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Smectite composition as a tracer of deep circulation: the case of the Northern North Atlantic

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Abstract

The link between smectite composition in sediments from the northern North Atlantic and Labrador Sea, and deep circulation is being further investigated through detailed studies of the X-ray pattern of smectites and cation saturations. This allows clear distinction of dominant terrigenous sources associated to the main components of the modern Western Boundary Undercurrent. Time variations of smectite characteristics in two piston cores from the inlet and outlet of the Western Boundary Undercurrent gyre in the Labrador Sea indicate: (1) a more southern circulation of North East Atlantic Deep Water during the Late Glacial; (2) a step by step transition to the modern pattern of deep circulation during the Late Glacial/Holocene transition, with intensification of North East Atlantic Deep Water and Davis Strait Overflow; (3) an expansion of Davis Strait Overflow and Labrador Sea Water circulation in relation to ice surges and deposition of detrital layers; (4) an intensified circulation of North East Atlantic Deep Water during the Younger Dryas; and (5) a very recent increased influence of Denmark Strait Overflow Water beginning between 4.4 and <1 kyr.

Keywords: Clays; Smectite composition; Sediment; Deep paleocirculation; Late deglacial; Northern North Atlantic

1. Introduction

In modern North Atlantic, deep circulation is driven by a contour-flowing bottom current, the Western Boundary Undercurrent (WBUC), which carries the main water masses involved in the formation of the North Atlantic Deep Water (NADW) along a counterclockwise gyre through the marginal North Atlantic basins. These water masses include: (a) the Northeast Atlantic Deep Water 1 (NEADW1) flowing from east to west and bathing the shallower parts of Reykjanes Ridge; (b) the deeper Northeast Atlantic Deep Water 2 (NEADW2) whose circulation is constrained by the morphology of Reykjanes Ridge, and flowing from the Northeast Atlantic through the Charlie-Gibbs Fracture Zone into the Irminger Basin where it forms a counterclockwise gyre along the ridge and the Greenland Margin; (c) the Denmark Strait Overflow Water (DSOW) that consists of cold surface waters from the Greenland and Norwegian seas that sink below 2700 m along the Eastern Greenland Margin to fill most of the deepest parts of the Irminger and Labrador basins; and (d) the Labrador Sea Water (LSW) characterized by cold water flowing from Davis Strait (Davis Strait Overflow, DSO) southwards along the Eastern Labrador Margin (Fig. 1, e.g. McCartney, 1992; Dickson and Brown, 1994; Lucotte and Hillaire-Marcel, 1994). Clay mineralogical investigation of surface sediments from the Northern North Atlantic has provided strong evidence for a link between the WBUC pathway and the relative abundance of smectites in associated deposits (Fagel et al., 1996).

Smectites derive from different sources and processes: meteoric weathering or pedogenesis of various substrates, hydrothermal or submarine alteration of basaltic volcanic materials (e.g. Biscaye, 1965; Chamley, 1989; Weaver, 1989). Their chemical and mineralogical characteristics display a wide range of variation, in relation to their origin and formation. Most trioctahedral smectites, mainly saponites, form through meteoric weathering or hydrothermal alteration of basalts. Dioctahedral smectites vary from an Al end-member to a Fe end-member. Montmorillonite and beidellite (Al end-member) mostly result from the chemical weathering of diverse substrates under a wide spectrum of environmental conditions. Fe-beidellites and nontronites (Fe end-member) commonly derive from meteoric weathering or hydro-thermal alteration of basalts; they are particularly abundant in active areas of mid-oceanic ridges (Haggerty and Baker, 1967; McMurthy et al., 1983; Parra et al., 1985, 1986).

Due to the complexity of water masses of different origins involved in the WBUC, smectites along its pathway are likely to result from different sources and processes. The aim of this study is: (a) to investigate the composition of smectites in surface sediments to detail further the potential sources of particles and their relation to the circulation of modern deep water masses involved in the NADW; and (b) to use time variations of smectite composition as a tracer of deep water changes that may have occurred since the Late Glacial.

Fig. 1. *Map of the study area, and location of surface sediment samples.* Deep (solid arrows) and surface (dashed arrows) circulation patterns are adapted from Dickson and Brown (1994), and from Lucotte and Hillaire-Marcel (1994). In the Northern North Atlantic, the Western Boundary Undercurrent (WBUC) carries along a counterclockwise gyre through the Iceland, the Irminger and the Labrador basins, the main water masses involved in the formation of the North Atlantic Deep Water (NADW), i.e. the North East Atlantic Water (NEADW) which is subdivided into an upper (NEADW1) and a lower water mass (NEADW2), the Denmark Strait Overflow Water (DSOW) and the Davis Strait Overflow (DSO). Lower Deep Water (LDW); Greenland Current (GC); West Greenland Current (WGC); Labrador Current (LC); Iceland Sea Overflow Water (ISOW); Norvegian Sea Overflow Water (NSOW); Wyville-Thompson Ridge Overflow (WTRO); North-West Atlantic Mid-Ocean Channel (NAMOC).

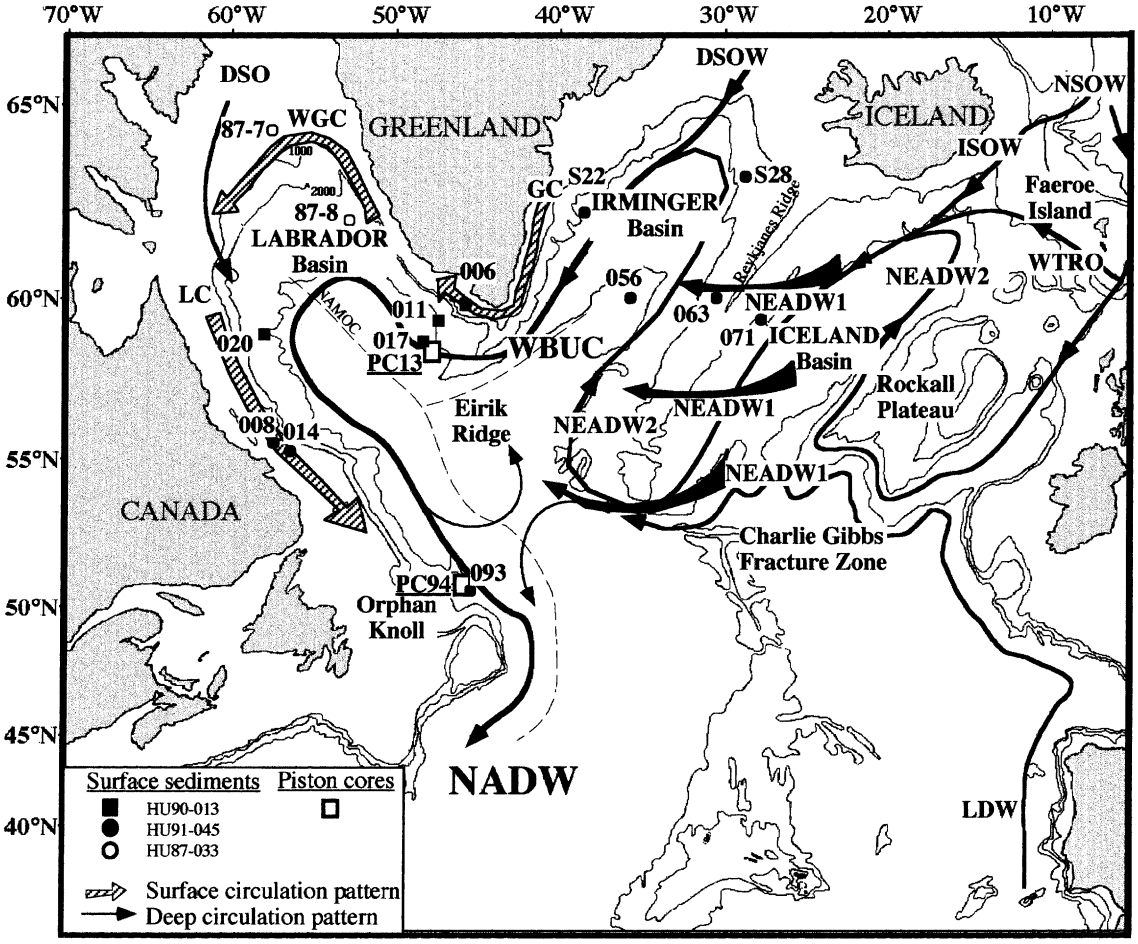

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Table 1: *Location and mineralogical data of surface sediments from the Northern North Atlantic basins.* Sites under the influence of the WBUC are underlined. Bottom water masses according to Lucotte and Hillaire-Marcel (1994). LSW, Labrador Sea Water; see Fig. 1 for other abbreviations. X-ray diffraction data obtained after ethylene-glycol solvation. Relative abundance of clay minerals in the <2 µm carbonate-free fraction. Smectites are characterized by: the position of the maximum intensity peak, *d*, in Angtröms, indicative of the global contribution of the mixed-layers (Lansson and Besson, 1992); the width at half-height of the (001) smectite reflection in 1/20° 2θ, $l_{1/2}$, indicative of the degree of "crystallinity" (or the degree of homogeneity of cristallite population) of the smectites; the vlp ratio defined by the height of the (001) smectite peak above the background p and the depth of the "valley" v on the low-angle side (Biscaye, 1965), this ratio which allowed an estimation of the amount of illite layers within the irregular illite-smectite mixed-layers by referring to the reference curves (Retke, 1981). The relative proportions of beidellite and montmorillonite are estimated from Li-saturated X-ray diffraction data

Sample						**Clay assemblage**					**Smectites**			**Smectitic layers in (10-14$_{sm}$) (%)**	**Beid.-Mont. proportion (%)**	**Beidellites abundance (%)**
Location	**Core**	**Lat. (°N)**	**Long. (°W)**	**Water depth (m)**	**Water mass**	**C (%)**	**I (%)**	**K (%)**	**V (%)**	**Sm. (%)**	***d*(001) (Å)**	**$l_{1/2}$ (1/20° 2θ)**	***vlp***			
Iceland Basin																
	91-045-071	58°56.42	28°44.44	2237	NEADW	18	10	5	0	67	16.7	10	0.70	80	50-50	34
Irminger Basin																
	91-045-063	59°40.61	30°21.46	1319	NEADW	16	12	7	0	65	16.7	10	0.62	77	36-64	23
	SU90-28	63°52.20	28°56.20	1625	NEADW	16	13	9	0	65	16.7	12	0.78	85	41-59	27
	91-045-056	59°38.07	36°07.53	3025	DSOW	14	16	9	0	61	16.6	16	0.00	<35	23-77	14
	SU90-22	62°32.50	38°50.00	2180	DSOW	26	24	12	0	38	16.6	12	0.00	<35	37-63	14
Labrador Basin																
Greenland margin	90-013-006	59°29.48	45°52.241	1105	LSW	25	33	10	0	32	16.4	16	0.76	75	15-85	5
Greenland margin	90-013-011	58°54.85	47°05.126	2805	DSOW	15	21	13	0	51	16.4	12	0.50	70	27-73	14
Greenland margin	90-013-017	58°12.51	48°21.61	3379	DSOW	14	26	8	0	52	16.4	13	0.00	<35	38-62	20
Davis Strait	87-033-008	62°38.91	53°53.07	2424	DSOW?	13	40	7	0	40	16.4	16	0.38	65	23-77	9
Davis Strait	87-033-007	64°24.01	57°25.20	823	WGC	16	57	7	0	20	16.5	14	0.00	<35	22-78	4
Canadian margin	90-013-020	58°21.55	57°27.38	2865	DSOW	21	32	12	0	35	16.6	16	0.50	70	20-80	7
Canadian margin	91-045-014	55°44.50	53°43.98	340	LC	29	36	8	27	0						
Canadian margin	91-045-008	54°42..97	55°35.05	300	LC	28	39	8	35	0						
Canadian margin	91-045-093	50°12.28	45°41.15	3448	DSOW	27	29	10	0	34	16.6	12	0.50	70	18-82	6
Arctic Basin																
Laptev Sea	PS2477-3	77°14.77	118°33.22	193		10	8	7	0	75	16.7	20	0.43	70	74-26	56
Kara Sea	KS4405	78°	120°	44		8	6	5	0	81	16.8	14	0.72	85	60-40	49

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Table 2: *Mineralogical data for Greenland Rise Piston Core HU90-013-013 (PC13).* The stratigraphic framework is based on AMS C dates, normalized to PDB and corrected by -400 yr for reservoir effect (Hillaire-Marcel et al., 1994). Ages reported for each sample depth were estimated by linear interpolation of ^{14}C dates, then interpolated ages were calibrated age using the curve of Stoner et al. (1998). YD, Younger Dryas; HE numbers refer to detrital Heinrich-like events, see Table 1 for explanation

Sample	Depth (cm)	Age		Clay assemblage				Smectites			Smectitic layers in 10-14$_{sm}$ (%)	Beid.-Mont. proportion (%)	Beidellites abundance (%)
		^{14}C (yr BP)	Calibrated (yr)	C (%)	I (%)	K (%)	Sm. (%)	*d*(001) (Å)	$l_{1/2}$ (1/20° 2θ)	*vlp*			
Surface													
90-013-017	0-1			14	26	8	52	16.4	13.0		<35	38-62	20
Stage 1													
	8-10	1310	< 1000	16	18	11	55	16.6	19.0	0.38	65	36-64	20
	98-100	3980	4424	9	10	7	75	16.5	18.0	0.67	80	41-59	31
	188-190	6810	8022	9	8	7	76	16.6	17.5	0.60	75	27-73	21
	218-220	7650	8432	9	11	9	71	16.7	17.0	0.60	75	20-80	14
	243-244	7837	8635	12	15	10	63	16.6	15.0	0.59	75	10-90	6
	274-275	8164	8934	10	14	8	68	16.6	17.0	0.57	75	10-90	7
	291-292	8341	9113	18	33	13	36	16.5	10.0	0.45	70	25-75	9
	325-326	8689	9549	9	17	8	65	16.5	17.0	0.50	70	29-71	19
	347-348	9020	9961	10	12	7	71	16.7	18.5	0.54	70	30-70	21
	356-357	9200	10151	12	11	9	69	16.8	20.0	0.57	70	21-79	14
	374-375	10157	11574	15	21	12	52	16.8	14.5	0.47	70	-	-
	382-383	10313	11819	9	14	9	68	17.0	19.0	0.50	72	20-80	14
YD	392-393	10546	11969	15	19	11	55	17.0	15.0	0.55	75	40-60	22
	401-402	10910	12169	14	20	12	54	16.8	13.0	0.56	75	40-60	22
	410-411	11482	12888	16	19	12	53	16.6	14.5	0.82	87	25-75	13
	418-419	11990	13465	15	22	12	51	16.6	18.0	0.64	80	19-81	10
	424-425	12266	13830	13	19	11	57	16.7	19.0	0.60	75	25-75	14
	434-435	12516	14148	17	23	12	48	16.7	20.0	0.63	75	28-72	13
Stage 2													
HE1	448-449	14150	16137	12	19	11	58	16.7	17.0	0.42	70	21-79	12
	459-460	14824	17460	14	16	13	57	16.5	19.0	0.42	70	31-69	18
	466-467	15254	18220	11	25	11	53	16.7	17.0	0.42	70	-	-
	480-481	17254	19928	14	24	13	49	16.8	15.0	0.75	85	24-76	12
	497-498	19498	22395	12	24	10	54	16.6	20.0	0.43	70	26-74	14
HE2	513-514	21250	24322	13	33	10	44	16.6	16.0	0.57	75	7-93	3
	529-530	22190	26064	16	34	13	37	16.4	15.5	0.42	70	23-77	9

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2. Material

In the Northern North Atlantic sediments along the high-velocity axis of the WBUC, i.e. at water depths of 2800-3400 m, smectites represent up to 50% of the clay fraction. In contrast, the clay assemblages of the upper slope and shelf off Greenland and Canada contain primarily illite and chlorite with no or only low amounts of smectites from adjacent continental areas. As smectites dominate the clay assemblages in the Eastern Irminger and Iceland basins, their occurrence in the deep Labrador Sea sediments has been related to distal supplies by deep currents through the WBUC (Fagel et al., 1996). Detailed investigations have been conducted on surface sediments from areas where the highest abundance of smectites is related to deep water transport. Fourteen surface samples (Table 1) have been selected from Iceland and Irminger Basins, Greenland and Canadian Rises, Davis Strait and Labrador Basin (cruises CSS Hudson 87-033, 90-013 and 91-045 and Suroit 90, Fig. 1). Samples from the shallow Russian Arctic basins (Laptev and Kara seas) have been added to test the hypothesis of an Arctic contribution to the detrital supply to the Irminger Basin (Nürnberg et al., 1994).

Clay mineral analysis of two piston cores from the deep Labrador Sea, both recovered at a water depth of 3400 m just below the maximum velocity core of the WBUC (Lucotte and Hillaire-Marcel, 1994; Wu and Hillaire-Marcel, 1994), indicates that discrete but continuous supply of smectites increases through the Late Glacial in parallel with an intensification of the deep water circulation, ca. 14.3 kyr (Fagel et al., 1997). Core 90-013-013 (PC13) is located on the SW Greenland Rise, at the inlet of the WBUC gyre into the deep Labrador Basin (Fig. 1). Core 91-045-094 (PC94) was taken from the Canadian Rise, at the foot of the Orphan Knoll near the outlet of the deep current gyre into the North Atlantic (Fig. 1). Their stratigraphic framework is based on accelerator mass spectrometry (AMS) ^{14}C dates, normalized to $\delta^{13}C$=-250‰ (PDB) and corrected by -400 yr for the carbon reservoir effect (Hillaire-Marcel et al., 1994). An absolute age (in years BP) was calculated for each sample by direct linear interpolation between two adjacent ^{14}C dates, assuming a constant sedimentation rate. Then for each sample depth, a calibrated age was assigned from the calibration curve by Stoner et al. (1998). This curve was derived by correlating oxygen isotope stratigraphies from individual geomagnetic paleointensities records to the SPECMAP chronostratigraphy.

Sediments in core PC13 essentially consist of clayey silts, silty clays and clays (Hillaire-Marcel et al., 1994). Twenty-three samples have been chosen, which cover the last 26 kyr interval. (Table 2). The sampling interval of 10-20 cm allows for a time resolution of ~400 yr during the deglacial stage, from 14 to 8 kyr. An ash layer, found between 350 and 400 cm, has been related to the Vedde tephra level by H. Haflidason (University of Bergen). Dated at 10.6 kyr BP (Mangerud et al., 1984), it corresponds to the climatic cold Younger Dryas event and is well-defined in PC13 in the oxygen isotope record (Hillaire-Marcel et al., 1994). From 360 to 240 cm (10.1-8.6 kyr), an increase in magnetite concentration and grain-size matches a drop in the smectite/illite ratio (with a minimum at 290 cm, 9.1 kyr; Stoner et al., 1995; Fagel et al., 1997). This layer (referred to in the text as the 9 kyr event) results from erosion during ice sheet retreat on Greenland from the coastline into the continental interior (Funder, 1989). Additional samples were collected from thin sandy layers at a depth between 440 and 450 cm (16.1 kyr) and ~505-515 cm (24.3 kyr). Both layers resulted from ice-rafted deposition and have been correlated with North Atlantic Heinrich events HE1 and HE2 (Bond et al., 1992).

In PC94, hemipelagic ooze alternates with abundant 10-40 cm thick sandy layers. Fourteen samples (nine from the dominant muddy sediment and five from the sandy layers) belonging to the last 20.4 kyr have been analyzed (Table 3). The time resolution is twice lower than in PC13, averaging ~900 yr between 14.7 and 6.9 kyr. Sandy layers (referred as LDC, DC0 and DC1) are characterized by a high detrital carbonate content and are related to ice surges occurring on the Hudson Strait Shelf (Stoner et al., 1996). In particular, the DC0 layer at ~180 cm corresponds to the HE0 event identified in Davis Strait (Hillaire-Marcel et al., 1994) and was coeval with the Younger Dryas based on AMS ^{14}C dates (Stoner et al., 1996).

3. Methods

Clay mineral have been identified by X-ray diffraction analysis of both surface samples and piston cores (Fagel et al., 1996, 1997). Irregular smectite-illite mixed-layers are assigned to the smectite group and referred to in the text as smectites. This study will focus on precise determination of these smectites sensu lato. For this, Li and Mg saturations were conducted on the carbonate-free (<2 µm) clay fraction previous X-ray diffraction analysis.

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Table 3: *Mineralogical data for Canadian Rise Piston Core HU91-045-094 (PC94). YD, Younger Dryas; BA, Boiling-Alleröd; LDC, light detrital carbonate layer; DC numbers refer to detrital carbonate layers identified by Stoner et al. (1998). See Tables 1 and 2 for explanation*

Sample	Depth (cm)	Age		Clay assemblage				Smectites			Smectitic layers in 10-14$_{sm}$ (%)	Beid.-Mont. proportion (%)	Beidellites abundance (%)
		^{14}C (yr BP)	Calibrated (yr)	C (%)	I (%)	K (%)	Sm. (%)	*d*(001) (Å)	$l_{1/2}$ (1/20° 2θ)	*vlp*			
Surface													
91-045-093	0-1			27	29	10	35	16.4	12.0	0.50	70	18-82	6
Stage 1													
	4.5-6.5	1656	1467	20	46	12	22	16.6	13.0	0.43	70	14-86	3
	33.5-35.5	2200	3930	20	24	12	44	16.6	15.0	0.75	85	42-58	18
LDC	82-83	6542	6944	27	26	17	30	16.5	14.0	0.42	70	10-90	3
	105-106	7622	8260	19	22	14	44	16.5	16.0	0.63	80	17-83	7
LDC	125-126	8500	9371	25	37	19	18	16.5	15.0	0.08	40	18-82	3
	150-151	9486	10736	20	28	16	35	16.6	17.0	0.47	70	36-64	13
YD/DCO	179-180	11395	12314	28	26	22	25	16.6	14.0	0.31	60	60-40	15
YD/DCO	181-182	11525	12441	25	27	20	28	16.6	24.5	0.49	70	45-55	13
BA	206-207	12850	13797	17	24	13	46	16.5	21.0	0.46	70	34-66	16
DC1	222-223	13429	14687	20	27	17	35	16.8	26.0	0.34	65	26-74	9
Stage 2													
	259-260	14745	16782	14	26	13	46	16.8	22.0	0.67	80	-	-
	282-283	16296	18109	19	32	16	33	16.8	21.0	0.24	55	43-57	14
	301-302	17110	19216	19	27	16	37	16.7	20.0	0.60	75	48-52	18
	323-324	17640	20388	19	31	14	36	16.6	19.0	0.60	75	34-66	12

3.1. Clay mineral preparation and identification

Aliquots of 1-2 g of dry bulk sediment were dispersed in distilled water, then sieved on a 63 µm mesh. Carbonate was removed with 0.1 N HCl. Deflocculation of clays was completed through repeated washings. The clay fraction was separated by decantation, the settling time being calculated from Stoke's law. Oriented mounts were made according to the sedimentation-onto-glass slide method (Moore and Reynolds, 1989). A Siemens diffractometer was used with a CoKα radiation (λ = 1.7890 Å), at scanning speed of 2° 2θ/min. Identification of the clay minerals was assessed according to the position of the (001) series of basal reflections on three diffractograms: (1) on the air-dried or natural sample (N scan); (2) after ethylene-glycol solvation during 24 h (EG scan); and (3) after heating to 500°C for 2 h (H scan). Semi-quantitative estimations (±5%) of the main clay species (illite, chlorite, smectites sensu lato, kaolinite and vermiculite) were based on the area of the (001) diffraction peaks of each clay mineral in EG diffractograms, i.e. at 10 Å for illite and at 17 Å for smectites. Estimation of chlorite and kaolinite was based on the area of the 7 Å peak, where the (001) of kaolinite and the (002) chlorite reflections are surimposed, their respective abundance being deduced by using the (004) chlorite/(002) kaolinite peak intensity ratio at 3.57 Å (kaolinite) and 3.54 Å (chlorite) on the air-dried scan. Minor contribution of illite-vermiculite mixed-layer was identified by the occurrence of a broad peak centered around 12 Å on the EG; this peak collapsed to 10 Å after heating. The intensities of the reflections at 7, 10, 12 (if present) and 17 Å were multiplied by their width at half-height, and the areas then summed to 100%.

3.2. Characterization of the smectites

The clays here referred to as "smectites" include minerals of different origins and chemistry, and irregular smectite-illite mixed-layers. The smectites do not correspond to a single well-defined peak at 14 Å that moves to 17 Å after glycolation On the air-dried X-ray pattern, smectites were recorded by a broad (001) peak encompassing most of the *d* range between 10 and 14 Å, reflecting a 10 Å component in the mixed-layer mineral. Sometimes, a single reflection defined a shoulder that was surimposed onto the dominant (001) smectite peak, or several small reflections were surimposed onto the smectite peak, but with decreasing intensities towards higher angle values. Expansion of smectite under glycolation varies from one sample to another, the position of the peak ranging from 16.4 to 17 Å. Characterization of smectites has been achieved through measurements of three parameters on X-ray patterns after ethylene-glycol solvation: the position of the maximum intensity of the smectite peak; the *vlp* ratio; and the crystallinity $l_{1/2}$ of the smectites (see Table 1 caption).

The X-ray patterns of the air-dried and the ethylene-glycol-treated smectites depend on the cation held in the exchange site (Moore and Reynolds, 1989). Post-treatments helped to further assess the composition of smectites (Schultz, 1969; Brindley and Brown, 1980; Thorez, 1998). Li-saturation tests have been conducted on all samples; additional Mg-saturation tests were only performed on selected samples. Saturation with Li allows to precise the composition of dioctahedral Al-Fe smectites, i.e. to distinguish montmorillonite s.s. (Al end-member) on the one hand and beidellite, Fe-beidellite and nontronite (Fe end-member) on the other. The layer charge of the montmorillonite originates primarily in the octahedral sheet whereas that of the beidellite is located in the tetrahedral sheet. The Fe^{3+} content of the octahedral sheet of dioctahedral smectites contains an average of 0.15 octahedral Fe. Nontronite is the Fe analog of montmorillonite and beidellite, with a Fe^{3+} content in the octahedral sheet higher than 1. When Fe values ranges from 0.15 to 1, the clay is referred to as Fe-rich smectite (definitions from Weaver, 1989). Montmorillonite s.s. displays irreversible collapse after Li saturation followed by heat treatment (300°C). Li ions neutralize the layer charge by migrating into the octahedral sites. The re-equilibrium of charge deficit converts the montmorillonite into a pyrophyllite-like mineral that does not expand anymore with ethylene-glycol (Moore and Reynolds, 1989).

For the Li-saturation procedure (modified from Lim and Jackson, 1986), clay particles were washed with aqueous LiCl·2N overnight. Samples were then rinsed with distilled water, and prepared as oriented mounts. Analyzes were conducted on air-dried slide (Li N scan), after 2 h heating at 330°C (Li 330°C scan), and then after overnight ethylene-glycol solvation (Li 330°C EG scan). The relative abundance of the montmorillonite and the beidellite when in admixture was estimated through comparison of the intensities of the 10 Å peaks on the three Li-saturated X-ray scans, assuming that the intensity of the illite (001) reflection remained constant (Thorez, 1998; see Fig. 2).

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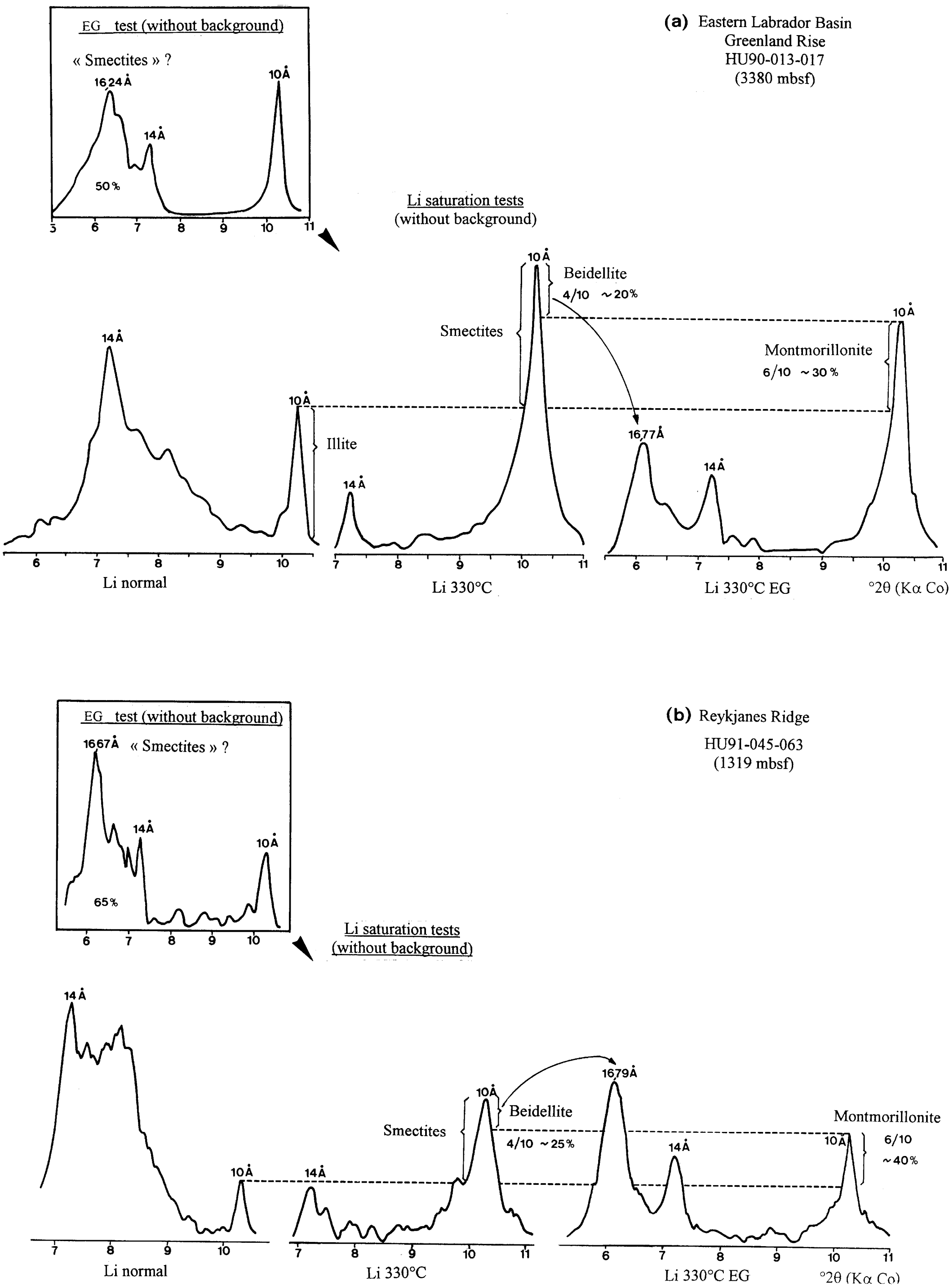
Fig. 2. *Estimation of the relative abundance of montmorillonite s.s. and beidellite from Li-saturation test*: (a) surface sample HU90-013-017, Greenland Rise, 3380 m water depth; and (b) surface sample HU91-045-063, Reykjanes Ridge, 1319 m water depth. The relative abundance of montmorillonite and beidellite when in admixture in smectites was estimated through comparison of the intensities of the 10 Å peaks on all three Li-saturated X-ray scans, assuming that intensity of the illite (001) reflection remained constant (Thorez, 1998). The peak height at 10 Å on the Li N scan corresponds to the content of illite. The peak height on the Li 330°C scan corresponds to the sum of illite and of the whole, collapsed smectites. After ethylene-glycol solvation, the decreased intensity of the 10 Å peak expresses further expansion for the beidellite fraction from 14 to 17 Å, whereas the (001) of montmorillonite remains stabilized at 10 Å where it contributes to an increase of the 10 Å illite peak. With Li treatments, beidellites and nontronites preserve their expandability after ethylene-glycol solvation.



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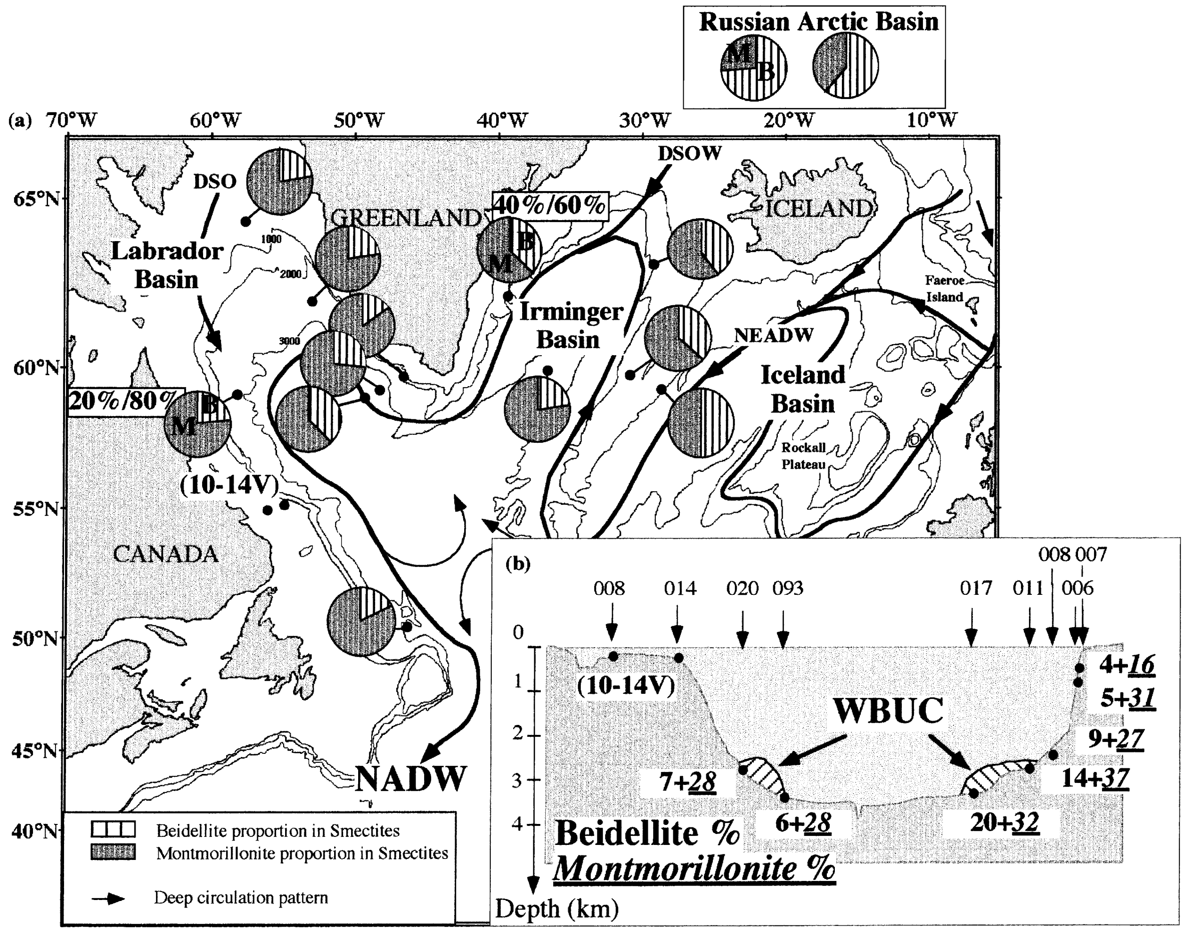
Among dioctahedral Fe-rich smectites, the Mg-saturation test allows identification of beidellite and nontronite. Saturation procedure for Mg and Li are identical (samples are washed with aqueous MgCl·2N). Two tests are critical: X-ray diffraction analysis of the air-dried Mg-saturated sample, and then glycerol solvation. The 14 Å reflection on the air-dried Mg sample expands up to 17 Å after glycerol solvation when nontronite is present, whereas beidellite (001) is stabilized at 14 Å.

The intensity ratio of the (002)/(003) reflections is useful for differentiating dioctahedral and trioctahedral smectites. However, the (002) and higher-order reflections are weak (Moore and Reynolds, 1989), and this method is not valid for differentiating smectites within complex marine clay assemblages like those from the Northern North Atlantic. The spacing of the (060) reflection also depends on the composition of the octahedral layer, and this character may distinguish the trioctahedral (peak at 1.54 Å) from the dioctahedral (peak at 1.49 Å) smectites when quartz is absent. However: (1) the quartz is ubiquitous in the Northwest Atlantic sediments and shows a peak at 1.54 Å that interferes thus with the possible 1.54 Å reflection of trioctahedral smectites (Robert, 1975); (2) saponite and nontronite have nearly identical *d*(060) values (Moore and Reynolds, 1989); and (3) nontronite and trioctahedral smectites are most of the time associated in weathering and hydrothermal alteration products of basalts where nontronite dominates (Weaver, 1989). As a consequence, occurrence or absence of nontronite is the clue for differentiating dominant volcanogenic from terrigenous smectites in complex clay fractions like those studied here.

Fig. 3. *(a) Map showing the relative proportion of montmorillonite and beidellite within the smectites; surface sediments; and (b) bathymétrie distribution of the beidellite and montmorillonite abundance in the clay fraction along a SW-NE transect across the Labrador Sea.*



4. Results

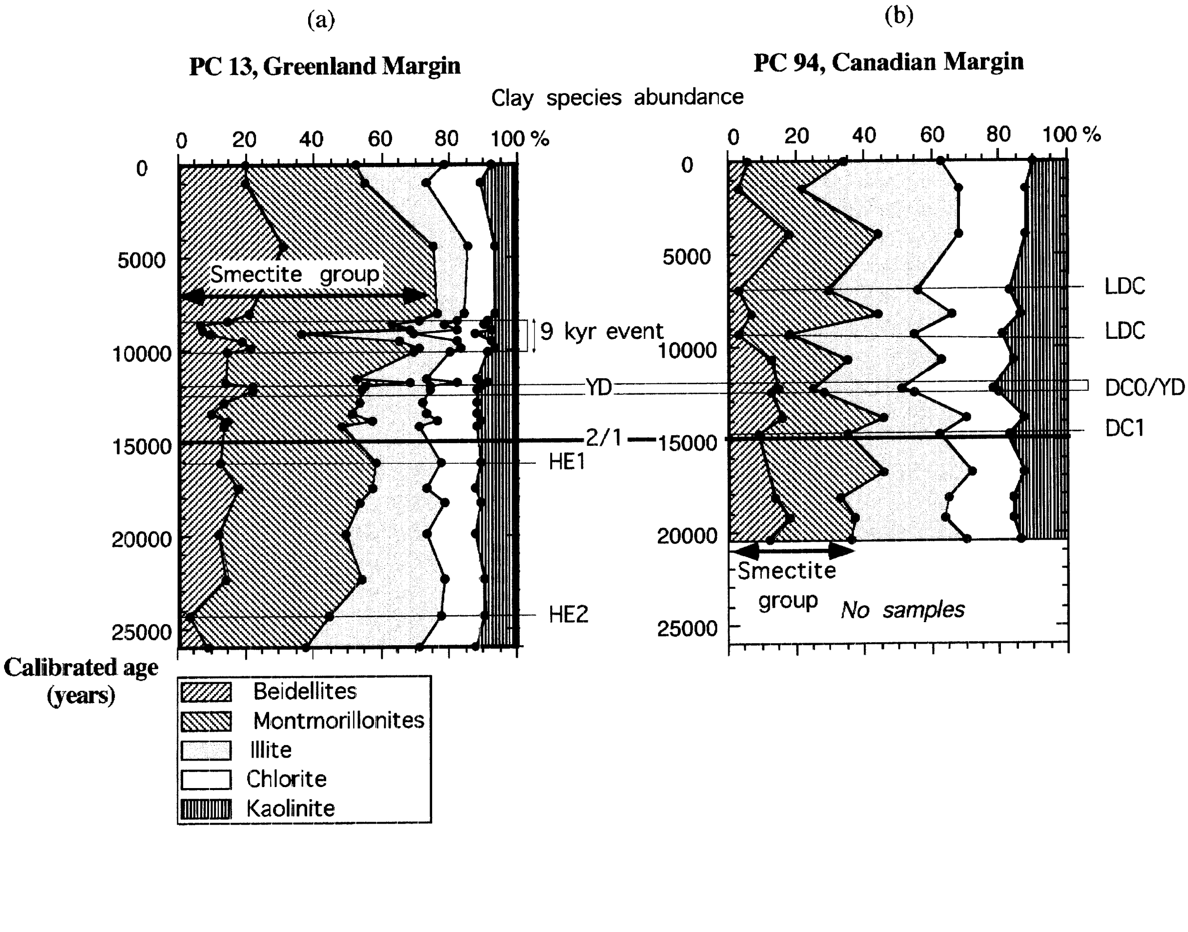
4.1. Surface data

The highest content of smectites (67%) in surface sediments has been evidenced in the Iceland and

Irminger Basins (Fagel et al, 1996), especially on the flanks of Reykjanes Ridge (071 and 063) and Southwest of Iceland (SU28). There, smectites show highest abundance of smectitic layers (70-85%), and a narrow (001) reflection (crystallinity ≥ 0.5° 2θ) that peaks at 16.7-16.8 Å after ethylene-glycol (Table 1). Sites 063 and SU28 are bathed by the NEADW1, whereas 071 is located in the NEADW2 (Fig. 1).

Smectites are slightly less abundant (61%) in the deep Irminger Basin (Site 056), and significantly less abundant (38%) on the Greenland Slope (Site SU22). There, smectites contain smaller abundance of smectitic layers (<35%) than on Reykjanes Ridge. Also, the expansion of the smectites after ethylene-glycol is less efficient (d = 16.6 Å), with a broader (001) reflection (crystallinity ≥ 0.6-0.8° 2θ). Site SU22 at 2180m water depth is located on the path of the DSOW that plunges southwest of Denmark Strait, whereas Site 056, at 3025 m water depth, corresponds to the deepest part of the Irminger Basin filled by the cold dense DSOW. Smectites in the Irminger Basin bathed by the DSOW do not show any significant relationship to the two surface sediments sampled in the Russian Arctic basins (Table 1).

Fig. 4. *Evolution of the clay mineral composition through time: (a) piston core PC13, Greenland Rise; and (b) piston core PC94, Canadian Rise.*



In the Eastern Labrador Sea, smectites increase with depth (1105-3379 m water depth) from 32 to 52% along the Greenland Slope. The abundance of smectitic layers is higher, from 65 to 75% as observed in areas bathed by the NEADW masses, with the exception of the deepest Site 017 (<35%) which shows affinity with areas bathed by the DSOW. However, the lowest expansion of smectites after ethylene-glycol, and variable crystallinities do not allow correlation with smectites from other areas. Mixing of water masses and lateral advection from Greenland may have resulted in a composite signal.

In the Western Labrador Sea, the shallowest sites, 008 and 014 (at 300 m water depth), off Southern Labrador do not contain any smectites but significant amounts of illite-vermiculite mixed-layers (Table 1). The deepest sites, 020 (2865 m water depth) to the north and 093 (3448 m water depth) at the outlet of the WBUC, contain 35% of smectites, among the lowest values of the whole study area. Smectites show affinities with samples from Iceland, Irminger and East Labrador Basins but again do not allow any correlation with specific area. At Site 007 in Davis Strait (823 m water depth), on the path of the DSO, relatively small contents (20%) of smectites contain minor abundances of smectitic layers (<35%), with intermediate crystallinity.

The Mg-saturation test does not allow identification of any major contribution of nontronite, as the 14 Å reflection after Mg-saturation does not expand upon glycerol. The Li-saturation test allows determination of both the montmorillonite s.s. and the beidellite. Montmorillonite dominantes the smectite composition in the surface samples (Table 1, Fig. 3), with the only exception of two samples recovered from the Russian Arctic Basin where beidellite dominates. On the Reykjanes Ridge, smectite compositions at Sites 063 and SU28 bathed by NEADW1 contain up to 65% of montmorillonite, whereas at Site 071 in the NEADW2 they contain about a same amount of montmorillonite and beidellite. Smectites at Site SU22, on the path of the diving DSOW along Greenland Slope of Irminger Basin, are composed by about 65% of montmorillonite. This value is very close to that found at locations bathed by NEADW1, but clay associations in both areas are clearly separated at the standpoint of smectitic content in the mixed-layers. At Site 056, in the deep Irminger Basin filled by the DSOW, a high proportion of montmorillonite (~80%) suggests some mixing, or advection from other sources.

On the Greenland Slope of the Labrador Sea, the high proportion of montmorillonite (85% of the smectites) at the shallowest site, Site 006 (1105 m water depth), decreases with depth to about 62% at the deepest site, Site 017 (3379 m water depth), in an area under of the DSOW. In the Western Labrador Sea at Site 020 (2865 m water depth) to the North, and at Site 093 (3448 m water depth) at the outlet of the WBUC, high proportions of montmorillonite (80%) are observed. These values are transitional between those at Site 007 (823 m water depth) in Davis Strait, bathed by the DSO, and those at shallow water depth on the Greenland Slope of the Labrador Basin (85% at Site 006, 1105 m water depth), suggesting some mixing of supplies from different water masses and/or a lateral advection of clay particles.

To summarize, the characteristics and the composition of the smectites in surface samples from the Northern North Atlantic allow a clear separation of clay mineral assemblages depending on their location. The distribution of these characteristics does not depend on water depth or on position of the sites relative to the ridge and the continental margins. Rather, it seems related to the different water-masses.

4.2. Core PC13, SW Greenland Rise

The clay mineral association of PC13 includes illite, chlorite, kaolinite and smectites (Fig. 4). Smectites represent 36-76% of the association, their modern value (site 017) being 52%. The lowest abundance of smectites (<40%) occurs in the lower part of the sequence (24-26 kyr) and at about 9 kyr. It is associated with the highest contents of illite and chlorite (due to the relative quantification approach and the more or less constant kaolinite content through the core). A high content of smectites (>60%) is punctually measured at 12 kyr. The smectite content remains higher than 60% from 10.1 to 8 kyr, with the exception of one sample at 9 kyr (~290 cm). A high smectite content (75%) at 4.4 kyr drops close to the modern values in the uppermost <1000yr sample (55% at 8 cm). There is no drastic mineralogic change during the Heinrich events or the Younger Dryas.

As for surface sediments, smectites include irregular mixed-layers. The proportion of smectitic layers is relatively high (65-87%, Table 2). Expansion of the smectites under glycolation varies from 16.4 to 17 Å (Table 2). The best expansion, which expresses the smallest abundance of mixed-layers, is observed from 12.2 to 10.1 kyr, encompassing the Younger Dryas. The lowest crystallinity is observed around the Younger Dryas, as well as in surface sediments. No specific variation of the characteristics of smectites is observed in the Heinrich-like layers.

The Mg and Li tests indicate the absence of nontronite, but the presence of montmorillonite and beidellite (Table 2, Fig. 5). The smectites are usually composed by 70-80% of montmorillonite and 20-30% of beidellite from 26 to 8 kyr. In the uppermost samples (4.4 and 1 kyr), the contribution of the montmorillonite remains dominant but decreases close to modern value (with ~60% montmorillonite and 40% beidellite within the smectites). The proportion of the montmorillonite reaches 90% during Heinrich event HE2 (up to 93%) and from 8.9 to 8.6 kyr (Table 2, Fig. 6). Such contributions of the montmorillonite are higher than any recorded in modern surface sediments (Table 1). A lower montmorillonite contribution within the smectites (60%) but close to the modern value of 62% characterizes the Younger Dryas.

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Fig. 5. *Evolution of the Li X-ray diffraction patterns (without background curve) through the late 24 kyr, PC13, Greenland Rise. The dashed area represents the beidellite contribution.*

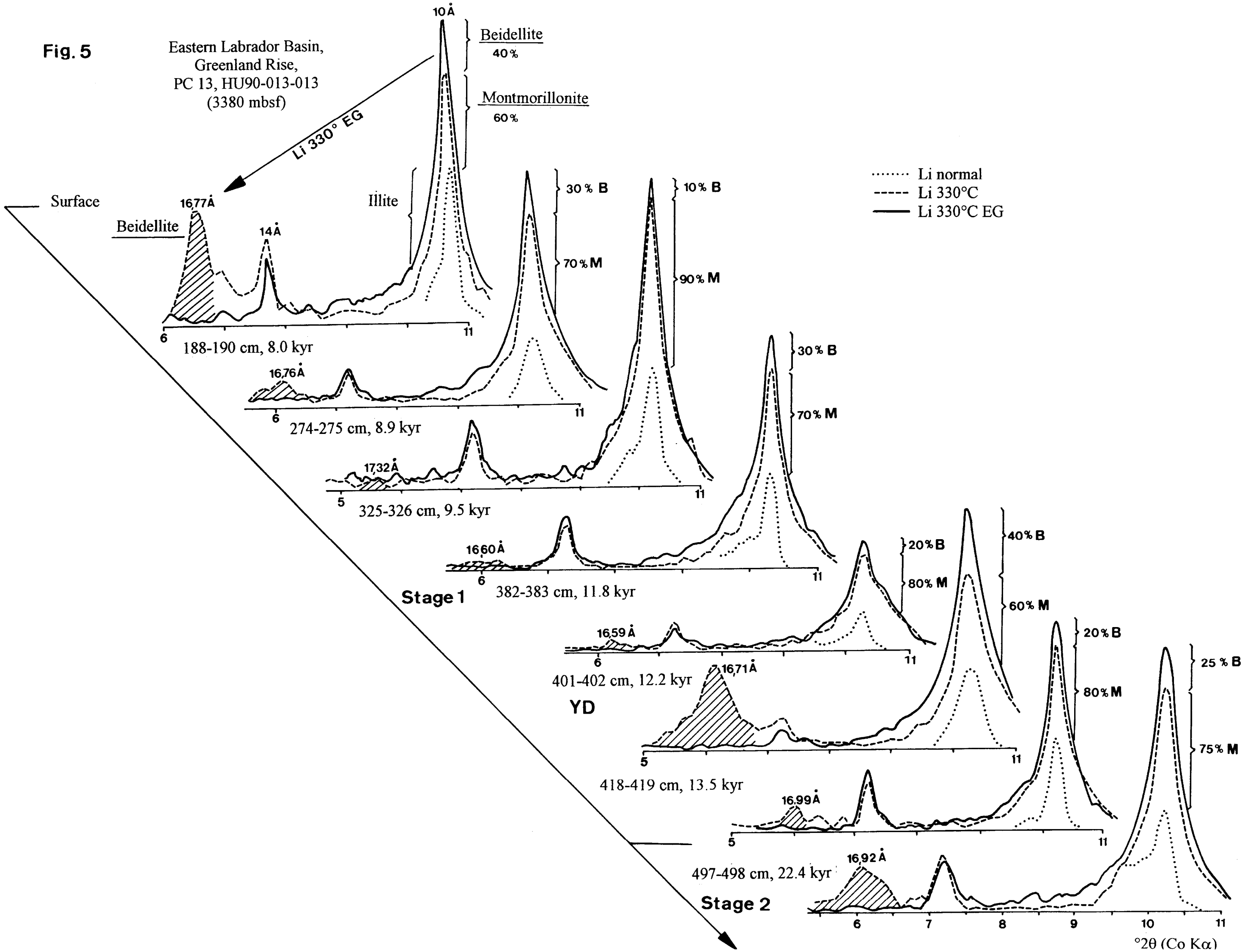

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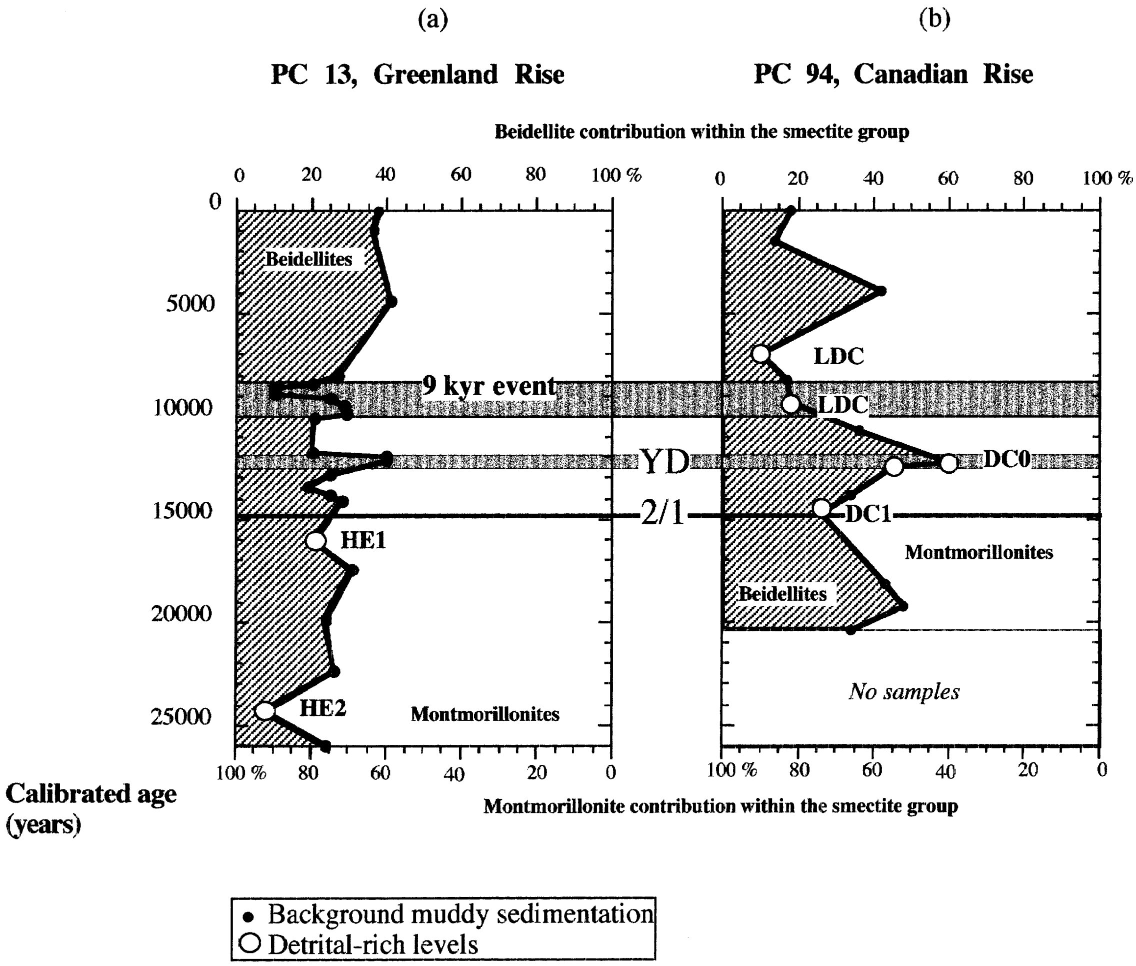
Fig. 6. *Evolution of the relative contribution of beidellite and montmorillonite: (a) piston core PC13, Greenland Rise; and (b) piston core PC94, Canadian Rise.*



4.3. Core PC94, Canadian Rise

The clay mineral association in PC94 includes illite, chlorite, kaolinite and smectites. Smectites represent 18-46% of the clay fraction, its modern abundance being 35%. These values are lower than those of PC13. The sampling resolution does not allow to define any temporal trend, but the detrital carbonate (DC) layers and the Younger Dryas event are characterized by the lowest abundance of smectites (Table 3, Fig. 4). The proportion of smectitic layers within the illite-smectite mixed-layers vary from 40 to 85%, the lowest values being again systematically recorded in the detrital carbonate intervals. After glycolation the main peak of the smectites varies from 16.4 to 16.8 Å, the highest expansion being recorded prior to 14 kyr. The crystallinity of the smectites is very poor ($l_{1/2}$ > 1.0° 2*θ)*, especially for the lower part of the sequence up to the Younger Dryas.

As in PC13 and in surface sediments, nontronite has not been observed in this core. The smectites mostly consist of montmorillonite and beidellite. Montmorillonite usually dominates (Fig. 6) up to 90% of the smectite composition at 6.9 kyr. The proportion of montmorillonite in PC94 is lower (rarely equal) than in equivalent age intervals of PC13, except at 8.2 kyr and in the uppermost (1.5 kyr) and surface samples. In hemipelagic sediments (DC excluded), smectite composition from the lower part of the sequence between 20.4 and 10.7 kyr closely matches those from surface sediments sampled along the WBUC in the Iceland and Irminger basins (35-50% of beidellite within the smectites, Table 1). Three detrital carbonate layers (LDC and DC1 — see Table 3) show an increased in montmorillonite. In contrast, the detrital carbonate layer associated with the Younger Dryas event (DCO, see Table 3) is characterized by an increased content of beidellite (up to 60%, i.e. the highest contribution of the past 20 kyr), at the expense of montmorillonite (Fig. 6).

5. Discussion

5.1. Origin of clay particles in the Northern North Atlantic

More than 50% of the clay fraction of surface sediments consist of smectites in most areas of the Northern North Atlantic (Biscaye, 1965; Grousset et al., 1982; Bout-Roumazeilles, 1995; Fagel et al., 1996); the highest abundances are recorded in the Eastern basins. High contents of smectites, proximity of active volcanic areas and mineralogical gradients have been used to infer a dominant origin from Iceland, Reykjanes Ridge and the Faeroes, through meteoric or submarine weathering of volcanic terranes (Yeroshchev-Shak, 1964; Grousset et al., 1982; Zimmerman, 1982; Bout-Roumazeilles et al., 1999). The lack of any correlation between glass shard occurrence and smectite abundance suggests that part of the smectites is derived from continental areas (Biscaye, 1965; Berry and Johns, 1966).

Only beidellite and montmorillonite are identified for surface and Late Glacial to Holocene sediments. The absence of nontronite at all sites indicates the absence or minor contribution of clays derived from hydrothermal alteration and/or meteoric weathering of basaltic materials below 1300 m water depth in the Northern North Atlantic, and at all depths of the Labrador Basin. Therefore, Iceland and the Mid-Atlantic Ridge do not constitute a major source for clays in the sediments bathed by the NEADW, and for sites located on the path of the WBUC. Several observations support this interpretation: (1) smectites are minor components in Icelandic soils where amorphous minerals (imogolite, allophane, ferrihydrite) dominate (Wada et al., 1992). No amorphous components have been found at North Atlantic sites where smectites are dominant (Fagel et al., 1996); (2) hydrothermal alteration of basalt to smectites occurs only locally in active areas of Iceland and of the Mid-Atlantic Ridge (Chamley, 1989), yielding formation of nontronite and trioctahedral smectites (e.g. Robinson et al., 1977); dioctahedral smectites in the studied sites do not include nontronite; (3) in active areas of mid-oceanic ridges, volcanogenic clays (smectites, celadonite, ...) are observed in and above weathered basaltic beds, but rapidly decrease within a few tens of centimeters in the sedimentary column (e.g. Chamley, 1989); and (4) Sm-Nd studies of the whole <2 µm fraction of surface sediments from the Reykjanes Ridge (site 063, Fig. 1) indicate a dominant terrigenous contribution (60%) from young crust components that may derive from Europe and/or from the Arctic (Innocent et al., 1997).

All these characters suggest that the origin of most smectites in sediments bathed by the NEADW and WBUC masses must be searched in upstream areas of these currents. Smectites sensu lato are common clays in the Northern North Atlantic, but they include in reality species with diversified chemical compositions, associated to illite-smectite mixed-layers. The presence of beidellite and montmorillonite only indicates that smectites here proceed mainly from chemical weathering of diverse substrates, and were eroded from soils and/or sediments.

5.2. Sources of terrigenous smectites

Terrigenous Al-Fe smectites may be supplied from several potential source-areas, i.e. (1) Northwest Europe, (2) Eastern Greenland coastal areas, (3) Arctic margins and (4) Northern Baffin Bay area.

1. Smectites are common clay constituents in modern soils from Western Europe where they are associated to vermiculite (e.g. Pedro, 1968; Righi and Meunier, 1995). Montmorillonite and beidellite are by far the most abundant smectites in temperate soils on various substrates, where they are associated to illitic mixed-layers (Gradusov, 1974; Weaver, 1989). For instance, montmorillonite with illite interlayering is common in soils of Ireland (Bain and Russell, 1980). However, the absence of vermiculite at the studied sites suggests that modern West European soils are not the dominant source for the terrigenous load of deep waters. The clay fraction of the late Jurassic and Cretaceous sediments from Western Europe contains 40-90% of smectites, most of them being montmorillonite (Weaver, 1989). Late Jurassic and Cretaceous sediments largely outcrop over large areas of the West European margins, especially in Ireland and Great Britain. They may have been eroded and transported to adjacent Northeast Atlantic basins where smectites frequently constitute the major part of the clay fraction both in surface and in late Quaternary sediments (Grousset et al., 1982; Zimmerman, 1982; Bout-Rouma-zeilles, 1995). Soils from semi-arid European and Mediterranean areas are dominated by smectites, which mostly consist of beidellite (Pédro, 1968; Righi and Meunier, 1995). Heavy rains in these areas ensure deep erosion and transport to the ocean. Al-Fe smectites contribute for 30-40% of the clay assemblages of surface sediments in the adjacent Bay of Biscaye (e.g. Debrabant et al., 1979) and may have been carried further to the North by the water deep circulation. Transport of smectites from Western Europe to the deep ocean may have been ensured by the North Atlantic Drift, that dives to the North and participates to deep water formation, and by intermediate to deep waters from the temperate Atlantic, that include a Mediterranean

Water component (McCartney, 1992; Dickson and Brown, 1994).

2. Part of the smectites may derive from erosion of fluvio-glacial sediments along the Eastern Greenland coast (Petersen and Rasmussen, 1980) where well-crystallized smectites formed by weathering of biotite during warmer intervals have been reported. Their composition has not been assessed; according to drainage conditions, biotite can evolve either into a mixed-layer clay and/or beidellite by transformation when hydrolysis is important enough, or into montmorillonite in confined conditions (e.g. Aoudjit et al., 1995).

3. Smectites have been locally reported in Siberian Arctic surface sediments, in particular in the Laptev Sea shelf area (20-40% of smectites, Nùrnberg et al., 1994). A recent synthesis demonstrates the variability of smectite content in surface sediments from the Eurasian shelf seas and the adjacent Central Arctic Ocean (Wahsner et al., 1999). Smectite contents are low (<5-20%) in Eurasian Arctic Ocean but increase in shelf areas, in the inner Laptev and Kara seas (mean smectite content of 26 and 60%, respectively). Maximum smectites content of up to 70% were being identified near the river mouths. These areas represent the main source of smectites out of the Arctic Ocean. Smectites were supposed to be derived from the erosion and weathering of Mesozoic basalt complexes in the Siberian Hinterland, then transported by rivers to the Kara and Laptev seas (see references in Wahsner et al., 1999). Smectite particles may have been transported by cold currents to the North Atlantic, a smectite maximum being evidenced along the pathway of the Transpolar Drift (Nùrnberg et al., 1994) which drives sea ice from the Siberian shelf to the Fram Strait. From there, the East Greenland Current carries cold waters and icebergs out of the Arctic (Stein et al., 1994). Note here that the clay fraction from the two samples collected in the Laptev and Kara seas, not representative of the Arctic Basin, contain up to 80% of smectites which largely consist of beidellite (Table 1). 4. Smectites represent 5-30% of the clay assemblages (mean 20%) in Baffin Bay sediments (Boyd and Piper, 1976; Piper and Slatt, 1977; Andrews et al., 1993). Montmorillonite, that was already reported by Piper and Slatt (1977), dominates the two samples from the Northern Labrador Sea (Table 1). The shallowest site (007) near the outlet of Davis Strait (Figs. 1 and 3) contains low contents of smectites (20%), with less than 35% of smectitic layers. Terrigenous particles including low amounts of smectites with a dominant montmorillonite may have been supplied through DSO waters to the WBUC gyre in the Labrador Sea.

To summarize, characteristics and composition of the smectites are consistent with a dominant terrigenous origin in areas bathed by the NEADW and the WBUC. The relative importance of the potential sources for smectites, that include Western Europe, Greenland, Siberian Arctic coasts and Baffin Bay, and their link to the modern circulation are discussed below.

5.3. Clay mineralogical imprint of modern deep water masses

According to their origin, specific mineralogical characteristics may be assigned to smectites driven by the main water masses involved in the WBUC. The sites bathed by the NEADW (all located on the flanks of Reykjanes Ridge between 1300 and 2250 m water depth) are characterized by smectite-rich and well-crystallized mixed-layers, characterized by a good expansion upon ethylene-glycol. Beidellite is significantly more abundant in smectite composition at Site 071, within NEADW2. This contrast most probably expresses differences in the origin and pathways of both sub-water masses. The upper part of the NEADW, i.e. NEADW1, mostly consists of Norwegian Sea outflow that plunges over the sill between Iceland and Scotland, and of North Atlantic surface waters that dive at the convergence (Mauritzen, 1996). This water mass is the most likely to contain mainly montmorillonite (associated to beidellite), which have been eroded by run-off from Northwest Europe, including Scotland and Ireland (e.g. Bain and Russell, 1980; Weaver, 1989). In the NEADW2, the main component from the Norwegian Sea outflow is mixed with warmer and more saline waters from the deep temperate Atlantic, with a small influx of Antarctic Bottom Water (McCartney, 1992; Dickson and Brown, 1994; Lucotte and Hillaire-Marcel, 1994). This composite NEADW2 contains a slightly different clay association, characterized by higher proportions of beidellite within the smectites probably of a distant origin. This allows a clear distinction of both water masses from their mineralogical content.

Site SU22, within the core of the DSOW near its overflow South of Denmark Strait, probably shows the most typical mineralogical imprint of this water mass (Table 1). Smectites are less abundant than in the NEADW although their proportions of beidellite and montmorillonite are quite similar. The surface sediment at Site SU22 also contains low smectitic layers, poorly crystallized, with low expansion after glycola-tion. No close correlation can be made actually with the two analyzed sediments from the Russian Arctic basins. As Arctic waters circulate at shallow water depth along the Greenland margin on their way to Denmark Strait, lateral advection of particles may have progressively modified the clay mineral association. Most of the characteristics of the smectites, as defined at Site SU22 at the inception of the DSOW in the Irminger Basin, are also present at the other sites bathed by the DSOW (Table 1, Fig. 3). However, higher contents of smectites occur within the DSOW South of Greenland at Sites 011 and 017, and at Site 056, in the deep Irminger Basin, together with a better crystallinity and more smectitic layers at the shallowest site (011) (2805 m water depth). Characteristics of these smectites are transitional between those observed in areas bathed by the NEADW and by the DSOW, and probably express some mixing of both water masses. These transitional smectites, with greater influence of DSOW supply with depth, also characterize the sites on the path of the WBUC in the Labrador Basin (Fig. 3).

The clay association from the shallowest site at the outlet of Davis Strait (007, Table 1) that mainly reflects DSO-driven supplies, contains a smaller abundance of smectites and lower proportions of beidellite than those from Site SU22 at the outlet of Denmark Strait. Its influence southward along the Canadian margin at sites within the WBUC is mostly reflected by a decreased content in smectites, particularly of the beidellite contribution, indicating inception of DSO waters within the main current. Lateral advection of particles within the WBUC is not considered here, due to the absence of smectites and presence of significant amounts of illite-vermiculite mixed-layers at shallow water depths of the Canadian margin (Table 1). The WBUC shows similar characteristics southward, at its outlet to the North Atlantic Basin. Comparable smectites are also present in the deep Irminger Basin (site 056), filled with deep waters with characteristics close to those of the DSOW that escapes from the main body of the WBUC North of the Charlie-Gibbs Fracture Zone (CGFZ) to form a deep cyclonic gyre (Lucotte and Hillaire-Marcel, 1994). Most of the modern DSO is not included within the core of the WBUC, but circulates at a shallow to intermediate water depth (LSW) and forms a recirculating loop in the Irminger and Labrador basins (Clarke and Gascard, 1983; Dickson and Brown, 1994). Site 006 off the southern tip of Greenland is located within this water mass. Its clay mineral content shows only small affinities with Site 007 at the outlet of Davis Strait (see content of beidellite, Table 1). This may be due to some mixing with other water masses (NEADW1) or, more likely, due to the lateral advection of detritals from Greenland.

The modern deep water masses in the northern North Atlantic contain specific types of smectites modified progressively in sites along the main path of the WBUC. This observation will be used to monitor time variations of the WBUC since the Late Glacial.

5.4. The Quaternary clay record of the past 26 kyr: evolution of the deep oceanic circulation

Based on a high-resolution sampling, the evolution of smectite percentages and smectite/illite ratios in cores PC13 and PC94 provided evidence for gradual intensification of WBUC circulation from the Late Glacial to the early Holocene (Fagel et al., 1997). In this study, only montmorillonite and beidellite have been evidenced at both sites, suggesting that major sources of smectites to the deep Labrador Basin remained the same for the past 26 kyr.

During the Late Glacial interval of PC13, the increase of smectites (that takes place) between 19.8 and 18.2 kyr (with an early peak at ca. 22.4 kyr) is associated with changes in XRD characteristics. In particular, the better expansion upon ethylene glycol solvatation, and higher proportion of beidellite (Table 2) may indicate a more important contribution of NEADW (especially NEADW2) waters as the WBUC intensified. In contrast, the intervals of low smectite content (<50%) show a poor expansion upon ethylene-glycol solvation, like those found at shallower water depth of the modern Greenland Rise bathed by the upper DSOW and the LSW (Tables 1 and 2). This is most probably related to a weak circulation of the WBUC, with a greater importance of the re-circulating gyres and of lateral advection of particles than in the modern ocean. Fluctuations of the characteristics of the smectites during the deglacial interval from 14.4 to 8 kyr suggest some variability of the regime of circulation. In the modern ocean, cold dense waters from the Norwegian Sea dive across the sill between Iceland and Scotland to reach the deep Atlantic where they mix with deep waters from the temperate Atlantic to form the NEADW2 (Dickson and Brown, 1994; Mauritzen, 1996). Dense water formation in relation to an increased salinity probably started in the Norwegian Sea as the surface temperature warmed, leading to full development of the NEADW during the Holocene (Boyle and Keigwin, 1987; Duplessy et al., 1988). In the uppermost part of the core, at least in the top 8 cm (no sample between 98 and 8 cm, i.e. between 4.4 and <1 kyr), the decreased percentage of smectites but associated with an increased contribution of beidellite (Table 2), also smaller percentages of smectitic layers and lower *vlp* values suggest a higher influence of the DSOW on the WBUC. The largely dominant influence of the DSOW at this depth (3380 m) of the Greenland Rise, may be very recent (less than 1 kyr), as evidenced from surface sediments (Table 2).

Late glacial proportions of beidellite (as well as their good expansion upon ethylene-glycol solvation; Table 3) in PC94 closely match these of the modern sediments bathed by the NEADW, suggesting a greater influence of this

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water mass on the composition of the WBUC near its outlet to the North Atlantic than at PC13. This implies a southward move of NEADW circulation at that time. This hypothesis is supported by oxygen isotope data indicating circulation of deep waters originating from the Central North Atlantic during glacial isotopic stages 4-2 (Duplessy et al., 1988; Labeyrie et al., 1992). Through the deglacial interval, the upward increased contribution of the montmorillonite within the smectites may reflect an intensified contribution of DSO waters to the WBUC through time (Table 3, Fig. 6).

The comparison of the smectite composition in both cores also indicates: (1) a relative enrichment in montmorillonite in detrital layers (LDC and DC1 in PC94; HE2 for PC13), and at about 9 kyr; (2) an enrichment in beidellite during the Younger Dryas. As these mineralogical changes occur in cores located at the inlet (PC13) and outlet (PC94) of the WBUC gyre in the Labrador Sea, they may be of both regional and global significance.

5.5. Terrigenous discharges

The detrital carbonate layers of PC94 at the outlet of the WBUC, characterized by smaller percentages of smectites (Fagel et al., 1997), reflect a massive terrigenous input. Andrews et al. (1993) have suggested that decreased contents of smectites resulted from dilution by strong pulses of carbonate-rich sediments from the Hudson Strait area, following local instabilities of the Laurentian ice-sheet (Andrews et al., 1995). With the exception of the detrital layer DCO closely associated to the Younger Dryas event, the smectites in all detrital carbonate layers from core PC94 show decreased *vlp* values, lower percentages of smectitic layers and higher proportions of montmorillonite. Comparison with the modern clay associations (Table 2, Fig. 3) suggests intensified contribution of DSO source areas during deposition of the detrital-rich layers. This is supported by changes in the Sm-Nd ratios of the carbonate-free clay fraction (Fagel et al., 1999).

In contrast, in PC13 at the inlet of the WBUC gyre, detrital Heinrich-like layers HE2 and HE1 do not show any significant decrease of the smectites (Fagel et al., 1997). Characteristics of the smectites do not vary notably, with the exception of the proportion of montmorillonite which increases in HE2 up to values similar to those recorded in the detrital carbonate layers of PC94. As surface samples indicate that the North Baffin Bay area is the only possible source for such amounts of montmorillonite, this implies significant contribution of this source area during the Heinrich-like event, HE2. This has been most probably achieved through intensified DSO and LSW circulation. We suggest that during Heinrich events (at least HE2) the recirculation loop of the LSW in the Irminger Basin (Clarke and Gascard, 1983; Dickson and Brown, 1994) expanded enough to ensure significant transport of terrigenous load to Site PC13.

5.6. The Younger Dryas and the early Holocene events

The Younger Dryas event is associated to a detrital carbonate layer (DCO) in PC94 (Canadian Rise), whereas only a minor increase of coarse fraction has been evidenced in coeval sediments from PC13 on the Greenland Rise (Hillaire-Marcel et al., 1994). The clay mineral association of this interval on the Canadian Rise contains higher percentages of chlorite, illite and kaolinite, and lower contents of smectites, indicating intensified erosion of high-latitude substrates, while no significant changes are evidenced on the Greenland Rise (Fagel et al., 1997). This also suggests persistent supply of smectites through deep circulation during the Younger Dryas. However, the smectites of the Younger Dryas interval in both cores contain significantly increased proportions of beidellite (Tables 2 and 3, Fig. 6). Contribution of the Arctic basins is not clearly expressed in the clay association. Comparison to surface data (Table 1) rather suggests an increased contribution of NEADW (especially NEADW2) to the deep current. The Younger Dryas event appears closely associated to very low values of precession (the minimum being centered at about 11.6 kyr) which correspond to maximum insolation at low latitudes and high meridional thermal gradients (Laskar, 1990; Crowley and North, 1991). Associated intensification of poleward heat transfer may have triggerred production of NEADW, which includes component waters from the Norwegian Sea and from the temperate Atlantic (Dickson and Brown, 1994). Poleward heat transfer also fostered precipitation in high-latitude areas and ice-growth (Sarnthein et al., 1995).

During the 9 kyr event, the beidellite contribution within the smectites that drops to 10% is close to the value presently measured in shallow sediments off Greenland (site 006, *B/M* ~ 15/85%, Table 1). At this time, sedimentological features and Nd isotopic signatures of the clay-size fraction (Fagel et al., 1999) evidence coarser sedimentary supplies from adjacent continent masses. As high proportions of montmorillonite are characteristic of DSO source areas, the youngest part of this interval (from <9.1 but >8.9 to 8.6 kyr) may correspond to an expansion of the LSW re-circulating gyre in the Irminger and Labrador basins, and an increased contribution of its terrigenous load to the sedimentation. This interval corresponds to maximum mean annual insolation at northern high latitudes, top values being reached at 9.3 kyr (Laskar, 1990). We suggest that increased energy favored ice-sheet retreat, and that increased availability of cold melting water may have forced DSO production and LSW circulation.

6. Conclusions

Clay mineralogical study of surface and late Quaternary sediments from the Northern North Atlantic and the Labrador Sea provided evidence for a link between abundance of smectites and deep water circulation. Detailed investigation of smectites documents the dominant terrigenous origin of clay particles and allows clear distinction of the different component waters of the deep ocean, and especially of the WBUC, from their clay mineral signature.

High amounts of smectites, including important proportions of beidellite and smectitic layers with a good crystallinity characterize the terrigenous load of the NEADW, especially that of NEADW2. Lower abundance of smectites with proportions of beidellite and montmorillonite similar to those carried by the NEADW, but more rich in illite layers, and poor crystallinity is associated to the DSOW. The small abundance of smectites largely dominated by montmorillonite rich in illite layers and poor crystallinity are typical of DSO-driven supplies and of LSW.

Time-variations of smectite characteristics allow recognition of major changes that concerned the deep circulation of the past 26 kyr, in relation to the evolving environment and climate. During late glacial interval, close resemblance of smectites at the most southern site (PC94) only with those from areas bathed by the modern NEADW indicates that the main body of deep water circulation flew southward of its modern pathway at a time of restricted formation of dense waters in the Norwegian Sea. During the late glacial/deglacial transition, occurrences of beidellite and smectitic layers-rich mixed-layers at the northern site (PC13) may result from higher contribution of NEADW2 waters in relation to the intensified circulation of the WBUC. This could be linked for a part to dense water production in the Norwegian Sea as warming of high latitude areas progressed. Upward increases of montmorillonite contribution within the smectites at Site PC94 are related to strengthened contribution of DSO waters to the downstream part of the WBUC during ice-cap receding. Heinrich-like event (at least HE2) in PC13 and detrital carbonate layers in PC94 contain higher proportions of montmorillonite and more illitic layers, indicative of increased contribution of DSO source areas. This implies an expansion of DSO/LSW circulation, including its re-circulating gyre in the Irminger Basin. The Younger Dryas interval in both cores is characterized by significant augmentation of beidellite contribution within the smectites, related to increased contribution of NEADW (especially NEADW2) waters to the deep circulation. Intensification of poleward heat transfer during the minimum of precession (centered at 11.6 kyr) may have triggered production and circulation of NEADW2 components, mainly deep waters from the temperate Atlantic and dense waters from the Norwegian Sea. As suggested by decreased percentages of smectites containing higher proportions of beidellite and more illitic layers, significant influence of DSOW waters to the WBUC is perceptible at ca. 4.4 kyr at Site PC13 off Greenland, where it may have increased very recently (between 4.4 and <l kyr).

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