3 Methods of investigation

The preparation of samples and the analyses of the samples were carried out in the laboratories of the Institute of Applied Geosciences at the Faculty of Civil Engineering and Applied Geosciences, Technical University of Berlin, Germany.

3.1 Mineralogical analysis

3.1.1 Separation of clay size fraction

From the original 144 samples, one hundred and one were chosen for powder XRD. Depending on the XRD powder results the samples were selected for clay mineralogy and XRF.

Fourty eight shale samples were analyzed by X-ray diffraction. The clay size fraction (less than 2μm) was investigated in order to give information about the clay mineralogy of the studied shales. About 25 g of the rock sample was soaked in distilled water after adding 5ml/l of 0.1m. $Na_4P_2O_7.10H_2O$, and disintegrated with a shaker machine. The clay fraction (<2 μm) was separated out from the sample by centrifugation. The <2 μm suspension was dried on glass slides. The oriented mounts were run under three conditions:

i) In air dry state.

ii) After ethylene glycol treatment.

iii) After heating to 550° C for 1 hour.

3.1.2 X – ray Diffraction (XRD)

The bulk samples and the clay fractions were examined by a Philips X-ray diffractometer PW1710, with Ni filtered CuKα radiation using 50 kV/30 mA.

X-rays are electromagnetic radiation, produced when an electron beam hits a substance and causes rapid deceleration of the electrons. In conventional diffraction, the X-ray tube is arranged so that electrons strike a target which produces X-rays of known wavelengths, which can be further filtered to produce radiation of a single wavelength which can be directed at the sample in the diffractometer. The wavelength of X-rays ranges from 0.05 to 0.25 nm. The sample is rotated in the beam so that crystallographic planes diffract X-rays as they reach the appropriate angle. The relationship of X-ray wavelength to the angle of diffraction and the characteristic lattice (or d) spacing of the mineral under examination forms the basis of all

X-ray diffraction (XRD) analysis and interpretation, and is known as Braggs Law (Dominic et al. 1993).

3.1.3 Petrographic microscopy

Thin sections were made both from the shales and from associated phosphate samples for mineralogical analysis with a petrographic microscope. The observed microfacies were described, discussed, interpreted and photographed.

Examination of standard and polished-thin sections is the mainstay of microscopic petrographic analysis. Because of the general softness of shales and mudstones, preparation of appropriate thin-sections often poses a challenge. The difficulty of preparing good petrographic thin sections of shales and mudstones is one of the reasons why acceptance and application of thin section microscopy of this rock type has been long delayed (Schieber and Zimmerle 1998)

3.1.4 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) for selected samples of different lithofacies was performed in order to diagnose and understand the microstructure and the diagenetic relationships among the main constituents and the matrix of the studied sediments.

Identification of different minerals through SEM was facilitated by comparing their characteristic morphologies with those shown in the SEM Petrology Atlas of Welton (1984). Identification was verified by X-ray diffraction analysis when possible. SEM analyses were carried out using a Scanning Electron Microscope Type S-2700 HITACHI.

3.2 Geochemical analysis

The present study includes major and trace element analysis of 55 carbonaceous shales from Egypt. The samples were crushed by a crushing machine to reduce the rock aggregate to <0.063μm particles. These samples were sieved to get the grain size fraction <0.063 μm.

3.2.1 X-ray Fluorescence (XRF)

The crushed samples were used to determine the major element composition by XRF. Analyses were carried out with a Philips PW 1404 WD-XRF via program "POWDER".

Mixture of 6g of sample powder with 1.5g of "HOECHST C-Wax" homogenised in vibrating device and pressed into Al-cups (40mm diameter) at 20t-pressure. Analysed major elements

were SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, SO_3 and P_2O_5 Trace elements analysed were F, Ag, As, Ba, Bi, Br, Cd, Cl, Co, Cu, Cr, Cs, Ga, Hg, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Th, U, V, W, Zn and Zr.

3.2.2 Determination of total organic carbon content (TOC)

The total organic carbon content was determined on each sample using a Hochtemperatur-TOC/TNb-Analysator (Liqui TOC) after decarbonating. The analyeses were performed at the TU, Berlin, Germany. Twenty-seven whole rock samples were analysed for TOC concentrates. About 200 mg pulverised sample was used for this analysis. Carbonate was removed by treatment with 10 % aqueous hydrochloric-acid. The residual materials were used for the determination of TOC by combustion analysis of temperatures in excess of 850C°. The evolved gas (CO_2) was measured quantitatively and simultaneously by infrared detectors and recorded as percentage of carbon.

3.2.3 Rock-Eval pyrolysis

The Rock-Eval pyrolysis was performed in the Applied Petroleum Technology AS, Norway. The TOC and Rock-Eval were determined on each sample using a Rock-Eval 6 instrument. The all procedures follow NIGOGA, 4th Edition.

The pyrolysis method is described in detail by Espitalie et al. (1977). For analysis 100 mg of each rock sample was used. The sample was placed in the instrument and heated at a rate of 25°C/min in a helium stream from 250°C to 550°C. Free hydrocarbons contained in the rock are expressed as an S1 peak; those released by the thermal breakdown of kerogen appear as an S2 peak which is produced by pyrolysis between 300°C-550°C. The quantity of hydrocarbon is measured by a flame ionisation detector (FID). Finally, an S3 peak representing CO_2 produced from the kerogen appears as a reflection of the oxygen content of the organic matter. The quantity of CO_2 is registered by a thermal conductivity detector (TCD).
The method leads to the calculation or measurement of two kinds of parameters:
i) Hydrogen and oxygen indices, which can be related to the type and thermal evolution of the organic matter. ii) The temperature at the maximum of the pyrolysis peak (S2 peak). This temperature is related to the thermal maturity of the organic matter (Espitalie et al. 1977; Peters, 1986).