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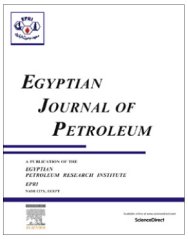

FULL LENGTH ARTICLE

Preliminary study of metalloporphyrins in some oil shales, red sea, Egypt

S.M. El-Sabagh, S. Faramawi, Fatma M. Harb *, M. Farouk

Egyption Petroleum Research Institute, Nassr City, Hei-Al-Zehour, 11727 Cairo, Egypt

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KEYWORDS

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Abstract Occurence and distribution of metalloporphyrins were studied in asphaltene and maltene fractions of some Egyptian oil shales from the main producing mines (Abu-Shegeili, El-Beida, El-Nakheil and Abu-Tundub I, II) in red sea area (Fig. 1).

Metalloporphyrins were extracted using adsorption column chromatography. The presence of Ni, Fe and Vo-porphyrins was monitored in each fraction by means of UV–Visible spectrometry, the result indicated that metalloporphyrins could be a mixture of Etio and DPEP types. Each fraction using UV–Visible spectrometry cannot differentiate between Ni and Fe porphyrins, so the extracted metalloporphyrins were subjected to purification and separation from each other by using thin layer chromatography (TLC).

HPLC was used for fingerprinting Vo, Ni and Fe-porphyrins, it was found that the different porphyrins exhibited wide different chromatograms. HPLC technique could be used as a successful tool to characterize Fe and Ni-porphyrins.

1. Introduction

1.1. Chemistry of metalloporphyrins

Oil shale can be defined as an organic rich sedimentary rock from which oil and or gas can be produced by pyrolysis [1]. Oil shales consist of organic and inorganic compounds [2]. The organic material is normally classified into two components, natural bitumen (smallest fraction) and kerogen (major fraction). The inorganic part consists mainly of quartz, clay, different types of carbonates ($CaCO_3$, $mgCO_3$) pyrite and Fe_2O_3 besides trace elements such as, B, Mo, Ni, V and Fe [3,4]. Trace elements have been used to characterize crude oils, soluble organic matter in sedimentary rocks, insoluble organic matter (kerogen) of petroleum source rocks and oil shales [5–7].

The most studied metal complexes associated with petroleum, in source rocks and oil shale are Ni and Vo porphyrins. Oil shale is generally known to have much lower concentrations of Ni and Vo (10 ppm in average) and have different metals in the porphyrins ring such as Fe [8]. The total metal content of crude oil can provide a distinctive fingerprint which has been used to correlate oils with source rocks [9] (see Fig. 1).

* Corresponding author.
E-mail address: fatmaharb1@yahoo.com (F.M. Harb).

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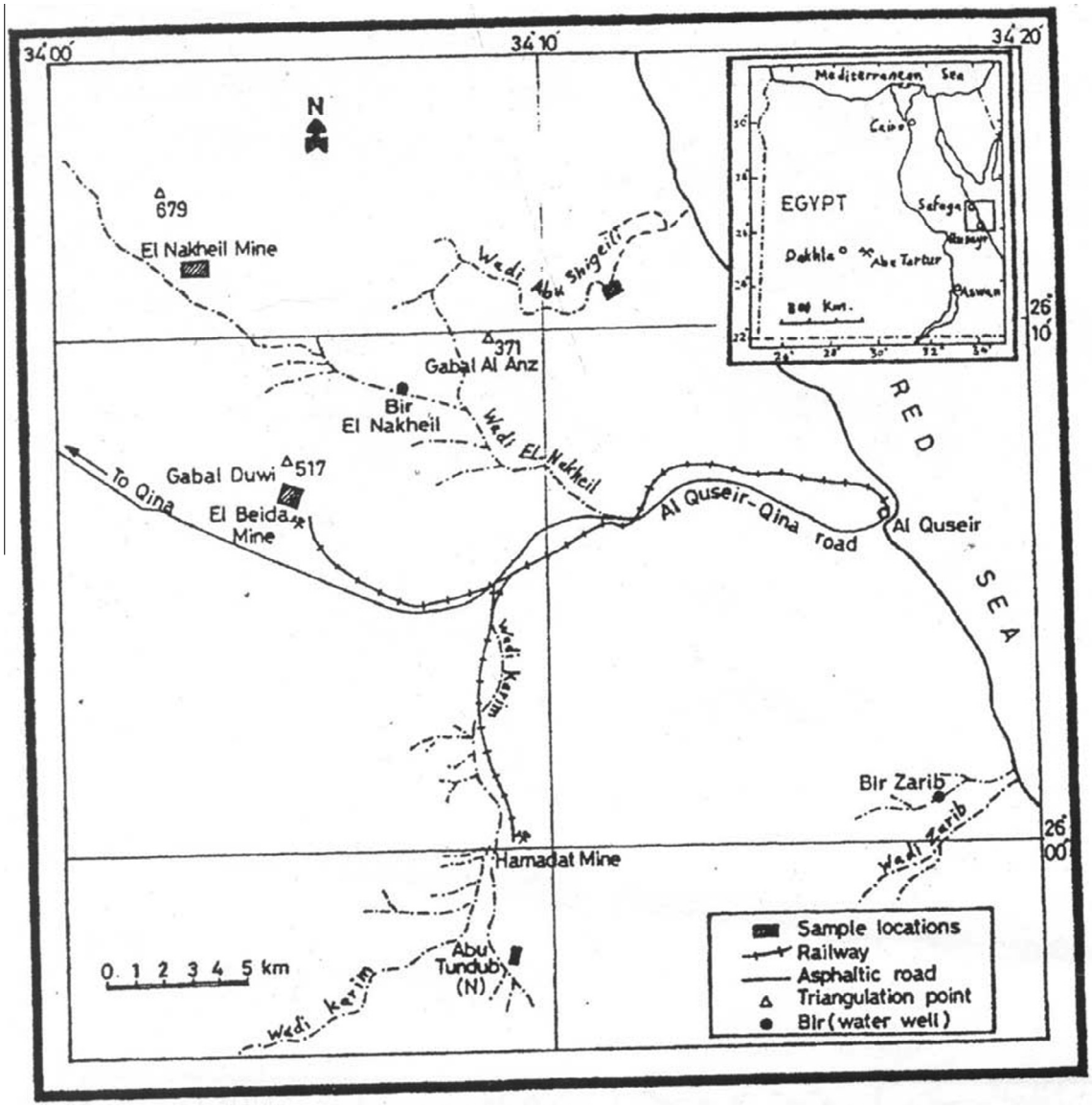

Figure 1 Location map of the oil shale samples.

1.2. Structure of porphyrins

Porphin nucleus consists of four pyrrole rings joined by four methene bridges giving a cyclic tetrapyrrole structure Fig. 2. Treibs [10] was the first one who isolated and identified the major metalloporphyrins in petroleum and oil shale and he proved that petroleum was derived from plant and animal organic remains and thus explained the origin of petroleum. Porphyrins are important biological markers in which their carbon skeletons are preserved after having undergone accumulation and diagenesis that can still be correlated with the original biological precursors.

The literature [11–13]reported the presence of five main porphyrins: two major types series, etioporphyrins (Etio) and deoxophylloerthroetioporphyrin (DPEP) and three minor series, tetrahydrobenzoDPEP (THBD), benzo (rahodo) Etio and benzo (rhodo) DPEP, Fig. 2.

In the present work the metalloporphyrins in bitumen fraction of five oil shale samples namely Abu-Shegeili, El-Beida, El-Nakheil and Abu-Tundub I, II were isolated and characterized by the aid of different techniques in order to shed light on the distribution of Ni, Vo and Fe-porphyrins, and finding an appropriate tool to differentiate between Ni and Fe-porphyrins.

2. Materials and methods

2.1. Preparation of oil shale samples

Five oil shale samples Table 1 were grinded, then sieved and an accurate weight of a portion of <200 mesh was dried over night at 100 °C then weighted and the percentage of moisture could be calculated from the weight loss.

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