kenig 2004) or in cores drilled in the ocean floor (van Bentum et al. 2012).

Hydrocarbons have also served to determine naturally caused fires in Earth's past (e.g. Marynowski, Simoneit 2009) and, in consequence, have made possible interpretations of climate (e.g. Jiang et al. 1998).

A separate issue is changes taking place in organic compounds when rocks heat up as they sink down into the earth's crust. The changes, often called maturity of organic matter, are connected with the generation of liquid hydrocarbons (thermally mature organic matter). In geology a number of maturity indicators are used based on the relative concentrations of compounds from various groups (e.g. Hunt 1996; Killups, Killups 2005; Peters et al. 2005).

Organic matter in rock is also affected by weathering, biodegradation or water washout. These factors lead to gradual depletion and, finally, complete removal of organic matter from the rock (e.g. Marynowski et al. 2011; Fischer, Gaupp 2005; Sinninghe Damsté et al. 2002; Bastow et al. 2007).

In the more general works of Hunt (1996), Killups and Killups (2005), Peters et al. (2005) or Fabiańska (2007) and in articles such as Greenwood et al. (2006), we can find more detailed information concerning the method discussed here.

The methods proposed by researchers in organic geochemistry can also be applied in archaeology. Such work has been done, for instance, by Krajcarz et al. (2013), or in the earlier mentioned research project whose objective is to describe varieties of chocolate flint (Fig. 2; Fig. 3; Table 1).

In the analyzed samples of flint, the main carriers of organic matter are hydrocarbons of polar fraction which represent the heaviest compounds (Fig. 3; Table 1). Their considerable share shows that the organic matter which occurs in flint has undergone great transformations connected with secondary processes (weathering, biodegradation, water washing). These processes have led to removal of lighter organic compounds and concentration of heavier hydrocarbons (e.g. Peters et al. 2005; Killups, Killups 2005; Marynowski et al. 2011).

On the complete chromatogram of the aliphatic fraction (saturated) the elevated background (marked as UCM; see Fig. 4) is clearly visible, evidence of the presence of an unresolved compound mixture. The presence of this mixture is one of the indications that the analyzed material is biodegraded (e.g. Peters et al. 2005; Killups, Killups 2005).

Important components of the aliphatic fraction are  $n$ -alkanes (Fig. 5). Their distribution begins with a hydrocarbon of 16 atoms in chain ( $n$ -C<sub>16</sub>) and takes on a monomodal character. The maximum of relative concentration was found in compounds with short hydrocarbon chains. Within hydrocarbons of long chains there was a dominance of compounds with odd numbers of carbon atoms in a chain.

The next analyzed group of compounds within the aliphatic fraction is tri- and pentacyclic triterpenoids (Fig. 6; Table 2, 3). All samples of the examined flint are characterized by similar distribution within that group. This indicates that the organic matter present in the flint came from a similar source and underwent similar diagenetic processes. The extracts also contained tricyclic triterpenes. The presence of this group is a good prognostic for investigations of correlations between particular occurrences of flint. This group is applied for correlations between crude oil and source rocks (e.g. Killups, Killups 2005; Peters et al. 2005).

Organic compounds from the sterane group also occurred in all analyzed samples and their distribution was similar in each of the analyzed extracts. Additionally, the presence of diasteranes was determined (low retention time; see Fig. 7). These types of diasteranes indicate the presence of clay minerals during the transformation of organic matter (e.g. Peters et al. 2005).

The most distinct differences appear within the distribution of tri- and pentacyclic triterpenoids. The most visible variations were present between samples from the

Wierzbica “Zełe” flint mine and from the quarry in Błaziny Górne (Fig. 6B). In the extracts from “Zełe”, the compound of relatively highest concentration was C<sub>23</sub> tricyclic triterpene, while in the extract from Błaziny Górne C<sub>30</sub>αβ pentacyclic triterpene. In this extract, the presence of hopanes with the βα configuration was determined. The extracts from “Zełe” did not contain this compound group. The difference probably results from the lower thermal maturity of the organic matter in the Błaziny Górne flint and/or from lesser influence of secondary processes (e.g. Peters et al. 2005).

The project aims to differentiate between flint materials from various localities. Should the results of analyses be positive, the method could serve in future to determine correlations between flint artefacts and prehistoric mines. However, it must be taken into account that in order to acquire an extract of organic matter dissolvable in solvents, the sample has to be ground before it can undergo extraction.

#### 4. Conclusion

This analysis provides the molecular composition of aliphatic and aromatic fractions. On the basis of thus identified organic compounds, it is possible to determine the original environment of the organic matter (e.g. plant, algal, planktonic, etc.), the environment in which sedimentation of organic matter occurred (e.g. open sea, shelf, delta, lake) or the conditions during sedimentation (e.g. aerobic, anaerobic, euxinic). The method also makes it possible to determine the conditions prevailing in the sediment after the organic matter had been deposited (aerobic, anaerobic) and secondary transformations of organic matter (biodegradation, water washout, weathering). Analysis of molecular composition of organic matter can determine correlations between oil and source rock, and could possibly be used to determine correlations between prehistoric flint artefacts and specific prehistoric mines.

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#### References

Allard, P., Bostyn, F., Gilignay, F., Lech, J. (eds.) 2008. *Flint mining in prehistoric Europe: interpreting the archaeological records*. BAR International Series 1891, Oxford: Archaeopress.

Balcer, B. 1976. Position and stratigraphy of flint deposits, development of exploitation and importance of the świciechów flint in prehistory. *Acta Archaeologica Carpathica* 16: 179–199.

Bastow, T. P., van Aarssen, B. G. K., Lang, D. 2007. Rapid small-scale separation of saturate, aromatic and polar components

in petroleum. *Organic Geochemistry* 38: 1235–1250. <https://doi.org/10.1016/j.orggeochem.2007.03.004>

Brown, T. C., Kenig, F. 2004. Water column structure during deposition of Middle Devonian-Lower Mississippian black and green/gray shales of the Illinois and Michigan Basins: a biomarker approach. *Paleogeography, Paleoclimatology, Paleoecology* 215: 59–85. [https://doi.org/10.1016/S0031-0182\(04\)00452-3](https://doi.org/10.1016/S0031-0182(04)00452-3)

Budziszewski, J. 2008. Stan badań nad występowaniem i prądziejową eksploatacją krzemieni czekoladowych. In: Borkowski, W., Libera, J., Sałacińska, B., Sałaciński, S. (red.), *Krzemień czekoladowy w prądziejach. Materiały z konferencji w Orońsku 08-10.10.2003. Studia nad gospodarką surowcami krzemieniami w Prądziejach* 7, Warszawa–Lublin: Państwowe Muzeum Archeologiczne, Instytut Archeologii UMCS, 33–106.

Budziszewski, J., Michniak, R. 1989. Z badań nad występowaniem, petrograficzną naturą oraz prahistoryczną eksploatacją krzemieni pasiatych w południowym skrzydle niecki Magoń-Folwarczysko. *Wiadomości Archeologiczne* 49/2: 151–190.

Budziszewski, J., Gruzdź, W., Jakubczak, M., Szubski, M. 2015. Chalcolithic raw material economy in light of new data from the „Przyjaźń” mining field in Rzeczkowo (Central Poland). In: Mangado, X., Crandell, O., Sánchez, M., Cubero, M. (eds.), *International Symposium on Knappable Materials „On the Rocks”, 7-11 September 2015, Barcelona, Abstracts*, Barcelona: Universitat de Barcelona, 56.

Dadlez, R., Marek, S., Pokarski, J. (eds.) 2000. *Mapa geologiczna Polski bez utworów kenozoiku, skala 1:1 000 000*. Warszawa.

Fabiańska, M. 2007. *Geochemia organiczna węgla brunatnych wybranych złóż Polski*. Katowice: Wydawnictwo Uniwersytetu Śląskiego.

Fischer, C., Gaupp, R. 2005. Change of black shale organic material surface during oxidative weathering: implication for rock-water surface evolution. *Geochimica et Cosmochimica* 69: 1213–1224. <https://doi.org/10.1016/j.gca.2004.09.021>

Grafka, O. 2013. *Ewolucja materii organicznej drobnoziarnistych utworów staropaleozoicznych Gór Bardzkich (Sudety)*. Doctoral thesis, University of Warsaw, Warsaw.

Greenwood, P. F., Leenheer, J. A. McIntyre, C., Berwick, L., Franzmann, P. D. 2006. Bacterial biomarkers thermally released from dissolved organic matter. *Organic Geochemistry* 37: 597–609. <https://doi.org/10.1016/j.orggeochem.2005.12.009>

Hunt, J. M. 1996. *Petroleum geochemistry and geology*. New York: W. H. Freeman and Company.

Jiang, C., Alexander, R., Kagi, R. I., Murray, A. P. 1998. Polycyclic aromatic hydrocarbons in ancient sediments and their relationship to paleoclimate. *Organic Geochemistry* 29: 1721–1735. [https://doi.org/10.1016/S0146-6380\(98\)00083-7](https://doi.org/10.1016/S0146-6380(98)00083-7)

Kamińska-Szymczak, J., Szymczak, K. 2002. Powierzchnie świeżych przełamów wybranych surowców krzemieniami z terenów Polski obserwowanych przy użyciu SEM. In: Matraszek, B., Sałaciński, S. (red.), *Krzemień świciechowski w prądziejach. Materiały z konferencji w Ryni, 22-24.05.2000*. Studia nad gospodarką surowcami krzemieniami w Prądziejach 4, Warszawa: Semper, 297–306.

Killops, S., Killops, V. 2005. *Introduction to Organic Geochemistry*. 2nd edition. Cornwall: Blackwell Publishing. <https://doi.org/10.1002/9781118697214>

Krajcarz, M. T., Krajcarz, M. 2009. The Outcrops of Jurassic Flint Raw Materials from South-western Margin of the Holy Cross Mountains. *Acta Archaeologica Carpathica* 44: 183–195.

Krajcarz, M. T., Cyrek, K., Gola, M. 2013. Osadnictwo paleolityczne w



- jaskini Biśnik w zapisie antropogenicznych biomarkerów. *Prace i Studia Geograficzne* 51: 57–68.
- Lech, J. 1980. Geologia krzemienia jurajskiego-podkrakowskiego na tle innych skał krzemionkowych. Wprowadzenie do badań z perspektywy archeologicznej. *Acta Archaeologica Carpathica* 20: 163–228.
- Marynowski, L., Filipiak, P. 2007. Water column euxinia and wildfire evidence during deposition of the Upper Famennian Hangenberg event horizon from Holy Cross Mountains (central Poland). *Geological Magazine* 144: 569–595. <https://doi.org/10.1017/S0016756807003317>
- Marynowski, L., Simoneit, B. R. T. 2009. Widespread upper Triassic to Lower Jurassic wildfire records from Poland: evidence from charcoal and polycyclic aromatic hydrocarbons. *Palaios* 24: 785–798. <https://doi.org/10.2110/palo.2009.p09-044r>
- Marynowski, L., Narkiewicz, M., Grelowski, C. 2000. Biomarkers an environmental indicators in carbonate complex, example from the Middle to Upper Devonian Holy Cross Mountains. *Sedimentary Geology* 137: 187–212. [https://doi.org/10.1016/S0037-0738\(00\)00157-3](https://doi.org/10.1016/S0037-0738(00)00157-3)
- Marynowski, L., Filipiak, P., Zatoń, M. 2010. Geochemical and palynological study of the Upper Famennian Dasberg event horizon from the Holy Cross Mountains (central Poland). *Geochemistry Magazine* 147: 527–550. <https://doi.org/10.1017/S0016756809990835>
- Marynowski, L., Kurkiewicz, S., Rakociński, M., Simoneit, B. R. T. 2011. Effects of weathering on organic matter: I. Changes in molecular composition of extractable organic compounds caused by paleoweathering of Lower Carboniferous (Tournaisian) maine black shale. *Chemical Geology* 285: 144–156. <https://doi.org/10.1016/j.chemgeo.2011.04.001>
- Michniak, R. 1980. Petrograficzka i geneza ciemnych krzemieni z dolnoturońskich osadów okolic Ożarowa nad środkową Wisłą. *Archiwum Mineralogiczne* 36: 83–106.
- Peters, K. E., Walters, C. C., Moldowan, J. M. 2005. *The Biomarker Guide. Vol. 2: Biomarkers and Isotopes in Petroleum System and Earth History*. Cambridge: Cambridge University Press.
- Přichystal, A. 2009. *Kamenné suroviny v pravěku východní části střední Evropy*. Brno: Masarykova univerzity.
- Přichystal, A. 2013. *Lithic raw materials in prehistoric times of eastern Central Europe*. Brno: Masarykova univerzity.
- Schild, R. 1971. Lokalizacja prahisterycznych punktów eksploatacji krzemienia czekoladowego na północnwschodnim obrzeżeniu Gór Świętokrzyskich. *Folia Quaternaria* 39: 1–61.
- Schild, R. 1976. Flint mining and trade in polish prehistory as seen from the perspective of chocolate flint of central Poland. A second approach. *Acta Archaeologica Carpathica* 16: 147–177.
- Schild, R., Sulgostowska, Z. (eds.) 1997. *Man and flint. Proceedings of the VIIth International Flint Symposium*. Warszawa: Institute of Archaeology and Ethnology, Polish Academy of Sciences Warsaw.
- Sieveking, G. de G., Hart, M. B. (eds.) 1986. *The scientific study of flint and chert*. Cambridge: Cambridge University Press.
- Sieveking, G. de G., Newcomer, M. H. (eds.) 1987. *The human uses of flint and chert*. Cambridge: Cambridge University Press.
- Sieveking, G. de G., Bush, P., Ferguson, J., Craddock, P. T., Hughes, M. J., Cowell, M. R. 1972. Prehistoric flint mines and their identification as sources of raw material. *Archaeometry* 14: 151–76. <https://doi.org/10.1111/j.1475-4754.1972.tb00061.x>
- Sinninghe Damsté, J. S., Rijpstra, W. I. C., Reichart, G.-J. 2002. The influence of oxic degradation on the sedimentary biomarker record II. Evidence from Arabian Sea sediments. *Geochimica et Cosmochimica* 66: 2737–2754. [https://doi.org/10.1016/S0016-7037\(02\)00865-7](https://doi.org/10.1016/S0016-7037(02)00865-7)
- van Bentum, E. C., Richart, G. J., Sinninghe Damsté, J. S. 2012. Organic matter provenance, paleoproductivity and bottom water anoxia during the Cenomanian/Turonian Oceanic Anoxic event in the Newfoundland Basin (Northern proto North Atlantic Ocean). *Organic Geochemistry* 50: 11–18. <https://doi.org/10.1016/j.orggeochem.2012.05.013>

## SKAM 2014 Article

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The conference papers are published in the Litikum Journal volumes as special contributions. Informations about the conference as well as the abstract book are available on the SKAM 2014 website: <http://skam.pannontenger.hu>

site	type of flint (archaeological name)	symbol of the sample	aliphatic	aromatic	polar
Wierzbica "Zełe", Radom District	"chocolate flint"	WZS-28	18.18	2.27	79.55
Wierzbica "Zełe", Radom District	"chocolate flint"	WZr81-1	22.78	6.33	70.89
Wierzbica "Zełe", Radom District	"chocolate flint"	WZ1B	0.58	0.10	99.33
Wierzbica "Zełe", Radom District	"chocolate flint"	WZ2B	9.89	6.59	83.52
Wierzbica "Zełe", Radom District	"chocolate flint"	WZ3B	0.00	100.00	0.00
Wierzbica – outcrop, Radom District	"chocolate flint"	WIK1	2.38	7.14	90.48
Orońsko, Szydłowiec District	"chocolate flint"	ORO1	15.91	3.41	80.68
Orońsko, Szydłowiec District	"chocolate flint"	ORO2	48.06	26.60	25.35
Orońsko "Mały Orońsk", Szydłowiec District	"chocolate flint"	MOR1	17.74	8.06	74.19
Tomaszów, Szydłowiec District	"chocolate flint"	TOM1	11.84	0.00	88.16
Polany II, Radom District	"chocolate flint"	POL1	50.59	26.49	22.93
Seredzice, Radom District	"chocolate flint"	SER24-B1	10.00	5.00	85.00
Seredzice, Radom District	"chocolate flint"	SER24-B2	4.55	4.55	90.91
Seredzice "Hapki", Radom District	"chocolate flint"	HAB1	8.70	6.52	84.78
Iłża, Radom District	"chocolate flint"	IL2-SCH	14.81	18.52	66.67
Błaziny Górne, Radom District	"chocolate flint"	BLG-CZK1	11.63	8.84	79.53
Seredzice, Radom District	striped flint	PSP-24BU1	7.32	2.44	90.24
Błaziny Górne, Radom District	striped flint	BLGPSP-1	25.00	12.50	62.50
Krzemionki Opatowskie, Ostrowiec Świętokrzyski District	striped flint	KO-GS1	13.79	1.72	84.48
Krzemionki Opatowskie, Ostrowiec Świętokrzyski District	striped flint	KO-GS2	3.72	87.19	9.09
Borownia, Ostrowiec Świętokrzyski District	striped flint	BOB?2	11.24	2.25	86.52
Borownia, Ostrowiec Świętokrzyski District	striped flint	BOB1	64.29	34.87	0.84
Świeciechów Lasek, Kraśnik District	gray white-spotted flint	SWLAS-1	5.88	5.88	88.24

**Table 1.** Percentage of aliphatic, aromatic and polar fractions for the exemplary attempts of analyze samples of siliceous rocks (see Fig. 3). //

**1. táblázat.** Alifás, aromás és poláris frakciók megoszlása a kovás kőzetminták próbaméréseinél (ld. 3. ábra).

Symbol	Name
C20	C20-tricyclic triterpene
C21	C21-tricyclic triterpene
C22	C22-tricyclic triterpene
C23	C23-tricyclic triterpene
C24	C24-tricyclic triterpene
C25	C25-tricyclic triterpene
C26	C26-tricyclic triterpene
C27	C27-tricyclic triterpene
C28	C28-tricyclic triterpene
C29	C29-tricyclic triterpene
Ts	18 $\alpha$ (H)-22,29,30-trisnorneohopan
Tm	17 $\alpha$ (H)-22,29,30-trisnorhopan
C29 $\alpha\beta$	C29-17 $\alpha$ ,21 $\beta$ -30-norhopan
C29 $\beta\alpha$	C29-17 $\beta$ 21 $\alpha$ -hopan
C30 $\alpha\beta$	C30-17 $\alpha$ 21 $\beta$ -hopan
C30 $\beta\alpha$	C30-17 $\beta$ 21 $\alpha$ -hopan
C31 $\alpha\beta$ 22S	C31-17 $\alpha$ ,21 $\beta$ -29-homohopan 22S
C31 $\alpha\beta$ 22R	C31-17 $\alpha$ ,21 $\beta$ -29-homohopan 22R
C32 $\alpha\beta$ 22S	C32-17 $\alpha$ ,21 $\beta$ -29-bishomohopan 22S
C32 $\alpha\beta$ 22R	C32-17 $\alpha$ ,21 $\beta$ -29-bishomohopan 22R
C33 $\alpha\beta$ 22S	C33-17 $\alpha$ ,21 $\beta$ -29-trishomohopan 22S
C33 $\alpha\beta$ 22R	C33-17 $\alpha$ ,21 $\beta$ -29-trishomohopan 22R

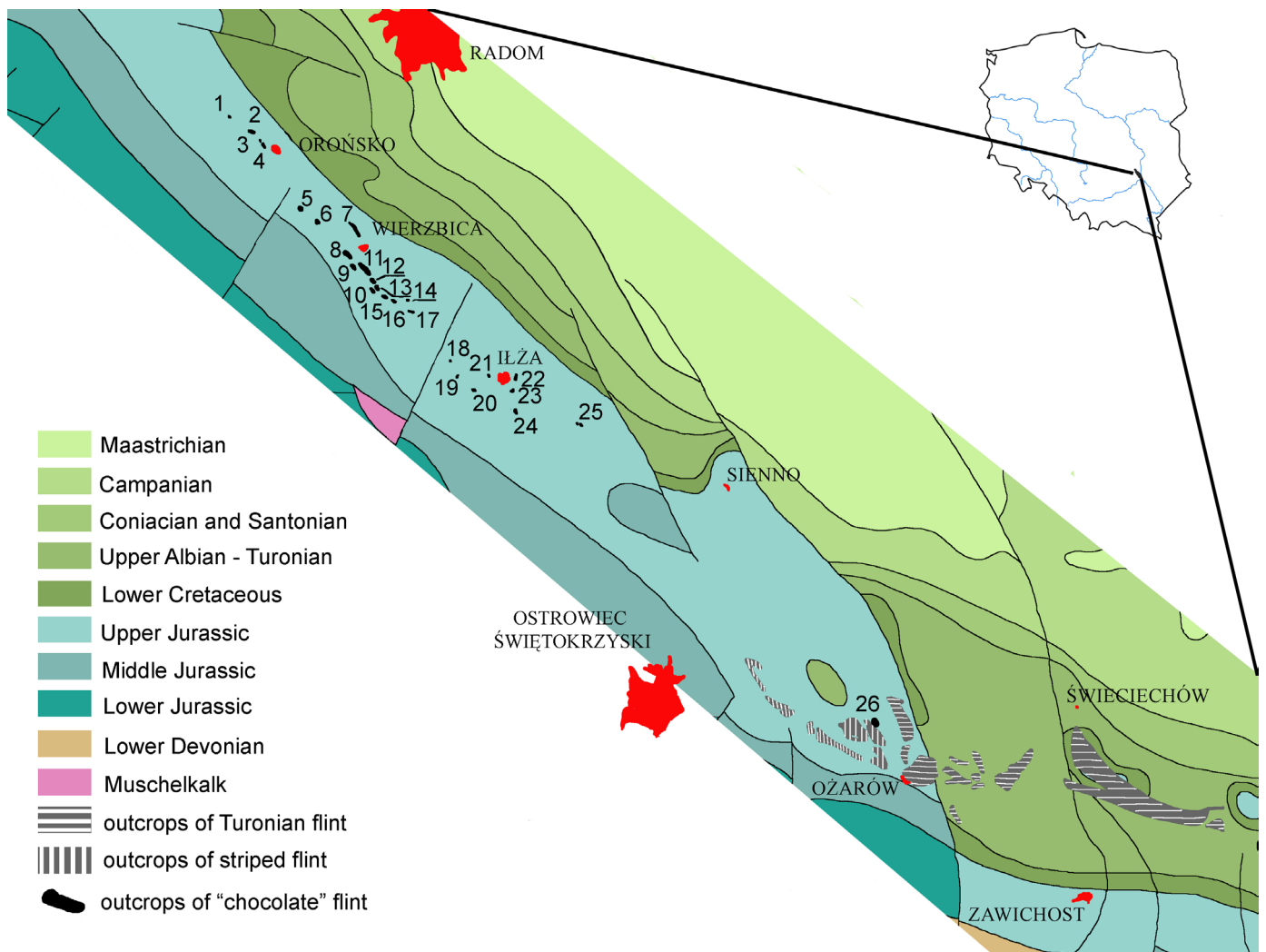
**Table 2.** Explanation of compounds name used for tri- and pentacyclic triterpenoids (see Fig. 6 and 7). //

**2. táblázat.** A tri- és pentaciklikus triterpenoidokra használt jelölések magyarázata (ld. 6–7. ábra).

Name	Symbol
C27 13 $\beta$ ,17 $\alpha$ -diasteran 20S	C27 $\beta\alpha$ 20S
C27 13 $\beta$ ,17 $\alpha$ -diasteran 20R	C27 $\beta\alpha$ 20R
C27 13 $\alpha$ ,17 $\beta$ -diasteran 20S	C27 $\alpha\beta$ 20S
C27 13 $\alpha$ ,17 $\beta$ -diasteran 20R	C27 $\alpha\beta$ 20R
C28 13 $\beta$ ,17 $\alpha$ -diasteran 20S (24S+R)	C28 $\beta\alpha$ 20S (24S+R)
C28 13 $\beta$ ,17 $\alpha$ -diasteran 20R (24S+R)	C28 $\beta\alpha$ (24S+R)
C27 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -steran 20S	C27 $\alpha\alpha\alpha$ 20S
C28 13 $\alpha$ ,17 $\beta$ -diasteran 20S	C28 $\alpha\beta$ 20S
C27 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -steran 20R	C27 $\alpha\beta\beta$ 20R
C29 13 $\beta$ ,17 $\alpha$ -diasteran 20S	C29 $\beta\alpha$ 20S
C27 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -steran 20S	C27 $\alpha\beta\beta$ 20S
C27 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -steran 20R	C27 $\alpha\alpha\alpha$ 20R
C29 13 $\beta$ ,17 $\alpha$ -diasteran 20S	C29 $\beta\alpha$ 20S
C29 13 $\beta$ ,17 $\alpha$ -diasteran 20R	C29 $\beta\alpha$ 20R
C28 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -steran 20S	C28 $\alpha\alpha\alpha$ 20S
C28 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -steran 20R	C28 $\alpha\beta\beta$ 20R
C28 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -steran 20S	C28 $\alpha\beta\beta$ 20S
C30 13 $\beta$ ,17 $\alpha$ -diasteran 20R	C30 $\beta\alpha$ 20R
C29 13 $\alpha$ ,17 $\beta$ -diasteran 20R i S	C29 $\alpha\beta$ 20R i S
C28 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -steran 20R	C28 $\alpha\alpha\alpha$ 20R
C29 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -steran 20S	C29 $\alpha\alpha\alpha$ 20S
C29 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -steran 20R	C29 $\alpha\beta\beta$ 20R
C29 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -steran 20S	C29 $\alpha\beta\beta$ 20S
C29 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -steran 20R	C29 $\alpha\alpha\alpha$ 20R
C30 5 $\alpha$ ,14 $\beta$ ,17 $\beta$ -steran 20R+S	C30 $\alpha\beta\beta$ 20R+S
C30 5 $\alpha$ ,14 $\alpha$ ,17 $\alpha$ -steran 20R	C30 $\alpha\alpha\alpha$ 20R

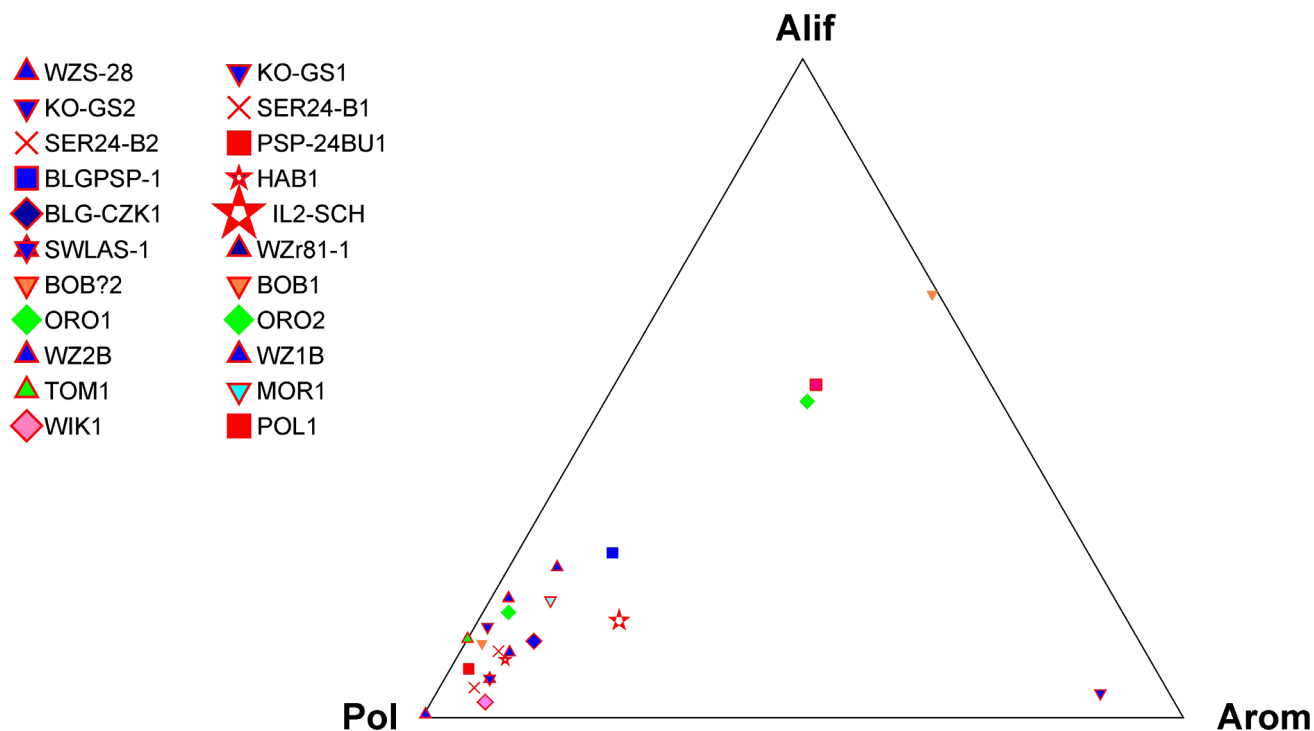
**Table 3.** Explanation of compounds name used for steranes and diasterans (see Fig. 6 and 7). //

**3. táblázat.** A szteránokra és diaszteránokra használt jelölések magyarázata (ld. 6–7. ábra).



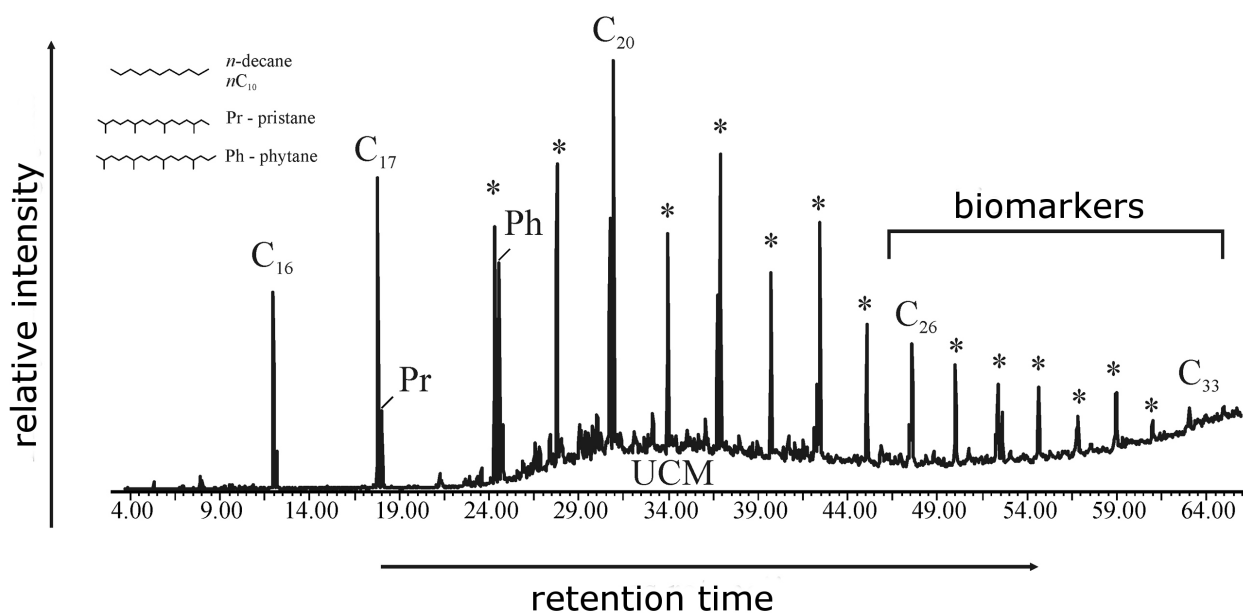
**Figure 2.** Occurrence of “chocolate” flint in pre-Quaternary formations on the northeastern outskirts of the Holy Cross Mountains. **1** – Chronów-Kolonia, Szydłowiec District; **2** – Guzów Szydłowiec District; **3** – Orońsko “Mały Orońsk” Szydłowiec District; **4** – Orońsko (Orońsk II) Szydłowiec District; **5** – Tomaszów Szydłowiec District; **6** – Rzeczków, Radom District; **7** – Wierzbica quarry, Radom District; **8** – Wierzbica “Zełe”, Radom District; **9** – Wierzbica “Krzemienica”, Radom District; **10** – Polany kolonie IV, Radom District; **11** – Polany kolonie I, Radom District; **12** – Polany kolonie II, Radom District; **13** – Polany kolonie IIa, Radom District; **14** – Polany III, Radom District; **15** – Polany kolonie III, Radom District; **16** – Polany I, Radom District; **17** – Polany II, Radom District; **18** – Pakosław, Radom District; **19** – Seredzice, Radom District; **20** – Seredzice “Kolonia”, Radom District; **21** – Iłża “Wąwóz Żuchowiec”, Radom District; **22** – Iłża “Krzemieniec” II, Radom District; **23** – Iłża “Krzemieniec” I, Radom District; **24** – Błaziny Górne, Radom District; **25** – Prędocin, Radom District; **26** – Gliniany “Wzgórze Kruk”, Opatów District (Schild 1971, 1976; Balcer 1976; Dadlez et al. 2000; Budziszewski 2008; Budziszewski et al. 2015). //

**2. ábra.** „Csokoládé” kova előfordulások a Szentkereszt-hegység északkeleti peremeinek negyedidőszak előtti formációiban. **1** – Chronów-Kolonia, Szydłowiec körzet; **2** – Guzów Szydłowiec körzet; **3** – Orońsko “Mały Orońsk” Szydłowiec körzet; **4** – Orońsko (Orońsk II) Szydłowiec körzet; **5** – Tomaszów Szydłowiec körzet; **6** – Rzeczków, Radom körzet; **7** – Wierzbica quarry, Radom körzet; **8** – Wierzbica “Zełe”, Radom körzet; **9** – Wierzbica “Krzemienica”, Radom körzet; **10** – Polany kolonie IV, Radom körzet; **11** – Polany kolonie I, Radom körzet; **12** – Polany kolonie II, Radom körzet; **13** – Polany kolonie IIa, Radom körzet; **14** – Polany III, Radom körzet; **15** – Polany kolonie III, Radom körzet; **16** – Polany I, Radom körzet; **17** – Polany II, Radom körzet; **18** – Pakosław, Radom körzet; **19** – Seredzice, Radom körzet; **20** – Seredzice “Kolonia”, Radom körzet; **21** – Iłża “Wąwóz Żuchowiec”, Radom körzet; **22** – Iłża “Krzemieniec” II, Radom körzet; **23** – Iłża “Krzemieniec” I, Radom körzet; **24** – Błaziny Górne, Radom körzet; **25** – Prędocin, Radom körzet; **26** – Gliniany “Wzgórze Kruk”, Opatów körzet (Schild 1971, 1976; Balcer 1976; Dadlez et al. 2000; Budziszewski 2008; Budziszewski et al. 2015).



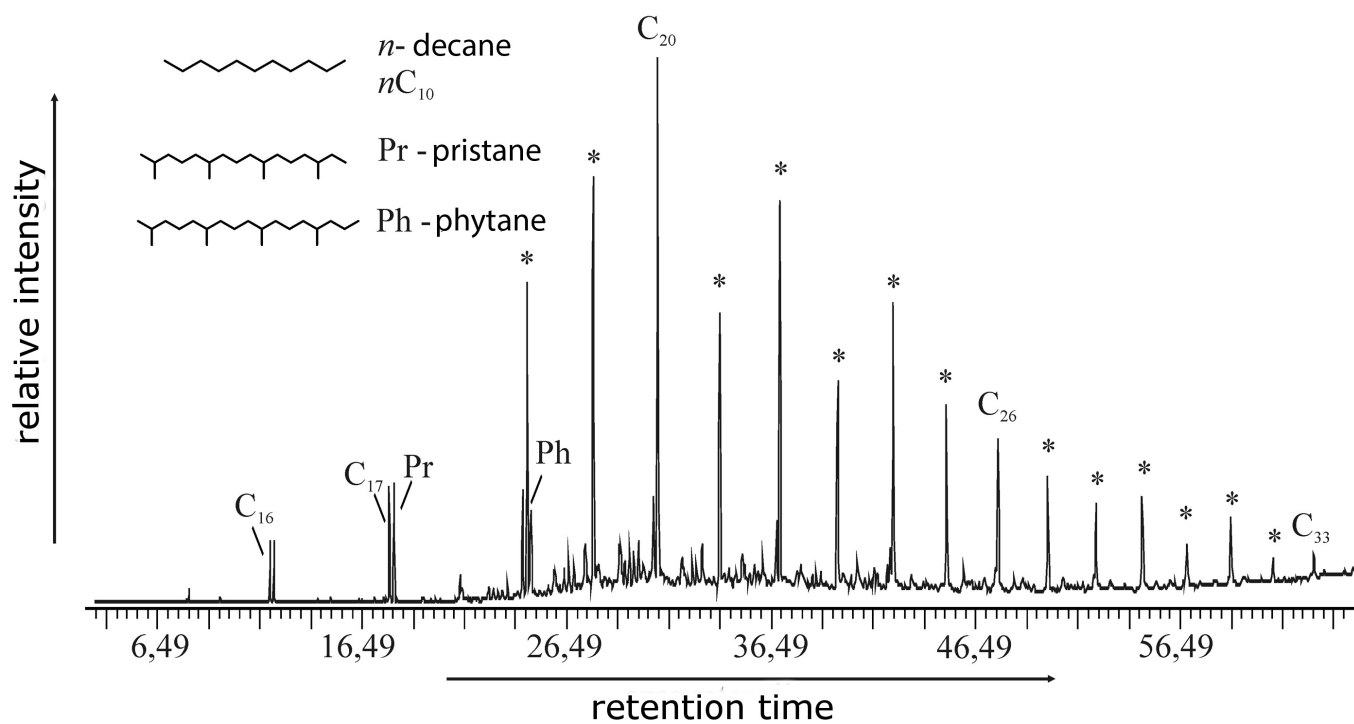
**Figure 3.** Ternary diagram showing the percentage of each fraction in the extract from the analyzed flint. 100% of the fraction in the corners (Pol - polar, Aliph - aliphatic, Arom - aromatic fractions; see Table 1). //

**3. ábra.** Háromszögdiagram a frakciók megoszlásával a kovamintákban. 100% a sarkokban (Pol - poláris; Aliph - alifás; Arom - aromás frakciók; ld. 1. Táblázat).



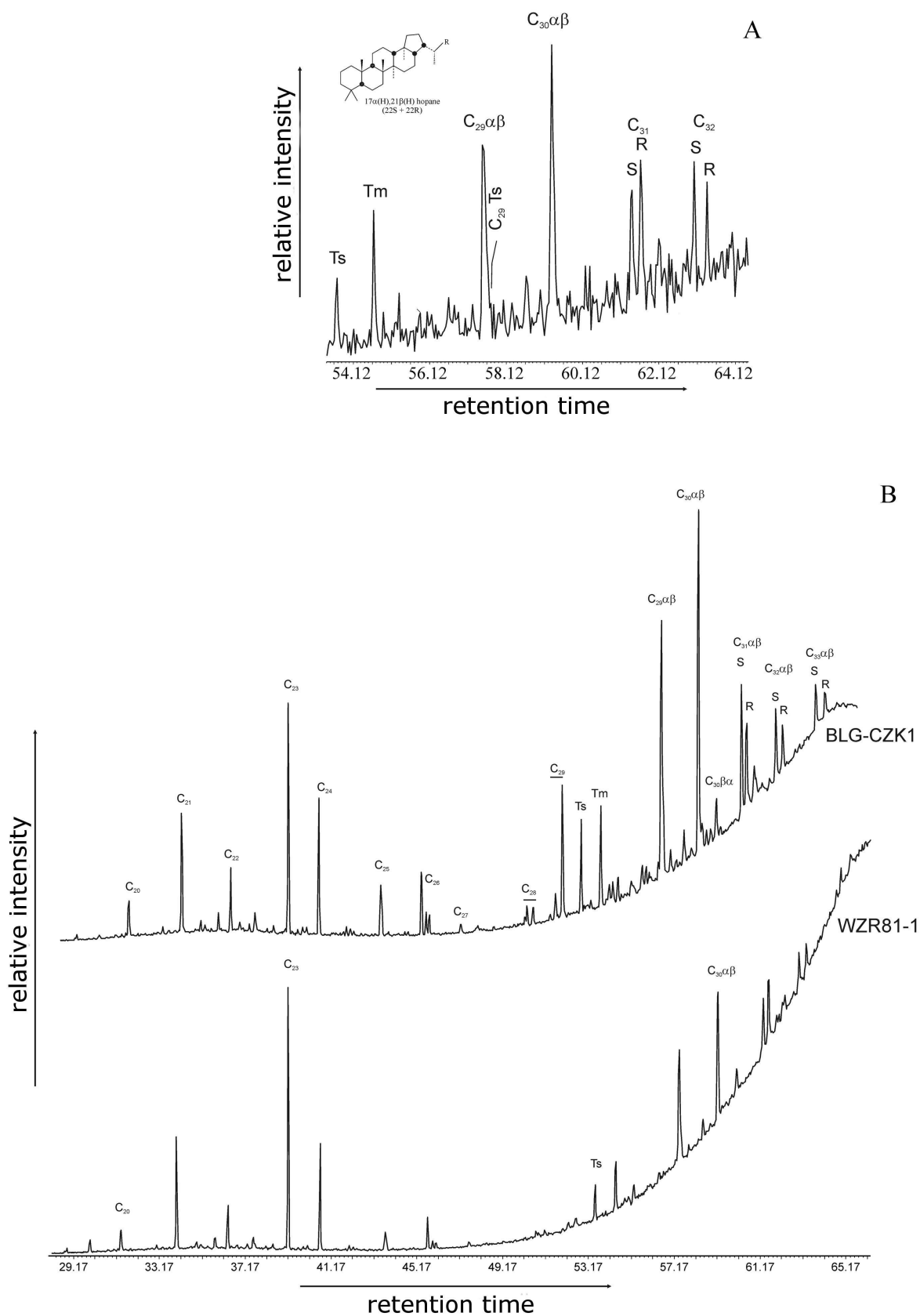
**Figure 4.** Total ion chromatogram (TIC) of aliphatic fraction. //

**4. ábra.** Az alifás frakció teljes ion kromatogramja (TIC).



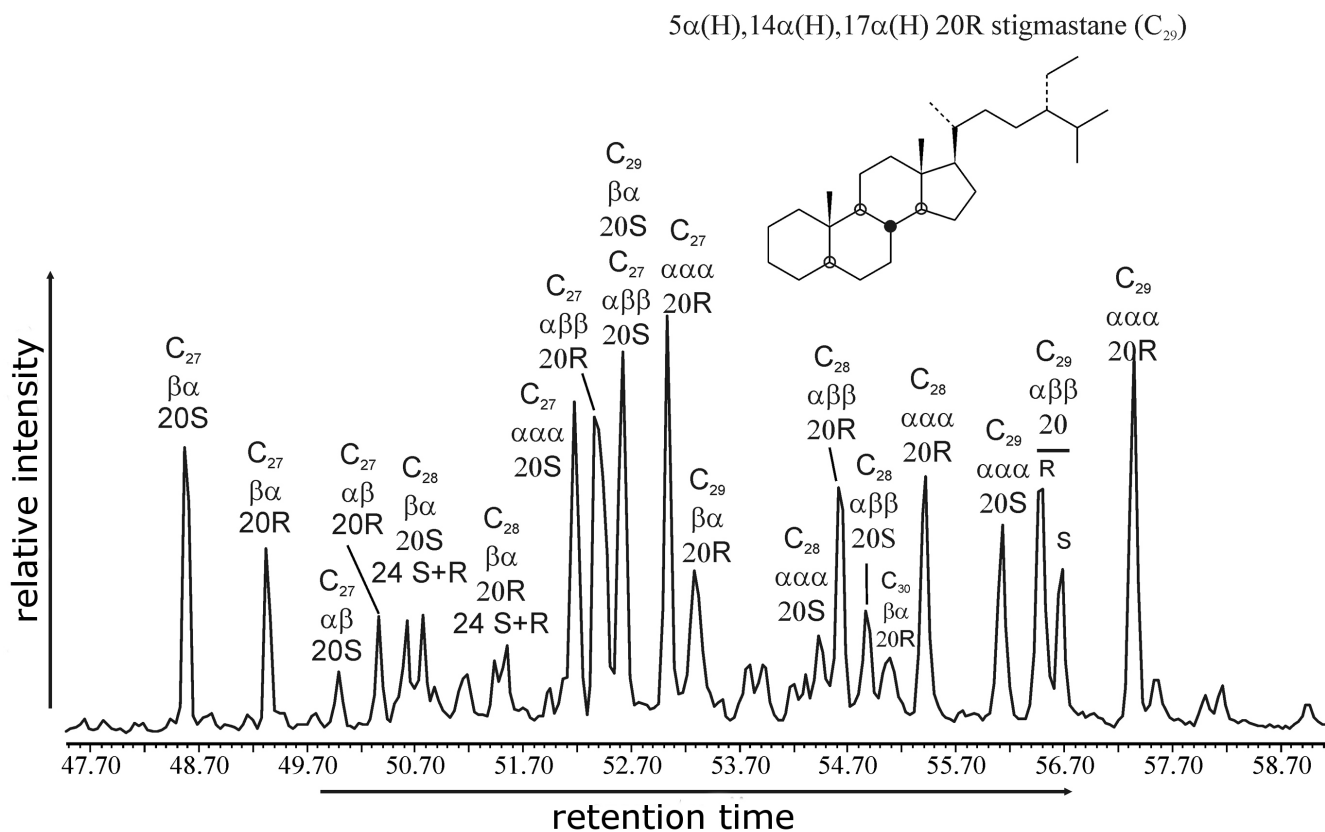
**Figure 5.** Distribution of  $n$ -alkane and isoprenoids ( $m/z = 71$ ).  $C_{16}$  –  $n$ -heptadecane, Pr – pristane, Ph – phytane, \* –  $n$ -alkanes. //

**5. ábra.**  $n$ -alkánok és izoprenoidok eloszlása ( $m/z = 71$ ).  $C_{16}$  –  $n$ -heptadekán, Pr – prisztán, Ph – fitán, \* –  $n$ -alkánok.



**Figure 6.** Fragmentograms with distributions (A) and comparison of distributions of pentacyclic triterpenoids ( $m/z = 191$ ) between flints from Wierzbica "Zełe" and Błaziny Górze (see Table 2 and 3 for identification). //

**6. ábra.** Fragmentogramok a pentaciklikus triterpenoidok ( $m/z = 191$ ) eloszlásával (A) és azok összehasonlításával (B) a Wierzbica „Zełe” és a Błaziny Górze forrásokból származó tűzkövek esetében (a jelmagyarázatot lásd a 2. és 3. táblázatban).



**Figure 7.** Steranes and diasterans ( $m/z = 217 + 259$ ) distribution for a flint from outcrop in Błaziny Górne (identification of shortcuts in Table 2 and 3). //

**7. ábra.** Szteránok és diaszteránok ( $m/z = 217 + 259$ ) eloszlása egy, a Błaziny Górne forrásból származó tűzkő esetében (a rövidítések feloldása a 2. és 3. táblázatban).