

First Report of Biomarkers from Tabriz Lignite Beds (NW Iran)

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Abstract Biomarkers are very useful tools for paleontologists, especially where the undistinguishable organic matters like Tabriz lignite cannot be attributed to particular fossils. In this study, the important detected biomarkers in Tabriz lignite beds are Oleananes (Olean-12-ene and Friedelane), beta carotene, Dibenzofuran and Gibberellic acid. The results indicate angiosperm higher and lower plants entering from adjacent areas into the lake sedimentary environment of the lignite beds. No biomarker of gymnosperm was found. The short chain even n-alkanes (C18 and C20) imply the contribution of marine microorganisms, C23 normal alkane is derived from terrestrial plants specially Sphagnum leaf wax, the existing simple methyl saturated alkanes (C11-C22) is derived from cyanobacteria and algae and thiophene formed by sulfate reducing bacteria. Thus, Tabriz lignite have two extrabasinal and intrabasinal origins that the first is made of the higher (angiosperms) and lower terrestrial plants have transported by runoffs into the basin and the second origin is made of seagrasses, cyanobacteria and algae within the lignite beds basin.

Keywords Biomarker, Cyanobacteria, Tabriz Lignite Beds

type, climate, facies variation during peat accumulation and the extent of organic matter degradation during diagenesis. In the past, coal petrological and palaeobotanical data were the primary source of information about the coal forming environment and the ecology of peat formation. In more recent times, biomarker analysis of the soluble organic matter of coal has increasingly contributed to the understanding of the palaeoenvironment in the mires and has provided clues to the botanical input involved in their formation [10-15]. The organic matter content of lake sediments can be small or large, but its paleolimnological importance is always great. Its composition includes a variety of elemental, isotopic, and molecular indicators or proxies that can be used to reconstruct paleoenvironments of lakes and their surrounding land areas. The organic matter originates from the complex mixture of lipids, carbohydrates, proteins, and other biochemical components produced by the various organisms that have lived in and around the lake. As an accumulation of “geochemical fossils”, the organic matter components in lake sediments provide information that can be used to reconstruct natural and human-induced changes in local and regional environmental systems [16]. In this paper, we study the biomarkers of Tabriz lignite beds and identify the organisms from which they originated.

1. Introduction

Biological markers or biomarkers [1, 2] are molecular fossils, meaning that these compounds originated from formerly living organisms. Biomarkers are useful because their complex structures reveal more information about their origins than other compounds [3]. Coal and lignite beds are important geological, paleontological and geochemical samples that can provide essential information for terrestrial paleoenvironment and paleoclimate as well as paleobotany. Recently, biomarker investigation of coal and lignite have been performed, and contributed to the understanding of coal-forming paleoenvironment [4-9]. The characteristics of coal are influenced by many different factors, like vegetation

2. Materials and Methods

2.1. Geological Setting

The Tabriz fault led to the formation of the Tabriz Basin in the Late Miocene [17]. The Neogene basin fill is composed from bottom to top of the Lignite Beds and the Fish Beds; the latter are overlain by Quaternary alluvial conglomerates [18]. Lignite and Fish Beds represent lake and swamp deposits with intercalations of volcanic ashes and tuffs. The Lignite Beds are up to 400 m thick and can be subdivided into a lower member, consisting of clay, mudstones, coarse-grained sandstones and conglomerates, and an upper member, comprising mudstones, fine-grained sandstones, thin carbonate layers and lignite [19].

2.2. Sample Collection

The study area is under the influence of Tabriz fault. The studied section is the complete section in sampling time that has located at 38° 03' N and 46° 25' E coordinates. The lignite samples were collected from the upper member of the

lignite beds at east of Tabriz city, on the heights of the Sari-Dagh Mountains at Baghmishah town (Fig. 1). The samples were collected in random. Each sample is about 40 gm. The geological map and the stratigraphic column of the studied section are shown respectively in Fig. 2 and Fig. 3.



Figure 1. A part of Tabriz overturn Lignite beds on Sari-Dagh Mountains at Baghmishah town. The white circles show some of random sampling positions.

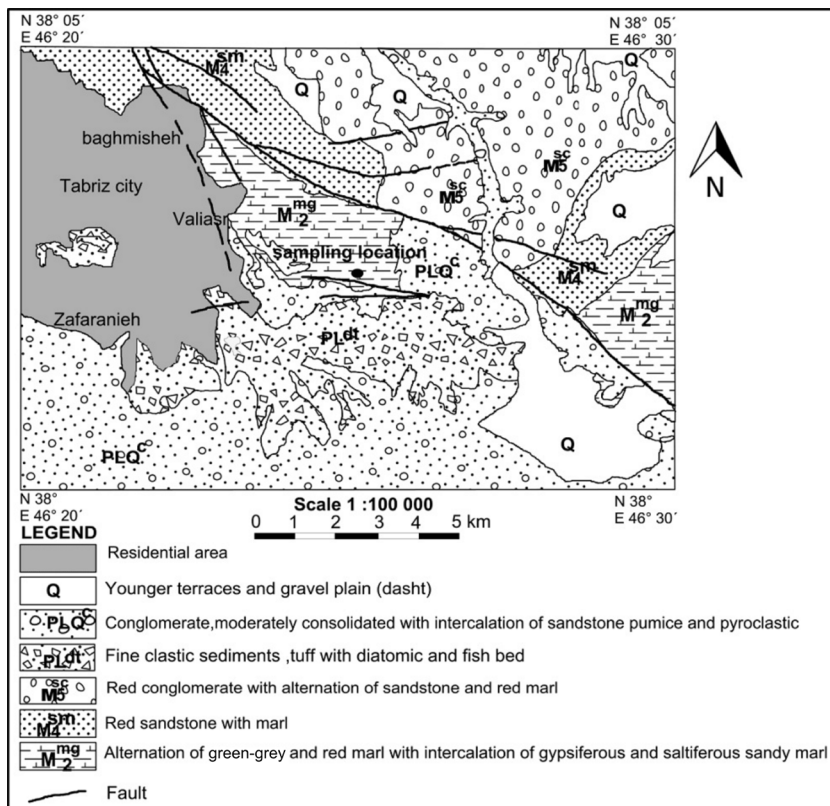


Figure 2. Geological map of the Tabriz Basin showing the location of the studied section on the lignite beds (M₂^{mg}) at Baghmishah. Source: Geological map of Tabriz 1:100000 [20].

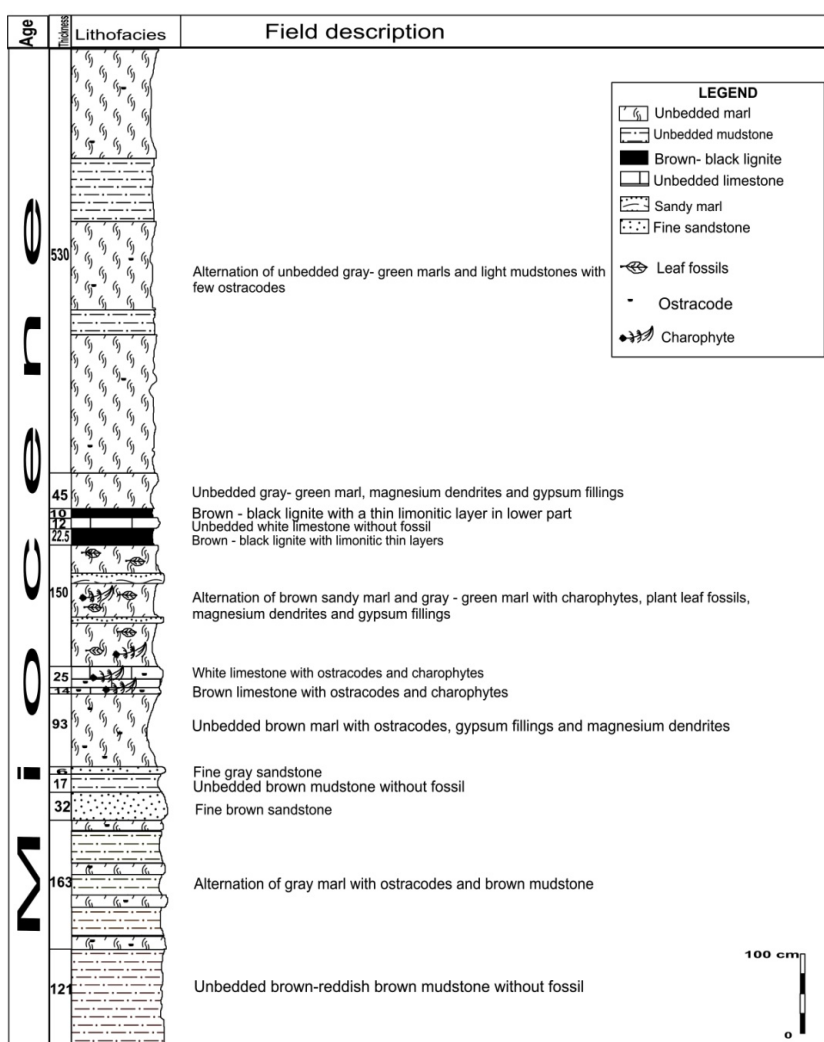


Figure 3. Stratigraphic column of the studied section on baghmisheh showing the lithofacies and the position of lignite beds.

2.3. Lab Analysis

Tabriz lignite beds are exposed at east of Tabriz city. Unfortunately, as for residential area development and excavations of Tabriz city toward east, the lignite beds were destructing and we tried to find more samples in a best a complete section. The experiments were performed on 24 handpicked lignite samples. The samples were crushed and powdered. We mixed them to obtain an average sample. The bitumen of 20 gm of the average sample was extracted by Soxhlet apparatus (for 40 h) with 500 ml of benzene and ethanol (1:1) solvent. For asphaltene precipitation, the sample was dissolved in chloroform and the obtained solution was poured in cold hexane (ice bath). After making filtration, for chloroform evaporation, the oil fraction (maltenes) was concentrated by rotary evaporator. Obtained maltenes in this step (0/107 gm), was dissolved in dichloromethane and was poured on a small amount of silica gel. The silica gel was leaved to dry the dichloromethane overnight. The sample covered the surface of the silica gel uniformly. This silica gel containing the sample was placed

on top of a small column of silica gel and the fractions were eluted as follows: Fractions were eluted with n-hexane (aliphatics or saturates), CH₂Cl₂ (unsaturates) and acetone (resins). Our biomarkers are saturated and unsaturated fractions that were detected by Gas chromatography– mass spectrometry. According to Stefanova [21], GC–MS analysis of the extracted fractions were performed on a Agilent6890n GC coupled to AgilentS973n quadrupole MS. Separation was achieved on a fused silica capillary column (HP 5MS, 0.25mm× 30mm× 0.25µm). The GC operating conditions were as follows: temperature hold at 65 °C for 2 min, increase from 65 to 300 °C at a rate of 6 °C/min with final isothermal hold at 300 °C for 20 min. Helium was used as the carrier gas. The sample was injected splitless with the injector temperature at 300 °C. The mass spectrometer was operated in the electron impact mode (EI) at 70 eV ionization energy and scanned from 50 to 650 Dalton [21].

3. Results

In the studied section, the lignite beds are two layers with 10 and 22.5 cm thickness (Fig. 1 and 3). They are brown-black. There is a layer of unbedded white limestone with 12 cm thickness, without fossil between the lignite beds. In bottom of the lignite we have brown sandy and gray-green marls with charophytes, plant leaf fossils, magnesium dendrites and gypsum fillings. These lignite beds are overlain by unbedded gray-green marls with magnesium dendrites and gypsum fillings. Fig.3 shows the stratigraphic column of the section on Baghmisheh area. Dominance of unbedded marls in bottom and top of lignite beds indicate fewer depths of sedimentary basin borders. Magnesium dendrites, gray-green marls and also the lignite beds indicate reduction conditions and the gypsum fillings imply the warm and dry climate. Thus, according to witnesses, the reduction and humid condition has been dominant. The sampling location has been specified at the east of Tabriz city on

alternations of marls with intercalation of gypsiferous sandy marl with M_2^{mg} symbol on the geological map of Tabriz basin (Fig. 2). The TICs (Total ion current) of the biomarkers containing fractions are shown in Figs. 3 and 4. They show abundance vs retention time of biomarkers. Each of the peaks represents the signal of a compound and we paid attention to essential biomarker compound peaks. Fig. 4 shows the saturated fraction. The important biomarkers in this fraction are Cholestane, Friedelane (a saturated oleanane), some simple branched alkanes, medium chain length C_{23} n-alkane and even n-alkanes (C_{18} , C_{24}). Fig. 5 shows the unsaturated fraction and the essential biomarkers in this fraction are Beta carotene, Gibberellin acid, Oleane-12-ene (an unsaturated oleanane), Dibenzophurane, and Thiophene. We interpreted these peaks and recognized the organisms which they have originated from them (refer to discussion).

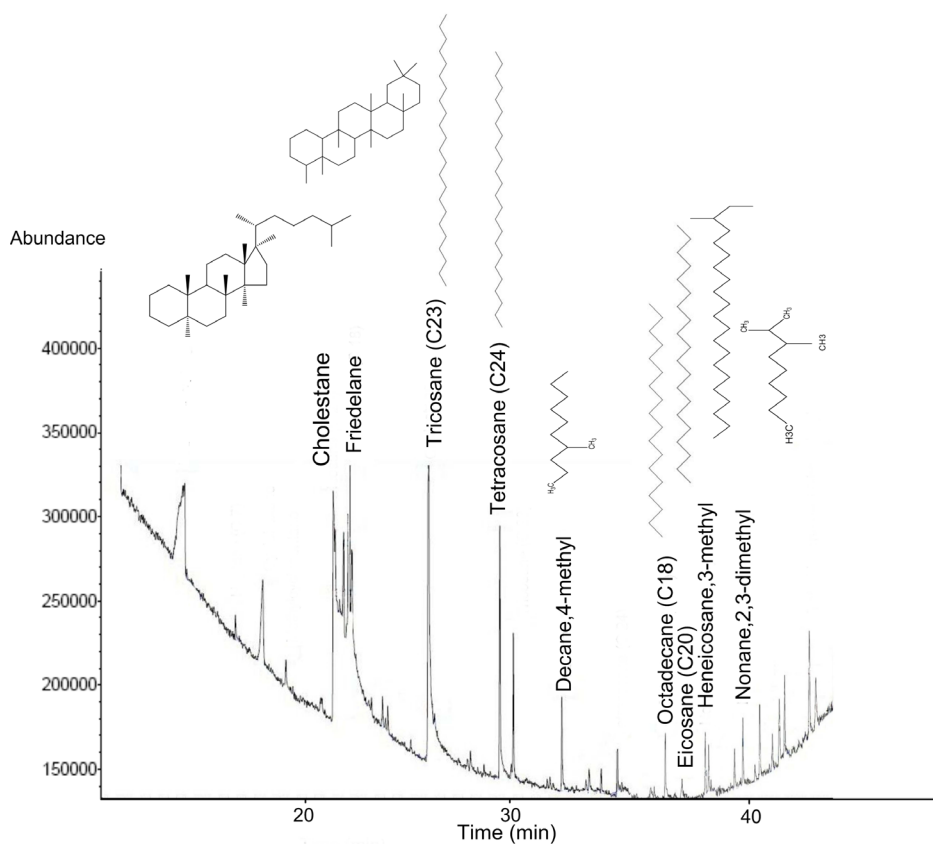


Figure 4. TIC (Total ion current) of the saturated fraction .

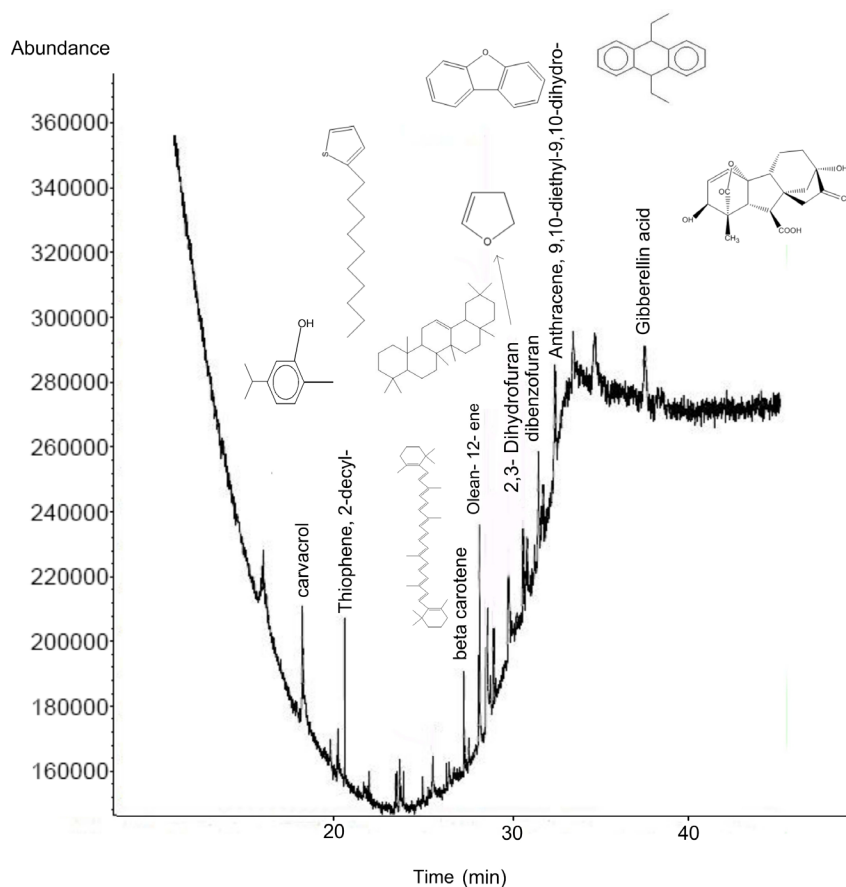


Figure 5. TIC (Total Ion Current) of the Unsaturated Fraction.

4. Discussion

Biological marker (biomarker) molecules are compounds that characterize certain biotic sources and retain their source information after burial in sediments, even after some alterations. Biomarkers in geologically old sediments and rocks are usually stabilized derivatives of their precursor compounds [16]. Here we have studied the saturated and unsaturated fractions for biomarkers.

4.1. Saturated Fraction

In saturated fraction (figure 4), we have the n-alkanes ranging from C18 to C24. The distribution of n-alkanes demonstrated the predominance of even carbon n-alkanes C18 and C20 and C24. The predominance of these short chain even n-alkanes (C18 and C20) indicates the contribution of marine microorganisms and petroleum products to the organic matter of sediments [23-25]. The C14 to C20 n-alkanes which are mostly derived from plankton and benthonic algae, are presumed to be abundantly available since Precambrian time [26]. Wiesenberg [27] showed that charring of grass biomass at 400 to 500°C produces exactly such n-alkane patterns. The long chain C23 odd carbon n-alkane was also present. This long chain odd carbon n-alkane is derived from terrestrial plants [28-32]. The dominance of C23 n-alkane has only been observed in

Sphagnum [33,34], submerged/floating aquatic macrophytes [35], seagrass and associated sediments [36,37], Antarctic soils [38] and laminated carbonates from the Franconian Alb, SW-Germany [39]. Common rust fungus (*Puccinia graminis* f. sp. *avenae*) contained high abundant n-C23 alkane in its airborne urediospores [40,41]. Also, Nichols [43] believe that sphagnum leaf wax is characterized by medium chain length (C23–C25) n-alkanes [33,42,43]. Simple branched alkanes are found in many species of cyanobacteria [44] and in algal mats and lagoonal sediments [45]. Therefore, it can be concluded that Decane, 4- methyl, nonane, 2, 3- dimethyl and heneicosane, 4- methyl branched alkanes maybe are derived from cyanobacteria and algal mats. Cholestane (C₂₇H₄₈) is a cyclic triterpenoid that represents in the saturated fraction. The dominance of cholestane may partly reflect the preservation of animal steroids [46]. Oleanane is a biomarker characteristic of angiosperms (flowering plants) found only in Tertiary and Upper Cretaceous rocks and oils [3]. Friedelane (a saturated oleanane) is a pentacyclic triterpene that is seen among the saturated biomarkers.

4.2. Unsaturated Fraction

Figure 5 has shown the unsaturated fraction. In this fraction we have these biomarkers: Carvacrol (2- methyl-5- (1-methylethyl)- phenol) (C₁₀H₁₄O) is a predominant monoterpenic phenol which occurs in many essential oils of

the Labiatae family including *Origanum*, *Satureja*, *Thymbra*, *Thymus* and *Corydothymus* species [47] that its frequency is significant. Olean-12-ene is an unsaturated oleanane that as said it implies to presence of flowering plants and the tertiary age. Beta-carotene, $C_{40}H_{56}$, is one of several carotene isomers occurring in many lower and higher plants [26]. This tetraterpane presence is significant in this fraction. Also, many phases of plant growth and development are affected by the "gibberellins", which can be grouped among the cyclic diterpenoids. They occur, usually in small quantities, in all higher plants [48,26]. Gibberellic acid ($C_{19}H_{22}O_6$) is a gibberellin that is seen in the second fraction. Dibenzofuran (DBF), the derivatives of methyl dibenzofurans (MDBFs) and dimethyl dibenzofurans (DMDBFs) were identified as the oxygen-containing Compounds. In general, DBF is derived from the lower plants such as lichen and/or polysaccharide in terrestrial soil [49,50,51]. Thiophene is a sulphur-containing compound. Sedimentary organic sulfur compounds result from a reaction of reduced inorganic sulfur species, formed by sulfate reducing bacteria, and functionalized lipids during early diagenesis ("natural sulfurization") [45].

For the first time, Reichenbacher [19] have described the fossil fish and ostracod fauna and the diatom assemblages from both the Lignite Beds and Fish Beds. All fossil groups are characterized by the occurrence of freshwater and brackish forms; additional marine– euryhaline taxa appear among the fishes and diatoms. They believe the fossil assemblages indicate a new palaeogeography for the Late Miocene of the study area, with temporary connections between the Tabriz Basin and the southern Caspian Sea, perhaps via an ancient Araks River passage [19]. On the other hand, the C11 to C23 n- alkanes are obtained in the organic matter extracts from the Rhaghavapuram shales indicate marine inputs to the sedimentary organic matter [22]. Then it could be said that the marine biomarkers (C18 and C20 n- alkanes) among the Tabriz lignite lake biomarkers are probably because of marine inputs of the southern Caspian Sea to Tabriz sedimentary basin. Then, organic matters formed within the Tabriz Lake have marine and lake origins. Also, Tabriz lignite contains abundant terrigenous organic compounds such as dibenzofuran concentration and continental plant debris; we suppose that the large amount of terrigenous matters were transported to the Lignite beds basin by runoffs during the Lignite beds formation time. Therefore, Tabriz lignite has form from continental, marine and lake organisms.

5. Conclusions

In this study, the biomarkers of lignite are extracted from Tabriz Lignite Beds for the first time. The biomarkers in this formation such as cholestane, beta-carotene and oleananes indicate clastic material of angiosperm higher plants inputs into the basin and by ignoring gibberellic acid that exist in all high plants, there is no gymnosperm biomarker among these

markers. In addition, the biomarkers such as normal and branched alkanes imply the presence of marine microorganisms (submerged /floating aquatic macrophytes, cyanobacteria and algae) and terrestrial plants at the formation time of this lignite. Therefore, lignite forming organic matters has two sources: extrabasinal and intrabasinal source. The extrabasinal source is debris of the high plants that were around the basin and the intrabasinal source is the seagrasses, cyanobacteria and algae that have lived within the basin during Miocene.

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