

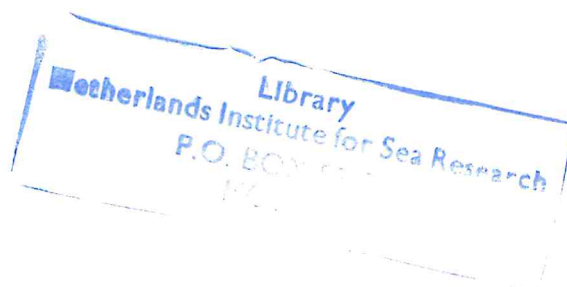
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A METHODOLOGY OF X-RAY DIFFRACTION AND INTERPRETATION OF  
X-RAY DIFFRACTION DATA ON THE CLAY-SIZED FRACTION OF  
CORES FROM THE NORTH ATLANTIC OCEAN BETWEEN THE  
FAEROE AND THE SHETLAND ISLANDS

SANKAR MAJUMDAR





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*Geological Survey of India*

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1. SUMMARY

As an introduction to using detailed techniques of X-ray diffractometry for estimating clay minerals in sediments, clay-sized fractions of two North Atlantic cores collected between the Faeroe and the Shetland Islands were examined. Molybdenum sulphide was used as internal standard. The relative quantities of the different clay minerals, based on peak heights, were measured and corrected at 50% and 100% relative humidities. Crystallinity of the swelling clay minerals was measured as width at half peak height. One core (NA81-5) appeared to be disturbed and comes out with confusing relations between the climatic periods on one hand, as determined from carbonate curve, and the X-ray parameters and CaCO<sub>3</sub> content on the other. The results core NA81-10, however, are highly significant and interesting.

In this core, the glacial period is uniformly marked by low contents of well crystalline combined swelling minerals, low amounts of vermiculite and high concentrations of smectite, while these values are uniformly the opposite in the warmer Holocene and interglacial periods. This pattern with regard to the climatic periods is also clearly reflected in the concentrations of kaolinite, chlorite and mica/illite, again with almost no exception. Similar patterns are also displayed by the CaCO<sub>3</sub> content, but with more exceptions. However, the two factors mutually support each other, thus affirming the validity and importance of the X-ray diffraction parameters in delineating the different climatic periods.

## 2. INTRODUCTION

This work stems from a co-operative programme for Indian research launches, financed by the Directorate General for International Co-operation, N.G.O. and Science Research, Ministry of Foreign Affairs, Government of the Netherlands.

The studies carried out at the laboratories of Netherlands Institute for Sea Research (NIOZ) had a two-fold objective: (1) Introduction to the techniques and methodology for examination of X-ray photographs of cores, collection of samples from selected depths within the cores, detailed treatment for separation of the clay-sized fractions, preparation of oriented mounts for the clay-sized fractions and unoriented mounts for homogeneously powdered bulk samples, programming of the diffractometer and identification of the minerals on the diffractograms, and (2) Computation, interpretation and analysis of diffractograms made from core samples collected in the North Atlantic Ocean.

The report embodies the results of X-ray diffraction on 24 samples chosen from two piston cores, NA81-5 and NA81-10, which had been collected in the North Atlantic Ocean in the channel between the Faeroe and the Shetland islands (latitudes: 60°N and 64°N; longitudes: 0°E and 5°W) (Fig. 1) during a cruise with the R.V. "Tyro" in 1981 by NIOZ. The cores represent alternate cold and temperate periods of sedimentation. Respective ages of the different periods were determined by the C-14 method, the oldest age exceeding 31 000 years for NA81-5 and 36 000 years for NA81-10 (Fig. 5).

### 2.1. PREVIOUS WORK ON NORTH ATLANTIC OCEAN

During the last few years, several investigations have been made on various aspects of the evolution of the North Atlantic. HOLTEDAHL (1959) examined geological and palaeontological aspects of cored sediments collected between 700 m and 3000 m depths from the southeastern part of the Norwegian Sea. BERRY & JOHNS (1966) observed that the clay minerals in North Atlantic-Arctic Ocean bottom sediments were derived primarily from terrestrial sources and were transported to environments of deposition by ice rafting and ocean currents. PUJOL, DUPRAT *et al.* (1974) collected information on the sediment sequence and stratigraphy of the Quaternary sediments from the Northeast Atlantic Ocean. KIPP (1976) tried to estimate sea-surface conditions from the distribution of planktonic foraminiferal assemblages in bottom sediments in the North Atlantic. MCINTYRE, KIPP *et al.* (1976) utilised transfer-function analysis of foraminiferal assemblages and water-mass-related assemblages of coccoliths and foraminifera as the basis for the reconstruction of temperature distribution in the surface water in the North Atlantic in 18 000 BP. KELLOG (1976) suggested, on the basis of surface-sediment distribution and stratigraphic analysis of sedimentary and faunal parameters in 6 piston cores, that during most of the last 150 000 years ice covered all of the Norwegian and Greenland seas. LATOUCHE & PARRA (1976) determined the origin and the process of transport and deposition of detritic fine-grained materials and biogenic carbonates of the North Atlantic Ocean between the Norwegian Sea and the Bay of Biscay during the recent Quaternary. YEMEL'YANOV, LOZOVAYA *et al.* (1977) came to the opinion that the modern sediments of the Icelandic region of the North Atlantic are being formed under the influence of the volcanoes of Iceland, Jan Mayen, the Faeroes

and Greenland. THIEDE (1977) used biogenous and terrigenous components of hemipelagic sediments to decipher the palaeo-oceanography of the southeastern North Atlantic Ocean during the last 150 000 years. NILSEN & KERR (1978) carried out petrographic and geochemical studies of a lower Tertiary lateritic paleosol resting on the Iceland-Faeroe Ridge and concluded that the ridge subsided in late Eocene and Oligocene time, permitting free interchange of marine waters between the Norwegian-Greenland Sea and the North Atlantic Ocean. KHARIN, SHEVCHENKO *et al.* (1979) studied the morphology of the smectites

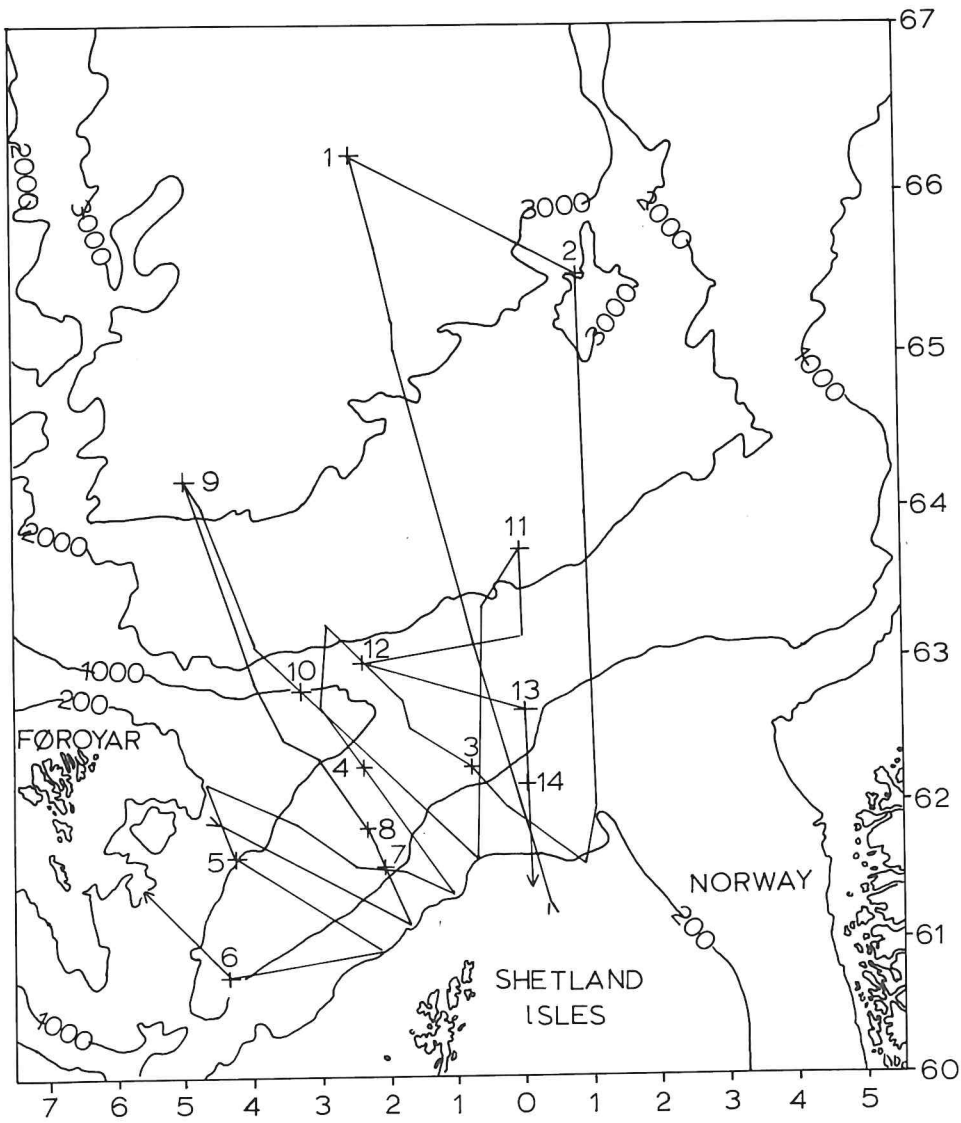


Fig. 1. Location map of core stations and cruise tracks.

formed in the altered basalt flows on the Norwegian Sea floor. DONN & NINKOVICH (1980) made an attempt to establish the history of major explosive North Atlantic Cenozoic volcanism from the distribution of volcanic ash layers intercepted in cores. KELLOG (1980) used composition and abundance of fauna represented in Norwegian Sea cores to derive sea-surface temperatures for the last glacial maximum (18 000 BP), the last interglacial (120 000 BP) and isotope stage 5a (82 000 BP). EISMA & VAN DER GAAST (1981) worked on terrigenous Late Quaternary sediments north and south of the Scotland-Greenland Ridge and from the Norwegian Sea and identified a basaltic province on the Iceland-Faeroe Ridge and an acidic province along the Scotland-Shetland shelf. GROUSSET & PARRA (1981) made an account of the northeast Atlantic Ocean and defined genetic groups to correlate them to their original sources. RUDDIMAN & MCINTYRE (1981) made a comprehensive treatment of the relevant factors associated with the last deglacial warming of the high-latitude North Atlantic. ZIMMERMAN (1981) pictured the distribution patterns of the nonbiogenic fine fractions of marine sediments in the context of the glacial recent North Atlantic Ocean. DUPLESSY, DELIBRIAS *et al.* (1981) carried out isotopic micropalaeontologic and pollen analyses of deep-sea cores from the Bay of Biscay and the northeastern Atlantic Ocean and suggested that the deglacial warming of this oceanic area was closely correlated with the palaeoclimatic evolution of the adjacent European continent. PARRA (1982) carried out mineralogical and geochemical studies of cored sediments from the main deep-sea basins of the North Atlantic and determined the distribution and origin of these materials during glacial, interglacial and postglacial periods. WOHLFEIL (1983) analysed sediment cores from the Iceland-Faeroe-Ridge region and tried to correlate different parts of the cores. DE LANGE (1983) depicted a massive slide in the southern Norwegian Sea, evidenced by geochemical and pore-water composition of cores. LEVER & McCAYE (1983) investigated on the clay mineralogy and grain-size distribution of quartz silt in pelagic sediment to outline the history of dust supply to the North Atlantic.

**Acknowledgements.**—The cores on which the present work was carried out was provided by T.C.E. van Weering who planned the work and also helped by offering fruitful suggestions. J. van Iperen assisted in selecting and collecting the samples from the cores, besides providing all previous informations collected on the cores. The work would not have been possible without the help of S.J. van der Gaast who right from introducing to the methodology of X-ray diffraction analysis of clay minerals to the computation and interpretation of the X-ray parameters and writing up of the report was part and parcel of the work. The author benefited from review and comments by D. Eisma who critically read drafts of the manuscript. F. Jansen kindly supplied reprints relevant to the work. Finally, the author likes to express his sincere thanks to J. Kalf, G. Berger, J. Hart and the staff members of Library and Drawing sections of NIOZ for their constant cooperation pertaining to the work.

### 3. METHOD

For diagnosis of clay minerals in natural sedimentary material, X-ray diffractometry provides the only effective and rapid method and thus has become almost a routine in many universities, research organisations and industries. While any sedimentary material

$< 2\mu\text{m}$  (less than 0.002 mm) effective spherical diameter is classified as clay, the principal minerals in clays are layer-lattice silicates (phyllosilicates) and some chain silicates (palygorskite-sepiolite group). The former include the major groups of kaolinite, smectite, mica/illite, pyrophyllite and talc, and chlorite. Besides, many non-clay minerals may be present within the size range of clay minerals. They include quartz, feldspar, calcite, dolomite, iron oxides, zeolites, titanium oxides, sulphides, sulphates, phosphates, gibbsite, etc. The presence of such and similar other non-clay minerals can also be found by X-ray diffraction provided individually they occur in about 1 per cent by volume or weight.

The X-ray diffraction apparatus gives a pattern of the principal crystallographic planes that cause the diffraction of the X-rays. Interpretation of the pattern, in turn, leads to identification of the minerals present in a sample. While the theory of X-ray diffraction and the operation of various X-ray units are given in detail in concerned books and manuals, the application of X-ray diffraction to clay minerals warrant important considerations, some of which are outlined in CARROLL (1970). As the mass absorption coefficient does not differ greatly for the majority of clay minerals, the orientation and crystallinity of the grains are of considerable importance. The X-ray diffraction patterns of clay minerals give strong basal spacings (001) in oriented mounts, that can be measured mainly from  $2-18^\circ 2\theta$  scanning with  $\text{CoK}\alpha$  radiation. This is sufficient for preliminary identification of any clay mineral present. In unoriented mounts the (hko) spacings are intensified. They can be measured from  $18-50^\circ 2\theta$  scan with  $\text{CoK}\alpha$  radiation, with also includes prominent reflections of quartz, cristobalite, feldspar, carbonates, amphiboles, pyroxenes and zeolites. For complete identification of the minerals on the diffractogram, certain tests are suggested (Table 9, CARROLL, 1970). Two principal treatments are glycolation and heating, which cause expansion and contraction respectively of swelling clay minerals. With prolonged heating at high temperatures, the crystalline structure of the mineral breaks down and amorphous mineral matter results. Pre-treatment with hydrogen peroxide or sodium dithionite (BRINDLEY, 1961) may be necessary for complete identification of clay minerals. Auxiliary techniques are chemical analysis, cation exchange analysis, petrological analysis, DTA/DTG and electron microscopy.

### 3.1. METHODOLOGY USED FOR THE NORTH ATLANTIC SAMPLES

The methodology used for the X-ray diffraction study of the North Atlantic cores was as follows:

(1) Thirteen sample points in core NA81-5 and eleven sample points in core NA81-10 were selected to represent the alternating cold and warm periods which, in turn, were found to be marked by distinctive  $\text{CaCO}_3$  values. About 25 gm sample was scooped out from the cores at the desired points and put into a 40 ml glass bottle.

(2) For separation of  $< 2\mu\text{m}$  fraction, 10 to 15 mg sample was taken in a 200 ml glass bottle, with two marks befitting the centrifuge capacity, mixed with demineralised water at room temperature ( $20^\circ\text{C}$ ) up to the lower mark and shaken well. More demineralised water was added upto the upper mark so that the bottles with their contents and lids have equal weight for each opposite pair.

(3) The samples were run in the centrifuge at 1500 R.P.M. for 1 min 55 sec, which was calculated on the basis of Stoke's Law to separate off the  $< 2\mu\text{m}$  fraction (at  $20^\circ\text{C}$  room temperature).



(4) The fluid (with clay fraction) in the bottle (up to the lower mark) was decanted and collected in 500 ml bottle, fitted to air exhaust system.

(5) For each sample, the procedures (2) to (4) were repeated for 15 times to ensure almost complete separation of  $< 2 \mu\text{m}$  size fraction.

(6) The fluid with clay-sized fraction was transferred into a 3 l glass beaker. About 20 gm  $\text{CaCl}_2$  powder was added to the content for complete flocculation to occur after 24 hours.

(7) After complete flocculation was ensured, the clear water above the settled clay was removed from the beaker, having only the wet clay remained.

(8) For Ca exchange, about 2 ml wet clay sample along with few drops of 1N  $\text{CaCl}_2$  and few drops of demineralised water were put into a 15 ml test tube. The contents were stirred well so that the entire clay went into suspension.

(9) The contents in the test tube were centrifuged at 2500 R.P.M. for about 5 minutes for complete precipitation of the clay.

(10) The clear water in the test tube was decanted and the procedures (8) and (9) were repeated twice more but only with demineralised water to make the clay free of excess Ca. In case the excess Ca was not completely removed, treatment with 2 or 3 drops of 1N  $\text{CaCl}_2$  and demineralised water was repeated until a sufficiently stable suspension of clay in water was obtained.

(11) For mixing with an internal standard (in this case  $\text{MoS}_2$  suspension), 200 ml (in some cases 150 ml) of each clay suspension was put, in triplicate, into an aluminium container (of about 8 to 10 mg weight) which had been pre-weighed in a microbalance and dried in an oven at  $120^\circ\text{C}$ . From the average weight of the dried sample, the weight of the clay material per 50 ml of suspension was computed to account for the weight of internal standard required.

(12) The clay suspension and the  $\text{MoS}_2$  suspension were put into a test tube at a weight proportion of 100 + 1 in such a way so as to contain about 25 mg of the sample, which amount is needed for each mount.

(13) For oriented mounts ceramic tiles of 20 mm x 15 mm size were used. The tile was put into the plastic holder of an exhaust system and pressed with rubber and plastic girders. The tile was washed with few drops of demineralised water to make its pore spaces free of air.

(14) Clay plus  $\text{MoS}_2$  suspended was drawn from the test tube in pipette and slowly put on the tile. Using the exhaust system, the water of the suspension was drained out, and the mount was ready for X-ray analysis.

(15) For the study of the bulk samples, the samples were powdered homogeneously in agate mortar and unoriented mounts were made in brass sample holders.

(16) To distinguish the respective peaks of chlorite and kaolinite, a clay suspension was used to prepare mount on a glass slide. For this purpose, ceramic tiles could not be used as they cause interfering reflections.

(17) X-ray diffraction analysis was carried out using a Philips PW1730 generator, PW1390 channel control, PW1394 motor control and PW1050/25 goniometer equipped with a curved graphite monochromator AMR, a helium-vacuum attachment and a computer-aided divergence slit (developed and to be published by S.J. van der Gaast and A.J. Vaars of NIOZ). The receiving slit and the anti-scatter settings 0.1 mm and  $0.5^\circ$  respectively.

(18) The samples were run at relative humidities of 100%, 50% and 0%. Some of the mounts were again run after 7 days and also after 3 months to see if there was any change in the crystallinity of the swelling clay minerals.

Attempts have been made by many workers from time to time to estimate the quantities of individual minerals in a mixture on the basis of diffractograms. KLUG & ALEXANDER (1962) recommend that under standardised conditions, using mixtures of minerals, all equally well crystallised, and an internal standard (generally fluorite) and making calibration curves, the weight of each component present in the mixture can be determined. NORISH & TAYLOR (1962) provided a comprehensive quantitative study of clay minerals using a methodology based on the intensity of diffraction and on the mass absorption coefficient of the mineral with respect to the radiation used. It is, however, mainly useful for estimating the iron content of samples. From diffractograms of powdered shale, aided by heat treatment and glycolation of the samples, SCHULTZ (1964) made a quantitative estimate of con-

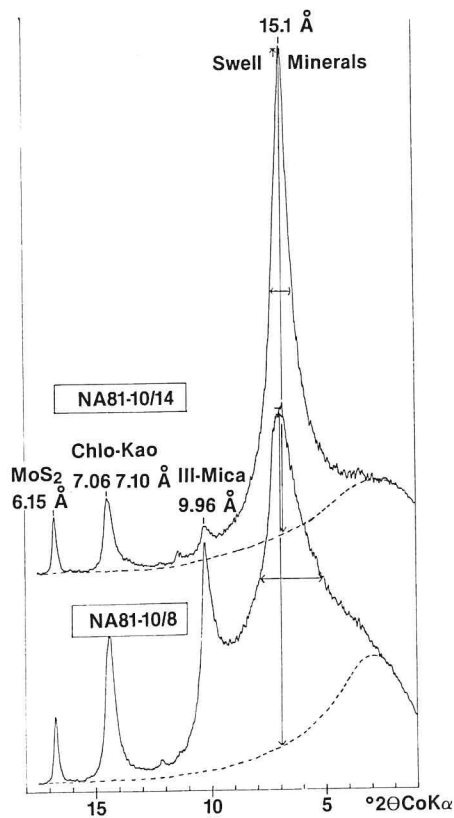


Fig. 2. Width at half peak height of Swell Minerals (combined swelling clay minerals) and the "d" spacings of Ill/Mica (illite/mica), Chlo/Kao (combined chlorite and kaolinite) and MoS<sub>2</sub> (internal standard) at 50% relative humidity.

stituent minerals. BISCAYE (1965) determined the percentages of clay minerals from the weighted peak areas, using different multiplying factors for different clay minerals. CARROLL (1970) used weight-percent mixtures of standard minerals and took into consideration the mass absorption coefficient of standard minerals and the efficiency of a Geiger counter over the X-ray unit to estimate quantitatively clay/silt size materials in the mixture. BRINDLEY & BROWN (1980) have commented that the application of these methods to clay is rendered difficult because of the variability of clay minerals, chemically and structurally.

The present author used  $\text{MoS}_2$  suspension (QUAKERNAAT, 1970) as internal standard mixed with a clay suspension of each sample in 1:100 weight proportion. The method used for computing the different parameters including the relative proportion of constituent minerals from the diffractogram was as follows:

(a) It is always to be expected that on diffractograms the background reflection (*i.e.* the base of a peak) will give more or less bulging depending on variations in particle size the

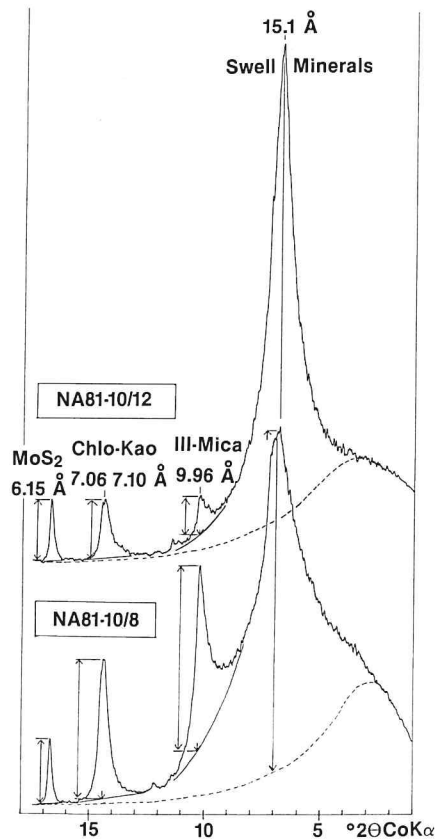


Fig. 3. Peak heights (from corrected base) of Swell Minerals (combined swelling minerals) III/Mica (illite/mica), Chlo/Kao (combined chlorite and kaolinite) and  $\text{MoS}_2$  (internal standard) at 50% relative humidity.

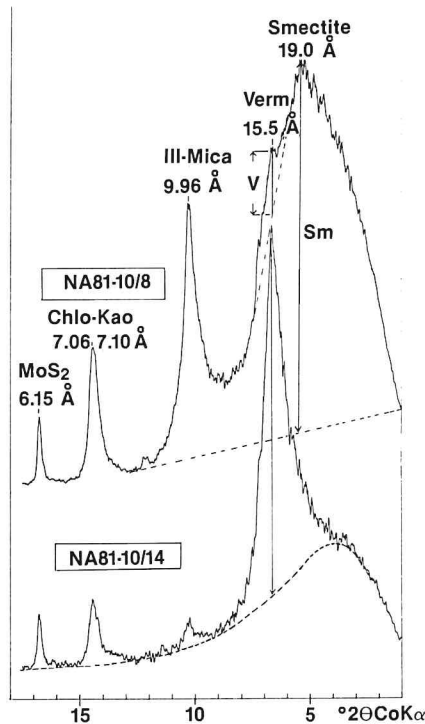


Fig. 4. Peak heights of Verm (vermiculite) and smectite at 100% relative humidity.

extent of crystal defects and the presence of micropores. For getting a correct basis, one sample was K-saturated and X-rayed at 0% relative humidity. The swelling minerals (smectite-vermiculite) then collapsed to higher angle side and provided a near-correct base, free of reflections due to chlorite and other associated minerals. For the diffractograms of all the samples, the base of the swelling minerals was corrected (drawn) with reference to the X-ray K-saturated base and accordingly the base lines for the kaolinite, chlorite, illite and  $\text{MoK}_2$  peaks was drawn. All measurements in respect of peak height etc were made with reference to the corrected base.

(b) At 50% relative humidity, the width (in mm) at half peak height was measured to define the crystallinity of the swelling minerals. The proportions of the width shared by vermiculite and smectite were taken tentatively as denoting the proportions of the two minerals. Measured at the same relative humidity, the individual peak heights of the swelling minerals, kaolinite, chlorite and muscovite/illite were divided by the corresponding peak height of the internal standard to obtain the corrected relative quantities of the concerned minerals.

(c) For determining the relative quantities of smectite and vermiculite separately on the diffractograms at 100% relative humidity, the bases for both minerals were separately drawn and the respective peak heights were accordingly measured and converted to percentages. The lowest peak height value (in percent) was subtracted from all peak height percen-

tages for smectite. The peak height percentages of vermiculite and the corrected peak height percentages of smectite were again computed to 100%. The values in percent thus obtained for the two swelling minerals were multiplied by the ratio of peak height of combined swelling minerals to that of the internal standard, measured at 50% relative humidity. All the aforesaid corrections were done to ensure a correct determination, though semi-quantitative, of the relative proportions of smectite and vermiculite. To illustrate the procedures involved in the above measurements, diffractograms are enclosed (Figs 2, 3 and 4).

#### 4. RESULTS

Twelve oriented mounts of clay-sized fractions of core NA81-5 were run in the X-ray diffractometer at 50% relative humidity. After three months the mounts were scanned again. It

TABLE I

Width at half peak height (WHPH) of combined swelling minerals and peak heights of clay minerals and Internal Standard ( $\text{MoS}_2$ ) at 50% relative humidity. Peak heights of swelling minerals (Sw Min), chlorite (Chlo), kaolinite (Kaol) and mica/illite (Ill) were divided by the corresponding peak heights of  $\text{MoS}_2$  to obtain their corrected peak heights. Individual peak heights of kaolinite and chlorite were calculated from their combined peak height (ceramic tile mount) and their peak height proportion (glass slide mount).

	WHPH		Peak heights (in cm)				Peak heights relative to $\text{MoS}_2$				Kaol/Ill ratio
	Sw Min	$\text{MoS}_2$	Sw Min	Chlo	Kaol	Ill	Sw Min	Chlo	Kaol	Ill	
NA81-10											
14	10.0	26.0	227	17.6	15.5	10	8.73	0.68	0.59	0.38	1.55
13	10.0	29.0	233	18.6	15.4	13	8.03	0.64	0.53	0.45	1.18
12	11.5	29.0	219	15.0	12.0	17	7.55	0.52	0.41	0.59	0.69
11	12.5	22.5	229	15.4	14.6	23	10.18	0.68	0.65	1.02	0.64
10	17.0	28.5	230	26.1	31.9	47	8.07	0.92	1.12	1.65	0.68
9	16.5	36.0	223	36.9	46.2	76	6.19	1.02	1.28	2.11	0.61
8	25.0	41.0	211	41.6	46.5	110	5.15	1.01	1.13	2.68	0.42
7	20.0	33.0	223	32.7	34.4	67	6.76	0.99	1.04	2.03	0.51
6	20.0	40.0	222	37.0	37.0	81	5.55	0.93	0.93	2.02	0.46
5	21.0	30.0	223	29.4	28.6	75	7.43	0.98	0.95	2.50	0.38
4a	13.0	26.0	235	14.3	14.8	21	9.04	0.55	0.57	0.81	1.04
NA81-5											
12	11.0	24.0	227	13.5	13.5	14	9.46	0.56	0.56	0.58	0.97
11	11.5	22.0	232	10.5	10.5	17	10.55	0.48	0.48	0.77	0.62
10	12.0	19.0	232	15.2	15.8	27	12.21	0.80	0.83	1.42	0.58
9	14.0	34.0	234	22.4	25.7	42	6.88	0.66	0.75	1.24	0.60
8	11.5	21.0	230	18.1	16.0	35	10.95	0.86	0.76	1.67	0.46
7	14.5	23.0	228	21.4	12.6	32	9.91	0.93	0.55	1.39	0.40
6	14.0	31.0	230	22.5	28.5	46	7.42	0.73	0.92	1.48	0.62
5	18.0	25.0	220	27.5	30.6	60	8.80	1.10	1.22	2.40	0.51
4a	10.5	21.0	233	10.4	9.6	10	11.10	0.49	0.46	0.48	0.96
4	15.0	21.0	225	26.7	28.3	58	10.71	1.27	1.35	2.76	0.49
3	11.5	18.0	233	17.4	23.7	25	12.94	0.96	1.31	1.39	0.94
2	17.0	21.0	220	23.9	31.1	60	10.48	1.14	1.48	2.86	0.52
1	19.0	27.0	218	69.0	60.0	96	8.07	2.55	2.22	3.56	0.62

TABLE 2

Peak heights of vermiculite and smectite measured at 100% relative humidity (RH) and corrected w.r.t. peak heights at 50% relative humidity.

	Peak height at 100% RH (cm)		Percentage values		After deducting lowest Smec value	Corrected percentages (a)		Quantity of Sw Min at 50% RH (b)	(a) × (b)	
	Verm	Smec	Verm	Smec		Verm	Smec		Verm	Smec
NA81-10										
14	21.75	8.20	72.60	27.40	6.50	91.8	8.2	8.73	801.4	71.6
13	21.60	5.70	79.10	20.90*	0.00	100.0	0.0	8.03	803.0	0.0
12	20.70	7.80	72.60	27.40	6.50	91.8	8.2	7.55	693.1	61.9
11	21.50	9.40	69.60	30.40	9.50	88.0	12.0	10.18	895.8	122.2
10	5.60	21.00	21.10	78.90	58.00	26.7	73.3	8.07	215.5	591.5
9	7.35	20.00	26.90	73.10	52.20	34.0	66.0	6.19	210.5	408.5
8	3.60	19.80	15.40	84.60	63.70	19.5	80.5	5.15	100.4	414.6
7	3.40	20.70	14.10	85.90	65.00	17.8	82.2	6.76	120.3	555.7
6	5.10	20.75	19.70	80.30	59.40	24.9	75.1	5.55	138.2	416.8
5	3.30	20.80	13.70	86.30	65.40	17.3	82.7	7.43	128.5	614.5
4a	22.40	12.90	63.50	36.50	15.60	80.3	19.7	9.04	725.9	178.1
NA81-5										
12	22.00	6.50	77.20	27.80	6.90	91.8	8.2	9.46	868.4	77.6
11	22.20	11.60	65.70	34.30	13.40	83.1	16.9	10.55	876.7	178.3
10	22.50	11.00	67.20	32.80	11.90	85.0	15.0	12.21	1037.9	183.2
9	22.00	14.40	60.40	39.60	18.70	76.4	23.6	6.88	525.6	162.4
8	22.60	10.60	68.10	31.90	11.00	86.1	13.9	10.95	942.8	152.2
7	24.30	12.30	66.40	33.60	12.70	81.6	18.4	9.91	808.7	182.3
6	21.70	15.20	58.80	41.20	20.30	74.3	25.7	7.42	551.3	190.7
5	5.40	21.60	20.80	79.20	58.30	26.3	73.7	8.80	231.4	648.6
4a	22.50	7.95	73.90	26.10	5.20	93.4	6.6	11.10	1036.7	73.3
4	25.70	14.25	64.30	35.70	14.80	77.3	22.7	10.71	827.9	243.1
3	20.00	13.00	60.60	39.40	18.50	77.3	22.5	12.94	1002.9	291.2
2	21.00	19.70	51.60	48.40	27.50	65.2	34.8	10.48	683.3	364.7
1	1.10	21.10	4.95	95.05	74.20	6.2	93.8	8.07	50.0	757.0

\* Lowest percentage peak height value of smectite (Smec) was deducted from all values of smectite and the corrected percentage peak heights of smectite and vermiculite (Verm) were multiplied by the corresponding corrected peak height values of combined swelling minerals measured at 50% relative humidity (Table 1).

was observed that during this time the crystallinity of the swelling clay minerals (vermiculite/smectite) decreased in eleven out of the twelve samples. From this the idea originated to examine how the crystallinity of the swelling clay minerals and the relative quantities of the other clay minerals in the two North Atlantic cores account for the CaCO<sub>3</sub> content of the corresponding samples and, in turn, the concerned climatic periods. While the CaCO<sub>3</sub>% was determined by Miss J. van Iperen of NIOZ, the aforesaid parameters were measured on the diffractograms (Tables 1 and 2) and were compared graphically against the CaCO<sub>3</sub>% and the estimated climatic periods (Fig. 5a and b). Good and significant results were obtained for core NA81-10, while core NA81-5 appeared to be disturbed with respect to various factors.

#### 4.1. CRYSTALLINITY OF THE SWELLING CLAY MINERALS

As shown in Fig. 5b, the  $\text{CaCO}_3$  percentages in core NA81-10 define the respective cold and warm periods, the  $\text{CaCO}_3$  contents ranging from 2 to 9% during the cold period and more than 15% during the warm periods. For the warm periods, however, samples No. 4a, 10a and 11 show low  $\text{CaCO}_3$  percentages of 1 to 2%. The crystallinity (of the swelling clay mineral), measured as width at half peak height, on the other hand, showed different climatic periods without any exception. Thus all peak width values for both the younger and the older warm periods fall below 15 mm (range: 10 to 13 mm) and all peak width values for the cold period exceed 15 mm, mostly ranging between 20 to 26 mm. To speak in terms of crystallinity, uniformly the swelling clay minerals are more crystalline in the cold period and poorly crystalline in the two warm periods. While high  $\text{CaCO}_3\%$  and low  $\text{CaCO}_3\%$  are associated with good crystallinity and poor crystallinity respectively of the swelling minerals, the above two factors combined can thus indicate a warm or cold period of sedimentation.

The picture is, however, somewhat different in core NA81-5. Both  $\text{CaCO}_3\%$  and crystallinity of the swelling clay minerals behave randomly in both cold and warm periods. Individually, most of the  $\text{CaCO}_3$  values, ranging from 5 to 10%, are distributed irregularly between the different climatic periods. In the case of the swelling minerals, on the other hand, the crystallinity is good (peak width range: 10 to 11.6 mm), for the younger warm period, moderately good to poor (peak width range: 11 to 15 mm) for the younger cold period, mostly good (peak width range: 10.5 to 18 mm) for the older warm period and poor (peak width range: 17 to 19 mm) for the older cold period. Thus only in the older sediments (below 3.25 m depth in the core), poor crystallinity occurs during the cold period and good crystallinity during the warm period, like core NA81-10.

#### 4.2. RELATIVE QUANTITIES OF VERMICULITE, SMECTITE AND COMBINED SWELLING MINERALS

For core NA81-10, the parameter, discussed earlier, for the relative quantity of vermiculite ranges from 700 to 900 in the warm periods and 100 to 215 in the cold period. The corresponding values of smectite range from 0 to 178 in the warm periods and 415 to 615 in the cold period. Thus, individually or combined together, the semiquantitative estimates of vermiculite and smectite characterise the climatic periods almost perfectly: as we will see below, it is likely that the cold period lasted somewhat longer than estimated from the carbonate curve. Although less clearly, also the relative quantity of the unclassified swelling minerals demarcates the climatic periods in the core, the low quantities of the swelling minerals (range: 5.15 to 7.43) falling in the cold period while the higher values (range: 7.55 to 10.18) are restricted to the warm periods. The highest value (7.43) of the former range and the lowest value (7.55) of the latter are from samples marking the upper and lower junctions of the different climatic periods.

For core NA81-5, again the relation between climatic periods and the relative quantities of vermiculite or smectite is either diffused or contradictory. For this core, while both the warm periods are marked, like the other core, by high quantities of vermiculites (ranges : 868-976 and 827-1037), the two cold periods also contain mostly higher estimates (range:

555-1038) of the mineral. Smectite behaves more erratically in the majority of its relative quantities range from low to moderately high values (73-300), haphazardly shared by the warm and cold periods. Similarly, the relative quantity of the swelling minerals with majority values ranging from 8.0 to 12.9, fails to delineate the different climatic periods.

#### 4.3. RELATIVE QUANTITIES OF KAOLINITE, CHLORITE AND ILLITE

The relative quantities of kaolinite, chlorite and mica/illite show similar changes and are reciprocal to that of the combined swelling minerals. They are uniformly low in the warm periods and uniformly high in the cold period and thus also act as good parameters to differentiate the climatic periods. In terms of numerical values, the kaolinite, chlorite and il-

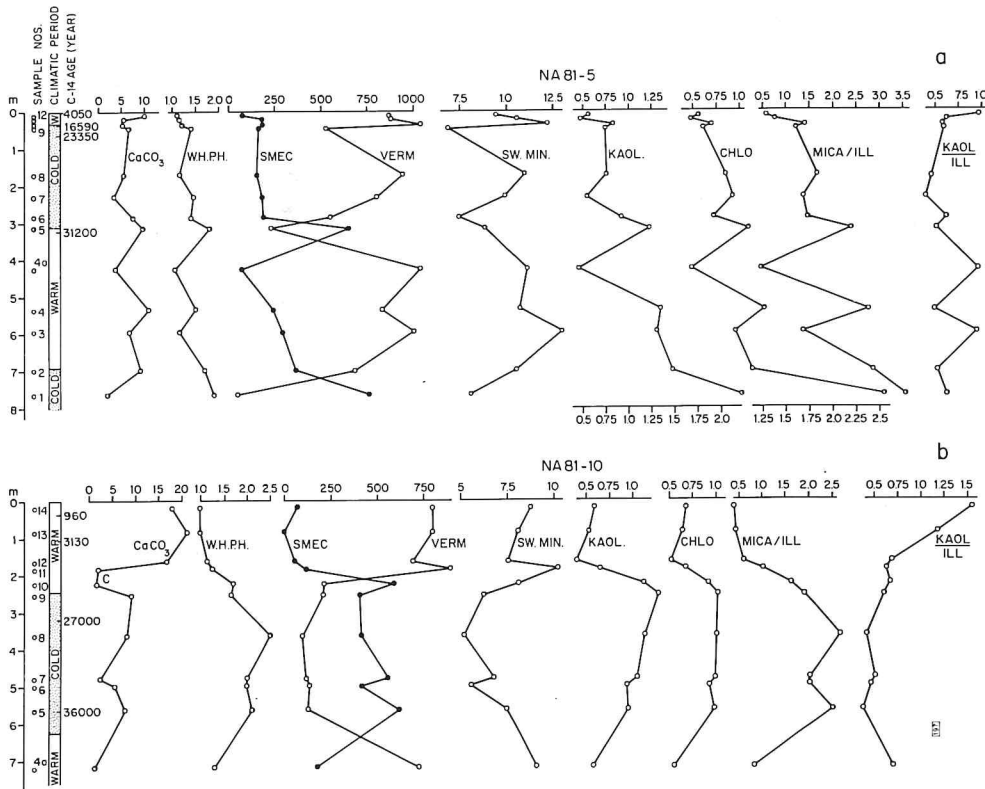


Fig. 5. Depths in core (in m). Calcium carbonate in percentage. Width at half peak height (in cm) of combined swelling minerals (WHPH) and peak heights of combined swelling minerals (Sw Min), kaolinite (KAOL), chlorite (CHLO) and mica/illite (MICA/ILL) corrected w.r.t. internal standard and ratio of kaolinite to illite ( $\frac{KAOL}{ILL}$ ) at 50% relative humidity. Relative quantity of vermiculite (VERM) and smectite (SMEC) calculated from peak height at 100% relative humidity and corrected w.r.t. that at 50% relative humidity.



lite show semiquantitative ranges of 0.4 to 0.6, 0.5 to 0.7 and 0.4 to 1.0 respectively in the warm periods and 0.7 to 1.30, 0.9 to 1.0 and 2.0 to 2.7 respectively in the cold period. From the Fig. 5a and b one more thing is apparent that for all the parameters, the break in the slope of the graphs is at the location of the sample No. 11 in the core. This suggests that the cold period of sedimentation might have continued later than was estimated.

Core NA81-5 continues to give a variable relation between the climatic periods and the relative quantities of the above mentioned three clay minerals. For the younger warm period and the older cold period in the core, the aforesaid parameters are uniformly low and high respectively with ranges, in order, of 0.5-0.6 and 1.48-2.22 (kaolinite), 0.5-0.6 and 1.2-2.6 (chlorite) and 0.6-0.8 and 2.9-3.6 (mica/illite). This is in conformity to the observation made in the other core. But, on the other hand, the same factors are erratic for the other climatic periods with low values during the younger cold period and high values during the older warm period, which is contrary to what was found for the other warm and cold periods. The only exception is mica/illite which for the younger cold has high values (range: 1.2 to 1.7) and conform to those observed in the other core.

The ratio of kaolinite to mica/illite was also computed and graphically represented (Fig. 5a and b) for both cores. For core NA81-10, a distinct change from very high values to very low values marks the change from the warm to the cold period, although the older warm period and the lower part of the younger warm period also show low kaolinite/illite ratios. The ratio is, however, always very low to low in the cold period. In core NA81-5, on the other hand, the relation between the climatic period and the kaolinite/illite ratio is not clear and does not suggest a definite pattern. But in general, in this core also higher ratios are associated with the warm periods and lower ratios with the cold periods.

## 5. DISCUSSION ON RESULTS OF NORTH ATLANTIC CORES

The X-ray diffraction parameters denoting the relative quantities of vermiculite, smectite, kaolinite, chlorite and mica/illite and the crystallinity and relative quantity of the unclassified swelling minerals in core NA81-10 show a significant correlation with the Holocene, glacial and uppermost last interglacial climatic periods. The picture is, however, very confusing in core NA81-5 in which  $\text{CaCO}_3$  content also shows a random-distribution pattern. In this core, Dr. Ganssen of Amsterdam University has observed that the carbon-14 datings are too low except for the Holocene, compared to oxygen isotope datings now being carried out (personal communication). Preliminary foraminiferal studies also have indicated that the core is disturbed and contains detrital older species, but the absence of dolomite in all the bulk samples X-rayed, discard the possibility that any detrital material from the Tertiary is present in the core. DE LANGE (1983), depicting a massive slide of a coastal fresh-to-brackish sediment "slab" in the southern Norwegian Sea, got evidence for an input of non-saline water in the pore space of one of the cores of this area but described the core NA81-5 as unaffected. The only possibility therefore remains that some material may have been removed randomly from the sediment column (core NA81-5). As follows from the results (chapter 3), the upper 3 km of the core is apparently more affected in this respect, than the lower part of the core.

Core NA81-10, on the other hand, really warrants attention and discussion, particularly in respect of observations made by various workers on the correlation of mineralogical

composition-distribution and climatology. In this core the relative quantities of the swelling minerals are about 8 to 10 times higher than those of the other clay minerals (Table 1). BERRY & JOHNS (1966) also noted the abundance of expandable clay minerals, relative to the other clay minerals, in the cored sediments of the Norwegian Sea. But while they found kaolinite in only one sample from the sea, this mineral with its characteristic X-ray peak is present in all our samples. Further, their conclusion that clay minerals cannot be used to determine palaeoclimatic horizons does not hold good in view of the present results which show a perfect matching with climatic conditions. In a core (No. V27-86) situated below the axis of the Norwegian Current and with an maximum warm water influence during the latest interglacial (KELLOGG, 1980), EISMA & VAN DER GAAST (1981) obtained a strong relation between concentration of swelling minerals and  $\text{CaCO}_3$  content. The similar parameters for the core NA81-10 support this observation not only for the last interglacial but for the entire climatic oscillations intercepted in the core. While the quantity of vermiculite and the crystallinity and quantity of the swelling minerals show the same pattern as the  $\text{CaCO}_3$  content, the quantities of smectite, kaolinite, chlorite and mica/illite along with the kaolinite/illite ratio increase or decrease with the enhancement or impoverishment of  $\text{CaCO}_3$  content. The only exception is a single  $\text{CaCO}_3$  value in the interglacial, which is too low for the warm period as compared to the carbonate pattern in the major part of the core column.

Also the observations of BISCAY *et al.*, (1976) and GROUSSET *et al.* (1981) indicate that for the entire North Atlantic carbonate content is low in cold periods and high in warm periods.

In the present case, all high values of smectite combined with all low values of vermiculite are restricted to the cold period, while for the warm Holocene and the interglacial the smectite contents and vermiculite contents are uniformly low and high respectively. This is in conformity with PUJOL *et al.* (1974), MOYES (1974) and LATOUCHE & PARRA (1976) who found that the glacial deposits of Faeroe area contained high percentages of smectite. For all their cores located around the Faeroe-Shetland ridge, EISMA & VAN DER GAAST (1981) noted, on the basis of X-ray diffraction parameters, that the content of swelling minerals varies independently whereas the concentration of kaolinite and also the ratio between mica/illite and kaolinite remains approximately the same throughout the core. This is in contrast to the present results which show that, like the swelling minerals, individually kaolinite, chlorite and mica/illite also act as good markers in analysing low for the Holocene, high for the glacial and again low for the latest interglacial. The ratio between kaolinite and illite behaves similarly, although the contrast is very sharp between Holocene and glacial and less prominent between the latter and interglacial. That EISMA & VAN DER GAAST obtained a different picture may be due to the fact that for clay mineral studies they collected samples from dried cores and used a different methodology, without reference to internal standard, for computing the X-ray parameters.

## 6. CONCLUSION

Much work have been carried out on sediments from North Atlantic and other oceans and seas. But only a few attempts have been made to search for factors and parameters other than microfauna and microflora to act as efficient guides towards tracing back the climatic

periods in a sediment column. The present work was a small-scale attempt in that direction, but shows that the relative quantities, with respect to internal standard, of unclassified swelling minerals, vermiculite, smectite, kaolinite, chlorite and mica/illite, based on corrected peak heights at 50% relative humidity, and the crystallinity of swelling minerals, indicated by the width at half peak height at 50% relative humidity, offer distinct patterns, with few or no exceptions, for cold and warm periods in core NA81-10. Calcium carbonate content also shows a similar pattern but with more exceptions. However, clay mineral data and CaCO<sub>3</sub> content mutually support each other. In a generalised way, the previous workers, discussed in section 4, came out with "lows" and "highs" in the CaCO<sub>3</sub> content and in the concentrations of different clay minerals for different climatic periods in the North Atlantic. These results do not contradict the patterns found in core NA81-10 and, in turn, reassure the validity and importance of the X-ray diffraction parameters. The results of core NA81-5 are not further considered here since this core clearly has been disturbed, as discussed earlier.

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