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EPXMA survey of shelf sediments (Southern Bight, North Sea): A glance beyond the XRD-invisible

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ABSTRACT

Shelf sediments of the southern North Sea, were studied with a microanalytical [electron probe X-ray microanalysis (EPXMA)] and two bulk [X-ray diffraction (XRD) and X-ray fluorescence (XRF)] techniques. The investigation proved that the promptness of the microanalytical method is combined with a reasonable analytical reliability. XRD studies of such a type of sediments with monotonous mineral composition are not able to provide mineralogical information beyond the main well-crystalline minerals and the mineralogical quantitative characteristic of the sediment based on XRD estimations are incorrect. The EPXMA mineralogical interpretations are based on the statistical evaluation of a huge data set (thousands of mineral particles) and provide a rather correct quantitative determination of the main minerals. The comparative EPXMA–XRF study revealed that the Al, Si, K, Ca, Fe and to some extent Ti contents estimated by EPXMA are fairly reliable. In this respect the accuracy of the EPXMA-based mineral identification of the pure silicates, pure aluminosilicates, and Al-, Ca-, Fe- and Ti-containing minerals with simple composition is very high. Mg-calcite, augite and apatite determinations are assessed to be correct. The supposed accuracy of the clay mineral determinations is slightly lower (70–80%) than that of the other main minerals due to the complex and varying composition of the clays. The identification of XRD-invisible accessory minerals and quantification of their presence in the sediments is an essential advantage of the EPXMA, which makes it a useful approach in tracing the origin of the sediments, the pathways of their transport and the geochemical processes they have undergone.

However, the EPXMA has several flaws, which need to be solved in the future sediment investigations: (1) calibration with natural standards is needed in order to provide a higher accuracy of the mineral determinations; (2) any EPXMA study of sediments needs to be secured with XRF examinations of selected samples since EPXMA gives only semi-quantitative information about the abundance of the elements; (3) ultra-thin window EPXMA of low-*Z* elements has to be used since some of them (O, C) are always present in the main sediment components: silicates, aluminosilicates, carbonates and metal oxyhydroxides; (4) the interpretations of the clay fraction have to be supported with detailed XRD investigations of selected samples, while the mineralogy of the silt and sand fractions needs to be backed up with optical microscopy studies. The information from different analytical techniques (EPXMA with XRF–XRD-optical microscopy of selected samples) combined with the knowledge about the most possible minerals in a given environment, would give the most reliable results in studying mineralogical composition of shelf sediments.

1. Introduction: "micro" versus "bulk" analysis

Sediments (marine, lacustrine, riverine) are conventionally analysed by bulk techniques as XRD, XRF, atomic absorption spectrometry, mass spectrometry, etc. In this way qualitative or quantitative information is obtained for a bulk sample. These methods, however, are time consuming in general and the sample amount required for many of them is substantial (0.01–2.0g) which makes them not applicable for studying extremely small samples (suspended matter, aerosols). Sometimes their detection limits are rather high which makes some minerals or elements invisible although they might be present in the samples.

Besides applying these bulk techniques, much effort was put into the development of microanalytical methods recently.

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Among the variety of microanalytical techniques, EPXMA is by far the most commonly used for single particle analysis: in its automated mode it can analyse huge numbers of individual particles with very high analytical efficiency in a relatively short time [1]. EPXMA is capable of simultaneously detecting the elemental composition, morphology and size of micrometer-size individual particles. In combination with cluster analysis and/or multivariate techniques it is a powerful tool for characterization of suspended (in water and air) particulate matter, soils and sediments.

Shelf sediments usually exhibit a monotonous composition over relatively large areas. The application of conventional bulk techniques is not always capable to throw light on the compositional differences of these sediments resembling each other. In order to figure out the possible sediment provenances and the sediment transport pathways there is a need for a tool able to investigate this type of sediments beyond the visible horizon of the ordinary facilities. Lately, single particle analysis by EPXMA has proved to be very powerful technique in studying micro-realm of the hydrosphere [2–4] and [5] and atmosphere [6,7] and [8] where very often the researchers are able to collect only extremely low amounts of sample. In order to explore whether the promptness of this microanalytical method is combined with its analytical reliability in the investigation of shelf sediments, we contemplated a comparative study of the shelf sediments of a well-studied basin with a microanalytical (EPXMA) and two bulk (XRD and XRF) techniques. The southern North Sea sediments, which are mostly sands with low mud content [9–12] and [13] provide this opportunity and the EPXMA seems to be promising in gaining insight into the details of their composition, especially of the features of their fine part. Here we report on the results of this investigation.

2. Material and methods

In October–November 1998, a scientific team from the Netherlands Institute of Applied Geosciences (NITG-TNO) onboard the R/V *Zirfaea* sampled the Netherlands Continental Flat (North Sea) at 12 sites [12 vibro-cores (6m barrel length) and 6 box-cores (1m barrel length)] (Table 1; Fig. 1) within the framework of a project for identification of tracers for sediment sources and transport in the North Sea [14]. The sampling sites covered 3 different sedimentary environments: the inshore coastal zone (Coarse-Grained Sands with Shells; Muddy Sands), the shallow shelf (Cross-Bedded Sands) and the deeper shelf (Oyster Grounds). In lab environment the sediment cores were split along into 2 halves. One halve was used to prepare lacquer peels for sedimentological analysis. After correlation of the sediment layers deposited at the same time or by one kind of process (e.g., migration of bed forms, storm deposit, etc.), the upper part of the sediment layers or "events" were sampled from the core's second half. The box-cores, designed to take undisturbed samples from the sediment surface layer, were sub-sampled with PVC tubes (7cm diameter). All the samples were sealed in plastic bags and stored at constant temperature (4°C) and humidity (100%) for further analyses.

200 sediment samples from these cores were analysed by means of XRF [14] and [15] immediately after the cruise. Prior to the analysis, a 10-g subsample was finely ground and subsequently pressed with wax into tablets in an automated grinding (WC mill) and pressing machine (Herzog HSM-HTP). The tablets were analysed for major and trace elements using an ARL8410 spectrometer with a Rh tube, with full matrix correction for major oxides (SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, SO_3) and Compton scatter method for trace elements (As, Co, Cr, Cu, Ni, Pb, V, Zn, Ba, Ga, Nb, Rb, Sr, Y, Zr). The XRF was calibrated using approximately 100 certified geological reference standards. Three standards were added to each batch of 50 samples to determine the precision (0.5–1% relative standard deviation) and accuracy (1–5% relative standard deviation).

We selected 46 sediment samples (from 12 vibro-cores and 3 box-cores; Fig. 1) from the ones analysed by XRF and further analysed them by means of EPXMA [16] five months after the cruise. Prior to the EPXMA, the samples were sieved over a 1-mm nylon sieve. 150.0mg of each subsample with a grain-size <1 mm was put in a plastic vial filled with 10ml de-ionised Milli-Q-water, placed in an ultra-sonic bath for 5 min and sieved over a 63-μm nylon sieve. The suspension with particles with grain-size <63 μm and the particulate matter on the 63-μm sieve were transferred into second and third plastic vials, afterwards filtered through 47-mm Nuclepore filters (0.4 μm pore-size) using a polycarbonate Sartorius filter holder in lab atmosphere and used for EPXMA measurements. Two blank samples were prepared following the same procedure. Each specimen (Nuclepore filter sector evenly loaded with particulate matter) was mounted with double side tape on a clean plastic plate which fits into the

Table 1
Investigated sediment cores

Core #	Latitude (N)	Longitude (E)	Water depth (m)	Core length (m)	Sampling device	Sedimentary environment
98dw406	51°45′50.7″	3°24′33.6″	29.5	3.00	Vibro-corer	Coarse-Grained Sands with Shells
98dw408	51°30′46.9″	3°03′01.5″	28.1	3.15	"	Muddy Sands
98dw410	51°55′18.8″	2°45′23.2″	40.2	5.30	"	Cross-Bedded Sands
98dw412	52°07′06.2″	4°11′38.1″	17.5	4.80	"	Coarse-Grained Sands with Shells
98dw414	52°09′23.2″	3°22′21.8″	33.2	4.30	"	Cross-Bedded Sands
98dw415	52°24′02.4″	3°13′40.1″	39.0	4.80	"	"
98dw417	52°47′25.6″	4°23′51.4″	23.7	2.60	"	Muddy Sands
98dw419	52°59′48.6″	4°13′45.1″	35.0	4.20	"	"
98dw420	53°03′57.6″	3°44′46.1″	27.0	4.90	"	Cross-Bedded Sands
98dw421	53°54′45.3″	4°31′20.4″	43.1	3.90	"	Oyster Grounds
98dw422	54°15′38.6″	4°32′06.5″	48.6	3.80	"	"
98dw423	54°31′01.5″	4°19′42.5″	50.2	3.50	"	"
98bc407	51°45′50.7″	3°24′33.6″	29.5	0.28	Reinck box-corer	Coarse-Grained Sands with Shells
98bc409	51°30′46.9″	3°03′01.5″	28.1	0.30	"	Muddy Sands
98bc411	51°55′18.8″	2°45′23.2″	40.2	0.35	"	Cross-Bedded Sands
98bc413	52°07′06.2″	4°11′38.1″	17.5	0.17	"	Coarse-Grained Sands with Shells
98bc416	52°24′02.4″	3°13′40.1″	39.0	0.23	"	Cross-Bedded Sands
98bc418	52°47′25.6″	4°23′51.4″	23.7	0.25	"	Muddy Sands