The Origin and Characterization of Soluble Organic Matter in the Phosphate Rock (Mardin-Mazıdağı-Turkey)

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Summary: In this study, the origin and structure of the soluble organic matter in the phosphate rock was investigated. The organic matter was extracted with n-hexane from the phosphate rock. Its structure was analyzed by using TG, GC-MS, FTIR and NMR. GC-MS results showed that the organic matter had a complex structure and had a modal distribution ranging between C_9 to C_{35} and maximizes at C_{10} and C_{14}. The presence of n-alkanes with even/odd carbon predominance indicates the intense microbial reworking of the organic matter taking place in this depositional environment. The Carbon Preference Index (CPI) was 0.71 in which major microbial sources exist. ^{1}H NMR and ^{13}C NMR spectra of the phosphate rock also confirmed these results. FTIR results showed that the bands obtained from organic matter exhibits a phospholipid characteristic which is a component only of living cells and, as such, a measure of viable biomass.

Keywords: Phosphate rock, organic matter, phospholipids, surface sediment, even n-alkanes.

Introduction

Most of the known world phosphate rock reserves are the sedimentary deposits of the Upper Cretaceous and Eocene ages of the Mediterranean phosphogenic province which exist in Morocco, Algeria, Tunisia, Egypt, Sahara, Israel, Jordan, Syria, Spain, Saudi Arabia, Turkey, and Iraq. The phosphate rock deposits in the Upper Cretaceous and Eocene ages are important reserves because of being more than 70% of the total world phosphate reserves [1].

It was reported that the Mazıdağı (Turkey) phosphate rock situated near the border with Syria was deposited during the Turonian and Senonian (Cretaceous) ages [2]. They investigated the phosphatic formations in Mazıdağı. They found that these phosphorite deposits occurred as a result of the following steps; erosion of calcitized deposits, redeposition in a phosphatizing environment, phosphatization of this detritus material and weathering causing an enrichment of the ores [2]. The Mazıdağı phosphate rock is mainly composed of calcite, fluorapatite, and carbonate-fluorapatite [3].

This organic matter emits volatile compounds that damage environment and lead to the formation of foam that complicate the process of filtering in the phosphoric acid production, known as wet process. The organic matter not only has harmful properties but also provides lower energy expenses in the retorting processes. In addition, when the phosphate rock is directly applied to enrich the soil, the organic matter is useful for providing the carbon needed [4].

Sedimentary hydrocarbons are complex structures. n-alkanes are one of the biomarkers in the geochemical literature. A biomarker can be best thought of as an organic compound in a geological sample which is structurally related to its precursor molecule, which in turn occurs as a natural product in higher plants, algae, bacteria, or any other potential source material [5]. If a specific set of biomarker parameters can be assigned to a clearly defined depositional environment, it will permit recognition of this type of environment in previously unexplored regions. In many cases the presence of a particular biomarker can be attributed to a specific organism that will grow only in definite conditions [6]. The distribution of n-alkanes can be defined by using chromatography techniques. These analyses show whether n-alkanes in both phosphatic and nonphosphatic shale have either odd or even carbon predominance. The Carbon Preference Index is given with the abbreviation of CPI [7]. This value indicates an odd carbon number predominance versus even carbon number predominance for n-alkanes. This analysis gives us information about the origin of organic matter. It was found that the normal-alkanes possessed no odd or even carbon predominance. Thus, it was derived from marine plankton and microorganism as a result of the analysis [8-10]. In the previous studies, it was frequently reported that n-alkane predominance with odd carbon shows the feature of higher plants [11]. There are very few studies about the unusual predominance of even-numbered alkanes which may indicate the microbiological origin or some petroleum pollutants.

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The lower CPI shows microbial sources of hydrocarbons [12-15].

The lipids (organic matter) are extracted with organic solvents from soils or sediments. Free lipids can be obtained by direct treatment, but bound lipids can only be obtained after acid destruction of the mineral matter [11].

The lipid compounds often contain the basic skeletal structure and functional group details of the original source [16]. Therefore, the investigation of lipid compositions in various recent depositional environments can provide much information about the source and diagnetic processes of organic matter and, furthermore, these data can be used to reconstruct paleoenvironmental conditions of the deposition [17, 18].

In this study, it is aimed to investigate the structure of soluble organic matter in the Mazıdagı phosphate rock by using GC-MS, FTIR, NMR and TG. It is expected to gain an understanding of the geological history of the phosphate genesis and elucidate the origin of embodied organic matter.

Results and Discussion

To check the purity of the soluble organic matter obtained after extraction, the sample was analyzed in TG between the temperatures of 25°C to 540°C. The TG curve of the soluble organic matter at a heating rate of 5°C min^{-1} in N_2 atmosphere is shown in Fig. 1. The mass loss took place on one stage up to 540°C which indicates the purity of the organic matter.

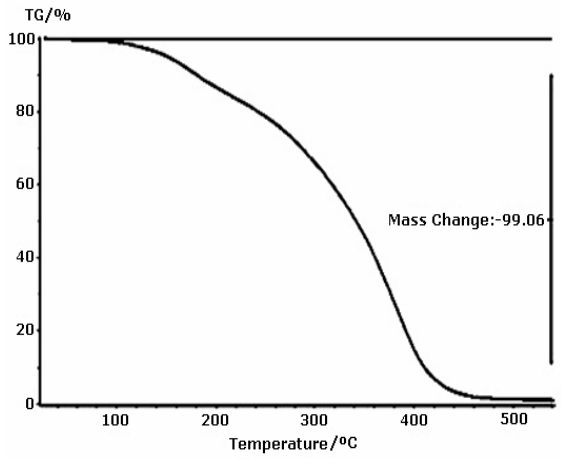

Fig. 1: TG curve of the hydrocarbons extracted from the phosphate rock.

^{1}H-NMR spectra of the oils obtained by extraction with hexane are shown in Fig. 2. The ^{1}H-NMR spectra were divided into three regions of interest based upon the chemical shifts of specific proton types. Aliphatic resonance, heteroatom (especially oxygen atoms) content in aliphatic (CH_3)-groups, and olefinic proton resonances obtained between the ranges of 0.8-2.4 ppm, 4.0-4.4 ppm, and 5.4-5.8 ppm, respectively.

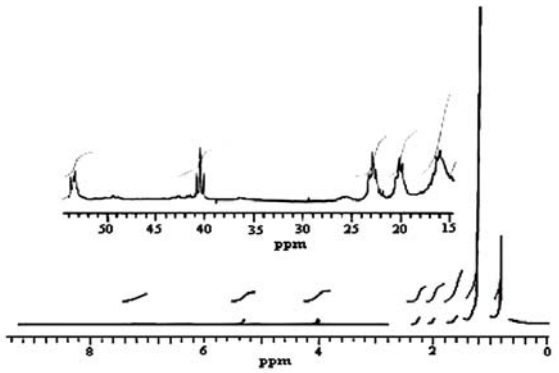

Fig. 2: ^{1}H-NMR (200 MHz, $CDCl_3$) spectra of hydrocarbons extracted from the phosphate rock.

The ^{13}C-NMR spectra are shown in Fig. 3. Quaternary carbon atom resonances, olefinic carbon atom resonances, and the large hydrogen content in aliphatic CH_3-, CH_2-, group resonances are observed in 175.6 ppm, 140-144 ppm, and 16-40 ppm, respectively.

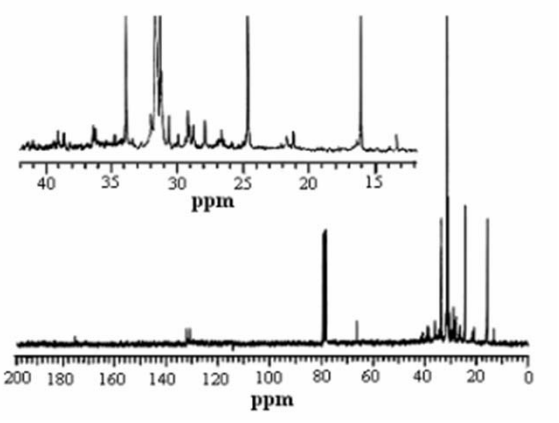

Fig. 3: 13C-NMR (50 MHz, CDCl3) spectra of hydrocarbons extracted from the phosphate rock

The infrared spectra data of hydrocarbons are shown in Table-1. The FTIR spectrum of the

extracted matter is illustrated in Fig. 4. The CH_2 stretching vibrations are the most intense vibrations in the infrared spectra of lipid structures. Their bands appear at the ranges of 3100-2800 cm^{-1}. The CH_2 asymmetric and symmetric stretching modes are generally located at 2925.07- 2854.31 cm^{-1}. These are the infrared bands due to CH_3 groups at 2954.65 cm^{-1} indicating asymmetric stretching. Methylene and methyl groups are located in the 1500-1350 cm^{-1}. The bands located at around 1470 cm^{-1} shows CH_2 bending. The symmetric deformation of the CH_3 group mode appears at 1377.35 cm^{-1} and the asymmetric deformation modes are switched off by scissoring bands [19].

Table-1: Major infrared bands of lipids.

Wave numbers	Assignment
2954.65	CH_3 asymmetric stretching
2925.07	CH_2 asymmetric stretching
2854.31	CH_2 symmetric stretching
1739.96	C=O stretching
1464.95	CH_2 scissoring
1377.78	CH_3 symmetric stretching
1171.19	CO-O-C asymmetric stretching
1081.25	PO_2^- symmetric stretching
969.64	$(CH_3)_3N^+$ symmetric stretching
721.89	CH_2 rocking

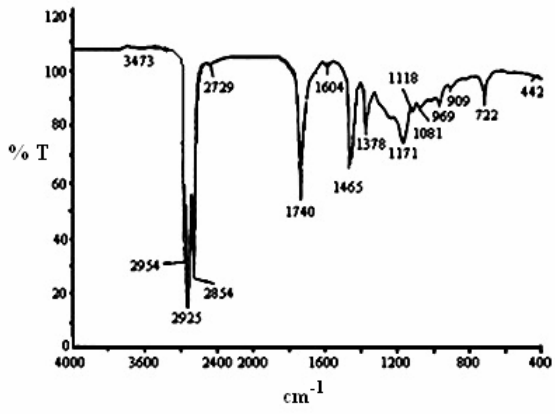

Fig. 4: FTIR Spectra of hydrocarbons extracted from the phosphate rock.

Hydrocarbons from extraction were analyzed by GC-MS. In Fig. 5, this chromatogram shows the presence of n-hydrocarbons. It is known that the distribution of n-alkanes is the most widely reported classes of biomarkers in the geochemical literature. The distribution of linear alkanes is given in Fig. 6. Gas chromatographic analysis reveals that the distribution of n-alkanes ranges from *n*-C_9 to *n*-C_{35}. This suggests that the extracted matter has a relatively large fraction of light and long chain hydrocarbons. The hydrocarbon concentration passes through a minimum near *n*-C_{20}. It is a maximum at n-C_{10} and n-C_{14}, there was a minor predominance in the *n*-C_{16} to *n*-C_{35} region. As can be seen from Fig. 6, it has the even carbon number predominance. It was found that CPI value was 0.71. This value (below 1.0) is unusual. Similar even/odd predominance of n-alkanes was observed at the surface sediments in the Arabian Gulf [13] and Black Sea [14]. A distribution in an apparently well-oxygenated system which may be resulted from an autochthonous origin possibly bacterial for these alkanes was also reported elsewhere [13]. The results may permit speculation on the even/odd predominance of n-alkanes that may result from marine organisms as well as specific conditions in the depositional environment [6, 12, 13, and 20]. The even predominant n-alkanes in the lower molecular range may also be attributed to some mixed petroleum pollutants [21]. The FTIR result of extracted organic matter was similar to the results of the phospholipids. The structure of phospholipids is given in Fig. 7. The structure of the phospholipid has a component only of living cells and, as such, a measure of viable biomass [22], because biogenic parameters are composed of C, N, and P elements.

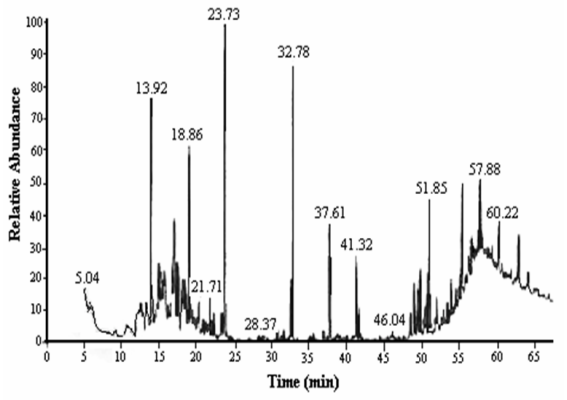

Fig. 5: GC-MS Spectra of hydrocarbons extracted from the phosphate rock.

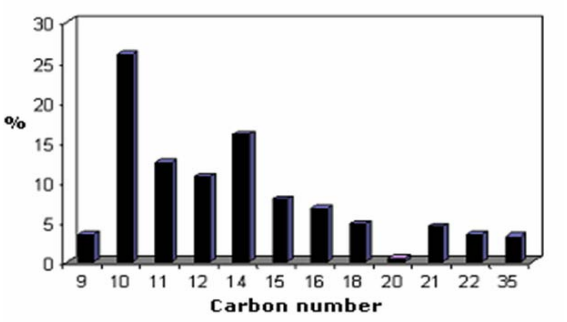

Fig. 6: Distribution of linear hydrocarbons extracted from the phosphate rock (percentage of the neutral fraction)

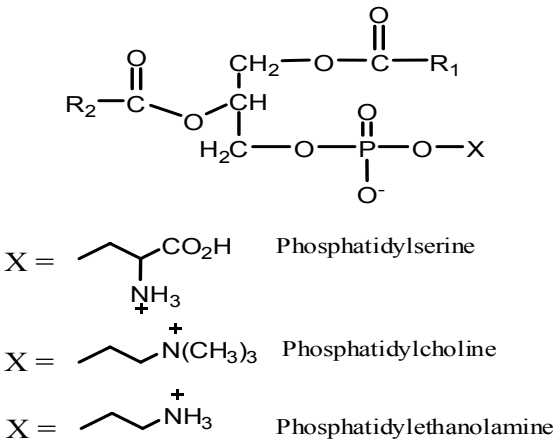

Fig. 7: Structure of phospholipids.

Experimental

Materials

Phosphate rock used in this study was provided from the Mazıdağı phosphate deposits. The sample was crushed, ground and then sieved to obtain a fraction of 100 µm. A detailed mineralogical study on the phosphate rock can be found elsewhere [23].

The results of X-ray powder diffraction analysis showed that the main minerals of the rock are calcite, fluorapatite and carbonate-fluorapatite. The chemical analysis of the phosphate rock was carried out by standard gravimetric, volumetric and spectrometric methods, and the results of chemical analysis are given in Table-2.

Sample Preparation

100 g of dried phosphate sample having particle size of 100 µm was extracted with *n*-hexane in soxhlet for 48 h. After the extraction, the extract was distilled on the rotavapor to remove *n*-hexane from organic matter. Then, the organic matter was dried at 80°C. Its structure was analyzed by using TG, GC-MS, FTIR and NMR.

Analysis

Gas Chromatography-Mass Spectrometry (GC-MS)

The analysis of the organic matter was performed using a Thermofinnigan Trace GC/ Trace DSQ/ AI 1300, (E.I Quadrepole) equipped with a SGE-BPX5MS capillary column (30 m x 0.25 µm). For GC-MS detection, an electron ionization system with ionization energy of 70 eV was used. Helium was the carrier gas, at a flow rate of 1 mL/min. MS transfer line temperature was set to 250°C. Temperature program was as follows; initial temperature was 50°C and raised to 150°C at a rate of 3°C/min, hold for 5 minutes at 150°C, raised to 270°C at a rate of 6°C/min and finally hold for 10 minutes at 270°C. Diluted samples (1/100, v/v, in methylene chloride) of 1.0 µL were injected manually in the split less mode. The components were identified based on the comparison of their relative retention time and mass spectra with those of standards, Wiley7N, TRLIB library data of the GC-MS system and literature data.

Thermogravimetric analysis (TGA)

TGA was performed to determine the purity of the soluble organic matter obtained after the extraction. TGA was carried out with a Netsch STA 409 PC Luxx thermal analyzer.

^{1}H NMR - ^{13}C NMR

The ^{1}H NMR spectra were recorded on an advance 200 MHz Varian NMR spectrometer. The chemical shifts are given with respect to tetramethyllesilane (TMS) taken as an internal reference.

Solid state ^{13}C NMR spectra of the soluble organic matter were obtained with a Varian spectrometer operating at 50 MHz and equipped with cross-polarization and magic angle spinning (CPMAS). The chemical shifts were calibrated with respect to tetramethyllesilane (TMS).

Fourier Transform Infrared (FTIR)

FTIR spectra of the soluble organic matter were recorded in the range of 4000-400 cm^{-1} on a Perkin Elmer spectrometer. Prior to recording of spectra, the disk was evacuated at 150°C until complete elimination of water.

Table-2: Chemical Analysis of the Phosphate Rock.

Compounds	P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	SiO_2	F_2	Loss on ignition	others
wt (%)	30.46	50.87	2.24	0.23	1.19	0.55	1.56	12.68	0.22

Conclusion

The structure and origin of the soluble organic matter in the phosphate rock was investigated. ^{1}H-NMR, ^{13}C-NMR studies indicated that it has rather aliphatic nature. GC-MS results supported that the organic matter has predominance of the even carbon and comprised of long and light hydrocarbon chains and showed a modal distribution in the ranges of *n*-C_9 to *n*-C_{35} and maximizes at *n*-C_{10} and C_{14}. n-alkanes in these ranges had considerably excess total amounts. The main components have even carbon numbers $C_{(10\text{-}12\text{-}14\text{-}16\text{-}18\text{-}20\text{-}22)}$. $C_{9\text{-}35}$ short modes are arised from the typical of organic matter resulting from the decomposition of micro-organisms. All lipids with < C_{20} are the microbial diagnetic process sources [15]. The FTIR results confirmed that the presence of sediment phospholipids is representative of the living biomass community within sediment and may closely reflect the ecological status of the community.

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