

Zeitschrift:	Eclogae Geologicae Helvetiae
Herausgeber:	Schweizerische Geologische Gesellschaft
Band:	86 (1993)
Heft:	1
Artikel:	Detrital silicates in Northeast Atlantic deep-sea sediments during the Late Quaternary : major element, REE and Rb-Sr isotopic data
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DOI:	https://doi.org/10.5169/seals-167240

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Detrital silicates in Northeast Atlantic deep-sea sediments during the Late Quaternary: Major element, REE and Rb-Sr isotopic data

By SYLVAIN HUON¹⁾ & RÜDIGER JANTSCHIK²⁾

Key-words: NE Atlantic Ocean, deep-sea sediments, detrital minerals, Rb-Sr isotopic data, geochemical data, Late Quaternary climate.

ABSTRACT

The major element content and the Rb-Sr isotopic composition of non-carbonate sediment residues have been determined on different size fractions of 14 samples and on 4 ice rafted dropstones from several deep-sea cores of the NE Atlantic Ocean ($47^{\circ}30'N$, $19^{\circ}30'W$), recovered within the framework of the NOAMP project (Northeast Atlantic Monitoring Program). Rare-earth elements compositions have also been measured on 15 bulk sediment samples. These results provide complementary data of a previous mineralogical and K-Ar isotopic study, carried out on the same samples (Jantschik & Huon 1992). The geochemical as well as the Rb-Sr isotopic composition of the detrital silicate fractions support the hypothesis of mixtures of several different mineral sources, according to the prevailing transport mechanisms. During the warm climatic periods (foraminiferal ooze) throughout the last 140 ky, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the clay-size fractions are lower (0.7241–0.7291) than during the cold climatic periods (diamictite, 0.7321–0.7407). This increase is best explained by a strong dilution of the basalt-derived material supply from the province of Iceland by an increase of the terrigenous input from the surrounding land masses (North America, Greenland). This change is not recorded by the K-Ar ages, due to the low ^{40}K and ^{40}Ar contributions of Tertiary-Quaternary basaltic material to the mineralogical mixtures. On the contrary, during several phases of enhanced ice-raffting in the Late Pleistocene (cemented marl) and of previous glacial periods (at about 250 and 400 ky), the K-Ar apparent ages of the silicate material increase to 1138 ± 18 Ma for the clay-size fractions and to 1338 ± 22 Ma for the coarsest size fractions ($> 63 \mu\text{m}$), whereas the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios remain comparable to those of the diamictite sediments. These ice-rafted layers display a different mineralogical composition, characterized by low Rb/Sr ratios and by high ^{87}Sr radiogenic content due to occurrence of Precambrian detrital minerals. The K-Ar and Rb-Sr isotopic signatures of detrital silicate fractions of deep-sea sediments provide complementary and substantial information for Late Pleistocene paleoceanographic and paleoclimatic reconstructions in the NE Atlantic ocean.

ZUSAMMENFASSUNG

Die Verteilung der Hauptelemente und die Rb-Sr-Isotopenverhältnisse wurden vom nichtkarbonatischen Sedimentrückstand von 14 Proben verschiedener Korngrösse und von 4 Dropstones bestimmt. Die Proben stammen aus Tiefseekernen aus dem Nordostatlantik (bei $47^{\circ}30'N$, $19^{\circ}30'W$), die im Rahmen des NOAMP-Projektes (Nord-Ost-Atlantisches-Monitoring-Programm) genommen wurden. Seltene Erden-Elemente (REE) wurden an 15 Proben des Gesamtsediments gemessen. Die Ergebnisse stellen eine Ergänzung zu mineralogischen Analysen und K-Ar-Isotopenuntersuchungen an Tiefseesedimenten dieser Region dar (Jantschik & Huon 1992).

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Die geochemischen, als auch die Rb-Sr-Isotopendaten und die REE-Verteilung der detritischen Sedimentfraktionen indizieren einen wechselnden Materialeintrag von verschiedenen Quellen, deren Einfluß von den vorherrschenden Transportmechanismen abhängt. In den letzten 140 000 Jahren sind während warmer Klimaphasen (Sedimenttyp: foraminiferal ooze) die $^{87}\text{Sr}/^{86}\text{Sr}$ -Werte der Tonfraktion geringer (0.7241–0.7291) als während kalter Klimabedingungen (Sedimenttyp: diamicton, 0.7321–0.7407). Diese Unterschiede können mit einer Verringerung des Eintrags von basaltischem Material (Island) durch ozeanische Bodenströmungen und einer gleichzeitigen Erhöhung der Zufuhr von kontinentalem Detritus von den umgebenden Landmassen (bevorzugt Grönland, Nordamerika) erklärt werden. Die K-Ar-Isotopendaten spiegeln diesen Unterschied nicht wider, weil im NOAMP-Gebiet der Einfluß von radiogenem ^{40}K und ^{40}Ar aus quartärem basaltischem Material auf die mineralogische Zusammensetzung des Detritus zu gering ist. Während einzelner, zeitlich begrenzter Phasen verstärkter detritischer Sedimentation durch Eisberge im letzten Glazial (Sedimenttyp: cemented marl) und zweier früherer Ereignisse um 250 und 400 ky steigen die K-Ar-Alter des silikatischen Sedimentanteils auf bis zu 1138 ± 18 Ma (Fraktion < 2 μm) und 1338 ± 22 Ma (Fraktion > 63 μm) an, während die $^{87}\text{Sr}/^{86}\text{Sr}$ -Werte in diesen Sedimenten denen des diamicton ähneln. Diese cemented marl-Horizonte haben eine unterschiedliche mineralogische Zusammensetzung, die durch geringe Rb/Sr- und hohe ^{87}Sr -Gehalte gekennzeichnet ist und mit dem Auftreten detritischer präkambrischer Minerale erklärt werden kann. Diese K-Ar- und Rb-Sr-Daten der detritischen Silikatfraktion von Tiefseesedimenten liefern wichtige Informationen über die spätglazialen ozeanographischen und klimatischen Bedingungen im Nordostatlantik.

RÉSUMÉ

La composition chimique (éléments-majeurs) et les rapports isotopiques Rb-Sr ont été déterminés pour différentes fractions granulométriques du résidu non-carbonaté de 14 échantillons de sédiments océaniques et pour 4 "dropstones" prélevés dans l'Atlantique NE ($47^{\circ}30'\text{N}$ – $19^{\circ}30'\text{W}$) dans le cadre du projet NOAMP (Northeast Atlantic Monitoring Program). La composition des Terres-Rares a aussi été mesurée sur 15 échantillons de sédiment total. Ces résultats sont complémentaires d'une étude minéralogique et isotopique K-Ar effectuée sur les mêmes échantillons (Jantschik & Huon 1992). Les compositions chimiques et isotopiques Rb-Sr sont cohérentes avec l'hypothèse d'un mélange de minéraux détritiques de plusieurs origines, en fonction du mode de transport dominant. Pendant les périodes climatiques chaudes (foraminiferal ooze) des derniers 140 ka, les rapports $^{87}\text{Sr}/^{86}\text{Sr}$ des fractions argileuses sont plus faibles (0.7241–0.7291) que pendant les périodes climatiques froides (diamicton, 0.7321–0.7407). Cette variation peut être interprétée comme résultant d'une forte dilution des apports en matériel d'origine basaltique depuis la province d'Islande et d'une augmentation de l'apport en matériel terrigène provenant des continents voisins (Amérique du Nord, Groenland). Les âges K-Ar n'enregistrent pas ce changement du fait des faibles contributions en ^{40}K et ^{40}Ar du matériel basaltique quaternaire-tertiaire dans le mélange minéralogique. Au cours de plusieurs phases où le transport par les glaces et les icebergs s'accroît et lors de périodes glaciaires plus anciennes (250 et 400 ka, cemented marl), les âges K-Ar du matériel silicaté augmentent jusqu'à 1138 ± 18 Ma pour les fractions argileuses et 1338 ± 22 Ma pour les fractions de taille supérieure à 63 μm , alors que les rapports $^{87}\text{Sr}/^{86}\text{Sr}$ restent comparables à ceux mesurés dans le diamicton des périodes froides. Ces valeurs reflètent un changement minéralogique important caractérisé par des rapports Rb/Sr faibles et par une forte teneur en ^{87}Sr radiogénique lié à la présence de minéraux détritiques précambriens. L'étude isotopique K-Ar et Rb-Sr de fractions silicatées détritiques des sédiments océaniques apporte une information importante pour la reconstruction des mécanismes de circulation océanographique et des conditions climatiques au cours du Pléistocène.

Introduction

In the Northeast Atlantic ($47^{\circ}30'\text{N}$, $19^{\circ}30'\text{W}$) the supply of detrital material into deep-sea sediments occurs by a variety of transport mechanisms. During the Late Quaternary (marine isotope stages 1–6), aeolian fluxes (Folger 1970; Windom 1975), surface and bottom currents (Grousset et al. 1983) and ice-rafting (Ruddiman 1977) provide non-carbonate mineral assemblages composed of mica, smectite, chlorite, kaolinite, which are mainly concentrated in the clay-size fractions (< 2 μm) and quartz, amphibole, K-feldspar, plagioclase, oligoclase and rare zeolite enriched in the coarser grain sizes

(Biscaye 1965; Ruch 1987; Jantschik 1991). The K-Ar apparent ages of these mineralogical mixtures average $413 + ^{+82}_{-63}$ Ma for the fine-grained fractions and $494 + ^{+126}_{-70}$ Ma for the 2–16 µm fractions (Jantschik & Huon 1992). This isotopic signature is roughly independent of the sediment types, characteristic of alternating cold (diamicton) and warm (foraminiferal ooze) climatic periods of the last 140 ky. The potential sources of fine detrital material, as inferred from K-Ar dating, are most probably the Caledonian-Precambrian terrains of Greenland and North-America (Bond et al. 1992, Jantschik & Huon 1992). However, the contribution of basalt-derived material from the province of Iceland (Parra et al. 1985; Grousset & Chesselet 1986) is not well resolved by this method. The most drastic changes in the composition of the detrital silicates occur during four of the six phases of enhanced ice-rafting of the cold interval corresponding to marine stages 2–4 (Heinrich 1988; Jantschik 1991; Broecker et al. 1992). Within these particular layers called cemented marls (Jantschik & Lohoff 1987), the relative contents of mica, chlorite, amphibole and feldspars increase, whereas smectite and kaolinite almost disappear. The K-Ar ages of these detrital mixtures increase to about 800–1140 Ma, reflecting an increasing input of Precambrian silicates, accompanied by a breakdown or a strong dilution of the supply of basalt-derived material, transported by bottom currents from the region of Iceland (Jantschik & Huon 1992).

The purpose of this study is to determine more precisely the different sources and mixtures of detrital silicates by chemical (major and Rare-Earth Elements, REE) and Rb-Sr isotopic analyses. This study is carried out on the samples already used for K-Ar dating (Jantschik & Huon 1992). Therefore, only the necessary mineralogical and some additional K-Ar measurements will be presented. More details can be found in Jantschik (1991) and Jantschik & Huon (1992). Extensive strontium isotopic data for Holocene deep-sea sediments have already been published by Dasch (1969), Biscaye & Dasch (1971), Grousset & Chesselet (1986) and Huon & Ruch (1992) for silicate residues of Holocene sediments. Geochemical and REE compositions, have also been published for various deep-sea sites (e.g. Boström et al. 1972; Bischoff et al. 1979; Dymond 1981; Grousset & Parra 1982; Grousset 1985; Nath et al. 1989; Grousset et al. 1988). These data provide information on oceanographic circulation patterns deduced from the potential geological sources of detrital minerals and the prevailing climatic conditions. However, no detailed downcore investigation has yet been reported from sediments of the Northeast Atlantic Ocean. The geochemical and isotopic data presented in this study detail the variations of the composition of detrital supplies, for the last 140 ky and for two older glacial events at about 250 and 400 ky BP.

Material and methods

Major element, REE, K-Ar and Rb-Sr isotopic analysis have been carried out on samples of piston cores ME-68-89, ME-68-91 and M6-7A-244/1, recovered during the NOAMP program ($47^{\circ}30'N$, $19^{\circ}30'W$; Meischner 1987, Heinrich 1989). This site is one of the permanent monitoring stations of the Joint Global Oceanic Flux Study (JGOFS) and provides optimal conditions for the study of Late Pleistocene climatic fluctuations in the NE Atlantic (fig. 1). Extensive geophysical, sedimentological and geochemical data have already been reported for the NOAMP region by Heinrich (1986a, 1986b, 1988, 1989), Meischner (1987), Jantschik & Lohoff (1987), Ruch (1987), Gabel (1989),

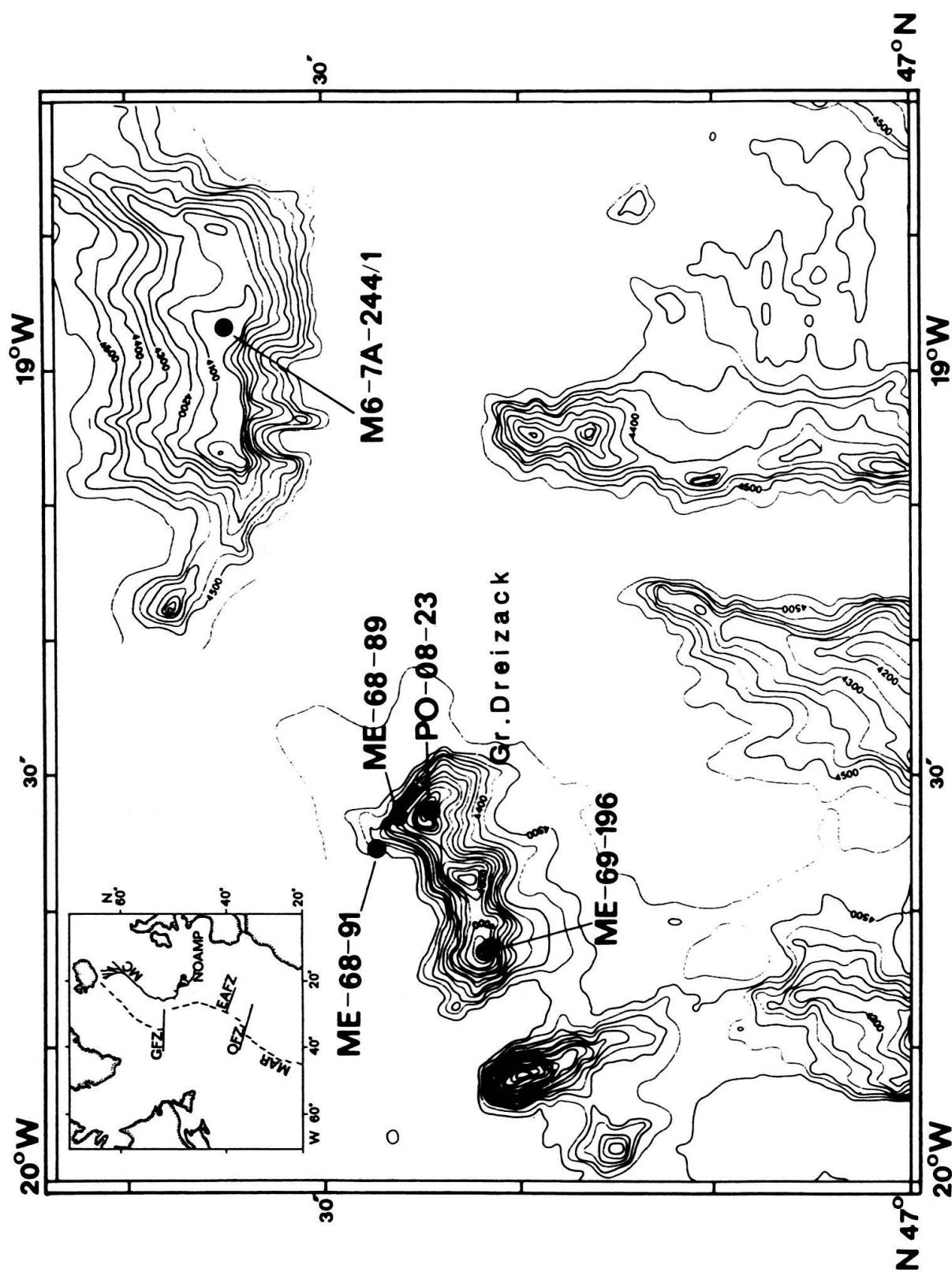


Fig. 1. Bathymetric map of the NOAMP site with core locations. Contour intervals are 50 m. MC = Maury turbidite channel. Small insert shows the NOAMP area in the North Atlantic. MAR = Mid-Atlantic-Ridge with main fracture zones.

Table 1. Rb-Sr isotopic data

Sample depth (cm)	Grain size (μm)	Sediment type (1)	Rb ppm	Sr ppm	$^{87}\text{Sr}/^{86}\text{Sr}$ $\pm 2s$ (2)	$^{87}\text{Rb}/^{86}\text{Sr}$ $\pm 2s$ (3)
<u>Core ME-68-89</u>						
1. 2-4	<2	FO	134	115	0.724067 (8)	3.377 (0.039)
2. 34-36	<2	CM ₁	136	189	0.735069 (8)	2.088 (0.056)
	2-16		89	239	0.726422 (10)	1.080 (0.023)
3. 58-60	<2	DI	169	134	0.732130 (8)	3.658 (0.026)
	2-16		122	143	0.725139 (17)	2.473 (0.132)
4. 65-67	<2	CM ₂	139	192	0.735457 (14)	2.100 (0.067)
	2-16		94	242	0.725811 (10)	1.126 (0.025)
5. 89-91	<2	DI	169	106	0.740627 (31)	4.628 (0.037)
	2-16		127	130	0.729047 (9)	2.832 (0.104)
6. 110-112	<2	DI	12	116	0.740683 (11)	4.304 (0.032)
	2-16		116	148	0.725624 (14)	2.272 (0.084)
7. 143-145	<2	CM ₃	165	174	0.742485 (10)	2.753 (0.133)
8. 153-155	<2	CM ₃	162	207	0.742217 (18)	2.272 (0.064)
9. 167-169	<2	DI-FO	160	123	0.729144 (12)	3.772 (0.027)
	2-16		115	157	0.722117 (10)	2.122 (0.060)
10. 187-189	<2	CM ₄	164	217	0.742053 (16)	2.194 (0.085)
11. 195-197	<2	FO	160	162	0.728741 (11)	2.864 (0.147)
	2-16		105	195	0.721686 (11)	1.560 (0.036)
12. 419-421	<2	DI	-	99	0.737058 (19)	-
D. 45	whole rock	diorite	63	220	0.735360 (18)	0.831 (0.025)
B. 224	whole rock	basalt	12	204	0.704602 (16)	0.166 (0.040)
<u>Core ME-68-91</u>						
13. 417-419	<2	TU	96	97	0.717961 (9)	2.867 (0.115)
	2-16		64	160	0.709891 (11)	1.158 (0.036)
<u>Core ME-69-196</u>						
G. 115	whole rock	granodiorite	59	527	0.714999 (18)	0.317 (0.083)
<u>Core PO-08-23</u>						
M. 104	whole rock	monzonite	272	155	0.850360 (16)	5.031 (0.105)
<u>Core M6-7A-244/1</u>						
14.	<2	CM ₆	-	117	0.744541 (33)	-
1083-1085	2-20		-	233	0.730693 (28)	-
	20-63		-	223	0.726443 (25)	-
	>63		-	183	0.728151 (37)	-

(1) FO = foraminiferal ooze, DI = diamictite, CM = cemented marl, TU = turbidite mud

(2) s = standard deviation, error on the two last decimals

(3) s = standard deviation.

whole rock = dropstones

Jantschik (1991), Huon et al. (1991), Jantschik & Huon (1992). The sediments are composed of foraminiferal oozes (FO), diamictons (DI, Harland et al. 1966) and cemented marls (CM), typical of alternating cold (DI, CM) and warm (FO) climatic fluctuations. Detailed lithological and stratigraphic sequences are presented in Jantschik & Lohoff (1987) and Jantschik (1991). Core ME-68-89 displays a complete sedimentary record down to marine isotope stage 6 (≈ 140 ky), whereas core ME-68-91 contains several turbidite horizons. The longest undisturbed sequence recovered, was found in core M6-7A-244/1 in which the carbonate content can be cross-correlated with reference cores down to marine isotope stage 12 (≈ 400 ky). All analytical data used in this study are given in tables 1–5.

Sample preparation, mineralogical and K-Ar analytical procedures, are described in Jantschik (1991) and Jantschik & Huon (1992). Two size fractions (<2 μm and 2–16 μm) have been chosen in the range of isolated silicate grains to avoid the influence of lithic fragments on isotopic analyses and to provide comparable material. Major element compositions, Rb and Sr contents were measured on fused preparations ($\text{Li}_2\text{B}_4\text{O}_7$) of silicate fractions by X-ray fluorescence (XRF), using US Geological Survey rock standards for calibration purposes (tables 1, 3). A set of 17 standards was devoted to the calibration of Rb ($r = 0.99950$) whereas, 12 acid-intermediate standards ($r = 0.99890$) and 7 basic standards ($r = 0.99991$) were used for Sr calibrations. Reproducibility was estimated by 8 measurements of 5 different fused preparations of standard DRN. The average Rb and Sr contents were 67.8 ± 2.9 ppm (± 1 s) and 404.6 ± 4.0 ppm (± 1 s), respectively. The major element analyses were also cross-checked by atomic absorption spectrophotometry. Strontium was separated by cation exchange chromatography after dissolution of samples in HCl-HF-HNO₃. The isotopic ratios (table 1) were determined in double measurement mode using a Finnigan MAT 261 mass spectrometer. Equipment reproducibility was controlled by measurements of the NBS-987 carbonate standard. During the course of this study the external reproducibility was 0.001 %. The REE

Table 2. K-Ar isotopic data (Core M6-7A-244/1)*

Core depth (cm)	Sediment type	Grain size (μm)	%K	$\%^{40}\text{Ar}$ rad.	[^{40}Ar rad] (10^{-9} mol/g)	K-Ar age $\pm 2\text{s}$ (Ma)
661-663	CM ₅	<2	2.98	93.1	6.429	946 ± 17
		2-20	2.48	93.6	6.819	1138 ± 20
		20-63	1.82	99.3	6.142	1320 ± 22
		>63	1.54	97.8	5.295	1338 ± 22
672-674	DI	<2	3.00	67.8	1.611	286 ± 7
		2-20	2.33	86.8	1.802	399 ± 9
		20-63	1.75	85.8	1.834	521 ± 11
		>63	1.80	97.0	2.330	625 ± 13
1083-1085	CM ₆	<2	3.07	86.2	4.458	688 ± 13
		2-20	2.81	98.0	6.626	1013 ± 18
		20-63	1.94	84.3	5.546	1171 ± 20
		>63	1.55	95.6	4.980	1275 ± 21

* for complete K-Ar isotope data see JANTSCHIK & HUON (1992)

Table 3. XRF data (size fractions and dropstones)

<u><2 µm</u>	1	2	3	4	5	6	7	8	9	10	11	13
SiO ₂	50.46	59.98	53.31	58.89	54.68	53.94	54.79	55.08	53.14	53.01	54.24	55.23
Al ₂ O ₃	16.22	16.22	19.69	16.50	19.13	18.59	18.08	17.28	18.86	18.72	17.53	14.13
TiO ₂	0.79	0.81	1.04	0.81	1.12	1.12	0.87	0.78	1.01	0.91	0.81	1.67
FeO	8.01	7.16	9.65	7.60	10.31	10.47	9.21	9.17	10.04	9.73	9.29	13.14
CaO	0.89	1.47	0.72	1.58	0.59	0.89	1.24	1.61	1.07	1.19	1.57	1.78
MgO	2.61	3.04	3.11	3.20	3.20	3.29	3.64	3.89	3.10	3.20	3.89	3.57
Na ₂ O	0.62	1.72	0.75	1.87	0.80	0.87	1.52	1.95	0.68	1.06	1.94	0.86
K ₂ O	3.14	4.07	3.93	3.92	3.84	3.71	4.05	4.06	3.48	3.64	4.02	2.31
MnO	0.42	0.09	0.13	0.05	0.09	0.10	0.08	0.07	0.06	0.06	0.08	0.08
P ₂ O ₅	0.26	0.16	0.13	0.16	0.14	0.22	0.10	0.15	0.19	0.12	0.08	0.11
P.F.	14.88	4.99	7.04	4.80	6.80	6.80	5.70	5.00	7.73	7.96	6.11	6.45
Total	98.30	99.71	99.50	99.38	100.7	100.0	99.28	99.04	99.36	99.60	99.56	99.33

<u>2-16 µm</u>	2	3	4	5	6	10	13	Dropstones	B	D	M	G
SiO ₂	71.48	64.11	67.88	67.29	64.37	67.59	58.02		47.86	52.90	66.73	66.20
Al ₂ O ₃	11.84	15.49	12.04	13.66	13.46	13.88	13.88		13.51	14.66	11.80	17.49
TiO ₂	0.71	1.03	0.66	1.05	1.11	0.91	1.84		2.31	0.75	0.35	0.35
FeO	3.00	6.71	3.28	6.06	6.18	5.35	9.21		13.54	11.19	3.08	2.71
CaO	1.60	1.23	1.83	1.04	1.05	1.54	4.29		9.52	8.80	3.92	4.35
MgO	1.11	2.31	1.21	1.94	2.01	1.86	3.40		7.08	5.37	3.26	1.06
Na ₂ O	2.22	1.45	2.39	1.53	1.69	2.07	1.95		2.85	3.02	0.99	5.02
K ₂ O	3.42	3.25	3.19	3.20	3.00	2.99	1.88		0.66	1.82	7.73	1.29
MnO	0.19	0.15	0.04	0.31	0.08	0.05	0.12		0.20	0.23	0.13	0.03
P ₂ O ₅	0.04	0.15	0.01	0.16	0.05	0.12	0.06		0.28	0.06	0.19	0.16
P.F.	4.19	2.94	4.05	3.96	7.11	2.25	4.07		1.57	0.98	0.77	0.99
Total	99.80	98.82	96.58	100.2	100.1	98.61	99.67		99.38	99.78	99.56	99.65

(Sample identifiers refer to Table I)

composition of 15 bulk sediment samples of cores ME-68-89 and ME-68-91 was analyzed by inductively coupled plasma emission spectroscopy (ICP) at the Centre de Recherches Pétrographiques et Géochimiques (Vandoeuvre-les-Nancy, France). The detailed analytical method is described in Govindaraju & Melville (1988). REE values and carbonate contents are detailed in table 5. The chondrite and shale normalized REE-plots are calculated on the basis of carbonate-free values in order to minimize the influence of biogenic carbonate.

Results

Geochemical data

1) Major element data

In order to support the following K-Ar and Rb-Sr isotopic data, the major element composition of a few selected DI, FO, TU and CM samples was determined. Additional

Table 4. Principal factors after varimax rotation for clay size fractions (high loading scores are underlined).

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
SiO ₂	<u>0.568</u>	-0.177	0.078	<u>0.757</u>	0.166
Al ₂ O ₃	-0.239	<u>0.950</u>	0.042	-0.084	0.059
TiO ₂	-0.398	-0.439	<u>0.773</u>	-0.039	0.143
FeO	-0.305	-0.226	<u>0.823</u>	-0.366	0.159
CaO	<u>0.698</u>	-0.613	0.061	0.010	0.247
MgO	<u>0.754</u>	0.050	0.475	-0.372	0.211
Na ₂ O	<u>0.954</u>	-0.002	-0.195	0.143	0.150
K ₂ O	0.507	<u>0.766</u>	-0.300	0.228	0.011
MnO	-0.454	-0.244	-0.590	-0.269	-0.442
P ₂ O ₅	-0.446	-0.081	-0.304	0.202	-0.769
Rb	0.081	<u>0.978</u>	-0.013	-0.133	-0.095
Sr	<u>0.855</u>	0.169	-0.390	0.044	0.243
Mica	0.152	<u>0.734</u>	-0.248	0.267	0.513
Chlorite	<u>0.661</u>	<u>0.535</u>	-0.025	-0.142	0.307
Kaolinite	-0.548	0.159	0.069	0.330	<u>0.657</u>
Smectite	-0.411	0.013	<u>0.777</u>	0.139	0.186
Quartz	0.518	<u>0.555</u>	-0.161	<u>0.534</u>	-0.197
Amphibole	<u>0.901</u>	0.204	-0.185	0.208	0.061
K-feldspar	<u>0.844</u>	0.321	-0.003	0.264	0.054
Plagioclase (1)	<u>0.896</u>	0.070	-0.059	0.111	0.059
Oligoclase (1)	-0.433	0.016	<u>0.770</u>	0.161	-0.241
K-Ar	<u>0.938</u>	0.143	-0.231	0.136	-0.052
Variance %	42.0	22.1	17.7	8.50	9.70

(1) Plagioclase and oligoclase are identified with CuK α_1 d-spacings of 3.18 Å and 3.22 Å, respectively.

analyses were carried out on several ice-raftered dropstones which represent some of the possible sources of detrital material from the surrounding land masses. A possible way of comparing the major element compositions of both the silicate size fractions and the dropstones is to use a conventional classification diagram, such as the one proposed by La Roche et al. (1981). All samples can be plotted in the R₁R₂ variation diagram, using their major cation contents (table 3, fig. 2). The dropstones display granodioritic, dioritic and basaltic compositions, consistent with microscope observations on thin

Table 5. REE data (bulk sediment)

Sample depth	Sediment type	La	Ce	Nd	Sm	Eu	Gd	Dy	Er	Yb	Lu
(Carbonate content)				(ppm)							
<u>Core ME-68-89</u>											
12-14 cm	FO (76.1%)	9.97	31.87	9.50	2.27	0.55	2.27	1.62	2.01	0.74	0.12
36-38 cm	CM ₁ (45.7%)	18.03	42.74	14.97	3.00	0.66	2.43	1.73	1.96	0.95	0.16
48-50 cm	DI (25.5%)	27.92	56.97	25.07	5.34	1.16	4.27	3.74	3.15	1.91	0.35
65-67 cm	CM ₂ (35.9%)	20.14	42.64	15.92	3.16	0.64	2.39	1.72	1.83	0.93	0.19
132-134 cm	DI (27.2%)	23.91	58.76	21.26	4.34	0.97	3.85	2.89	2.48	1.55	0.25
158-160 cm	CM ₃ (34.8%)	20.10	42.27	15.54	3.04	0.61	2.15	1.69	1.70	0.91	0.21
185-187 cm	CM ₄ (22.7%)	26.55	51.56	21.00	4.21	0.92	3.36	2.33	1.94	1.23	0.21
251-253 cm	FO (73.2%)	12.25	33.76	11.71	2.59	0.56	2.53	1.99	1.29	0.87	0.19
332-334 cm	FO (84.6%)	9.73	31.75	9.68	2.21	0.49	2.44	1.62	1.96	0.75	0.15
370-372 cm	DI (27.2%)	26.32	65.34	25.59	5.20	0.82	3.72	3.10	2.51	1.66	0.28
<u>Core ME-68-91</u>											
51-53 cm	CM ₁ (40.6%)	21.52	47.56	16.38	3.29	0.80	2.73	1.78	2.20	0.99	0.18
101-103 cm	CM ₂ (45.3%)	21.68	57.90	16.84	3.11	0.66	2.62	1.65	2.12	0.86	0.12
185-187 cm	TU (9.0%)	23.10	54.85	25.71	6.42	1.88	6.23	5.57	4.00	2.68	0.51
255-257 cm	CM ₃ (39.2%)	23.22	54.50	19.03	3.91	0.76	3.13	2.08	2.21	1.07	0.20
438-440 cm	TU (11.2%)	23.43	50.65	26.93	7.01	2.03	6.51	5.95	3.85	2.82	0.48

sections (Jantschik & Huon 1992). However, the two size fractions of the sediments obviously do not provide source rock compositions. All points fall within the granitic composition field. Except for the TU sample, the coarse 2–16 µm fractions yield higher silicium contents ($3420 < R_1 < 3870$) than the corresponding clay-size fractions ($2520 < R_1 < 3000$). This deviation is related to differences in quartz content. On the contrary the higher R_2 values calculated for the fine-grained concentrates (410–535) indicate a greater phyllosilicate content compared to that of the 2–16 µm fractions (342–398). These general observations are consistent with the mineralogical compositions inferred from X-ray diffraction analyses (Jantschik & Huon 1992). The two size fractions of the different sediments types more or less match a mixture of at least one

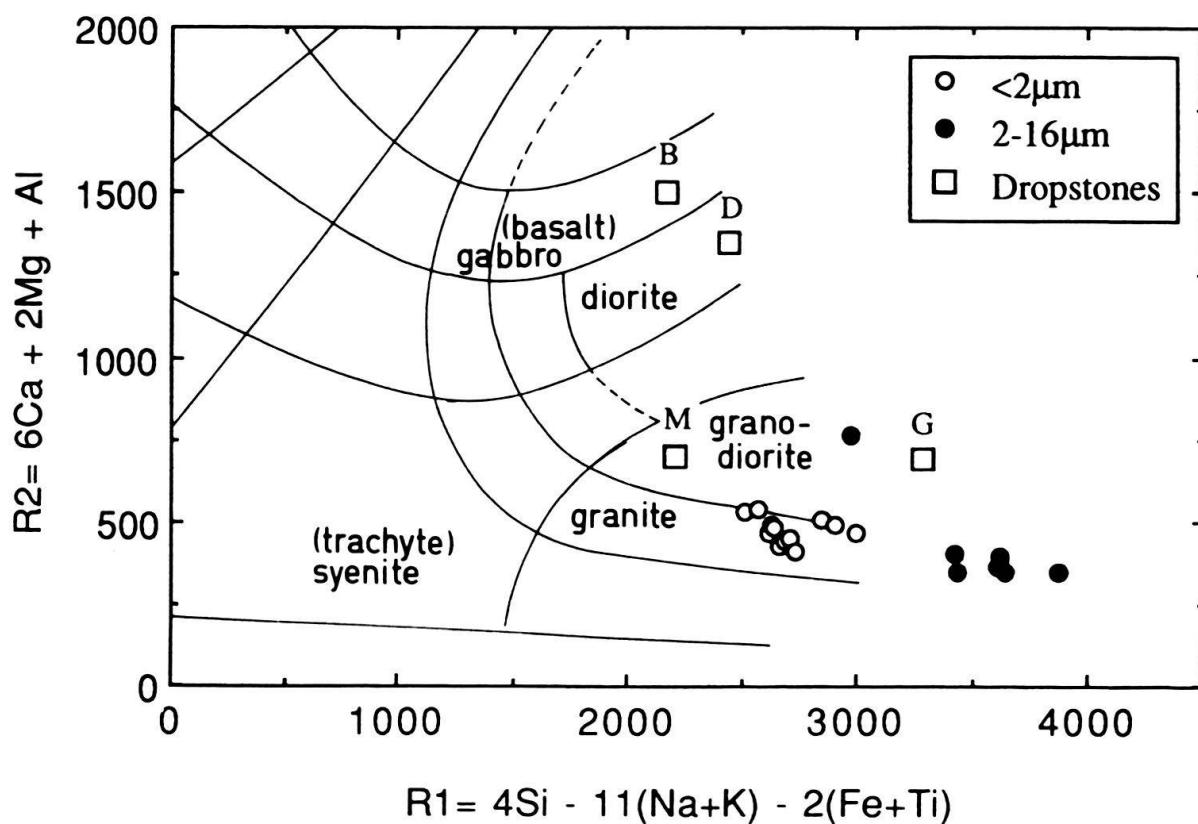
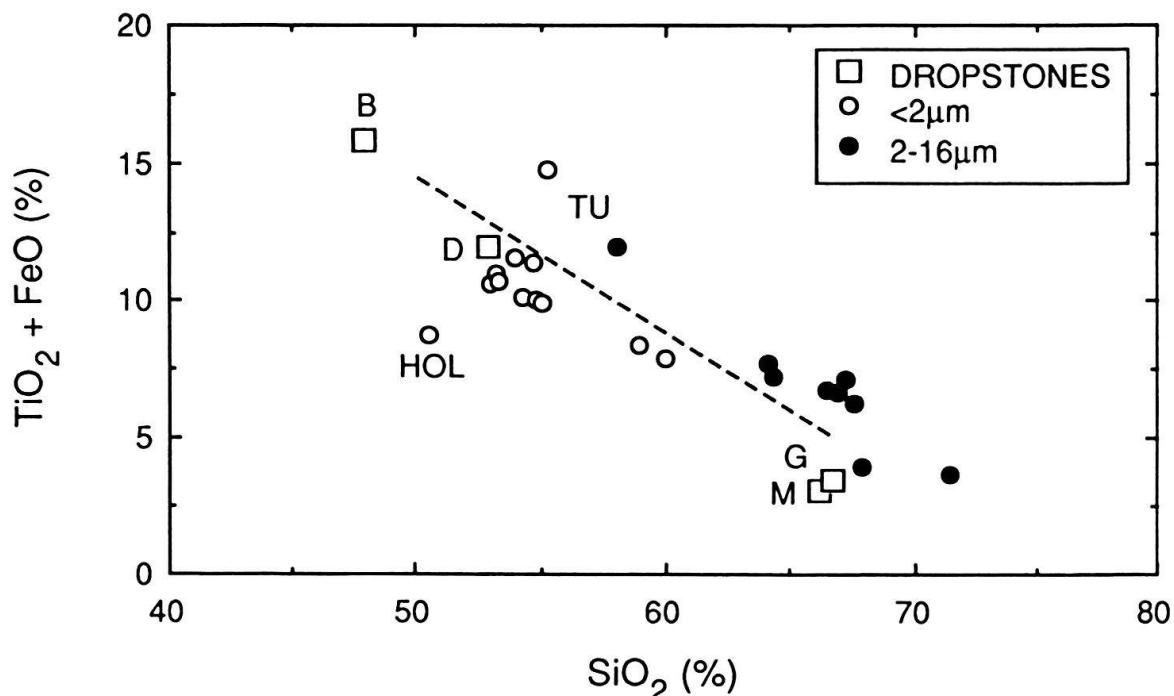


Fig. 2. Simplified R_1 - R_2 variation diagram of plutonic rocks (La Roche et al. 1981) for non-carbonate size fractions of sediments from cores ME-68-89 and ME-68-91 and whole-rock compositions of dropstones. Volcanic compositions are shown in brackets.

basaltic and one granitic component. In a $\text{TiO}_2 + \text{FeO}\%$ versus $\text{SiO}_2\%$ diagram, the clay fractions display an intermediate position between the granitic and the basaltic compositions of the dropstones (fig. 3). The 2–16 μm fractions fall close to the granitic compositions, according to a relative enrichment in quartz and feldspar.

Additional information is inferred from principal component factor analysis, using a varimax rotation procedure. The correlation matrix was built up with the available data for the clay-size fractions: the major constituents (in % oxides), the Rb and Sr contents (in ppm) and the relative content of each mineral component as estimated from XRD $\text{CuK}\alpha_1$ peak intensities. The K-Ar age values (Jantschik & Huon 1992) were added to the factor analysis in order to separate more precisely the potential mineral groups. The three principal factors account for 81.8% of the proportionate variance contribution (table 4). Factor 1 is dominated by the $\text{CaO}-\text{MgO}-\text{Na}_2\text{O}-\text{Sr}$ and chlorite-amphibole-K-feldspar-plagioclase-K-Ar age groups. The $\text{CaO}-\text{Na}_2\text{O}-\text{Sr}$ constituents are consistent with K-feldspar and plagioclase, whereas MgO is more characteristic of the chemical compositions of chlorite and amphibole. The age values also display a high loading score, indicating that the K-bearing phases associated with this group are mainly responsible for the rise of the K-Ar ages. This variation is best explained by an important statistical weight of the CM samples, enriched in K-feldspar, plagioclase and amphibole, which also provide higher K-Ar apparent ages than the remaining DI-FO-TU samples (Jantschik & Huon 1992). Therefore, this factor most likely accounts for the increase in ice rafted



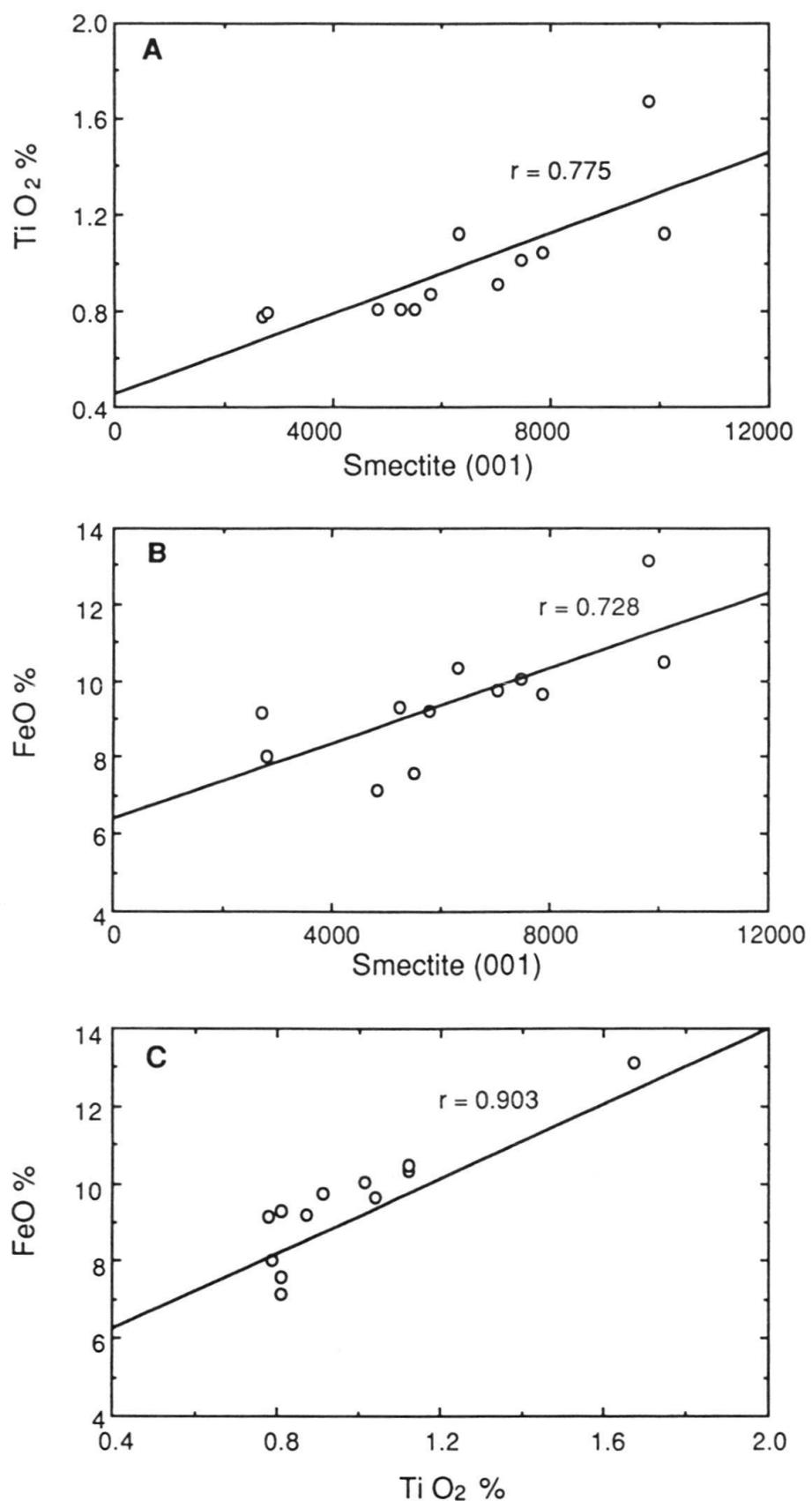


Fig. 4. Plots of TiO₂ %, FeO % and smectite contents for clay-size fractions of sediments from cores ME-68-89 and ME-68-91. Smectite content is estimated from XRD peak intensities (Jantschik 1991).

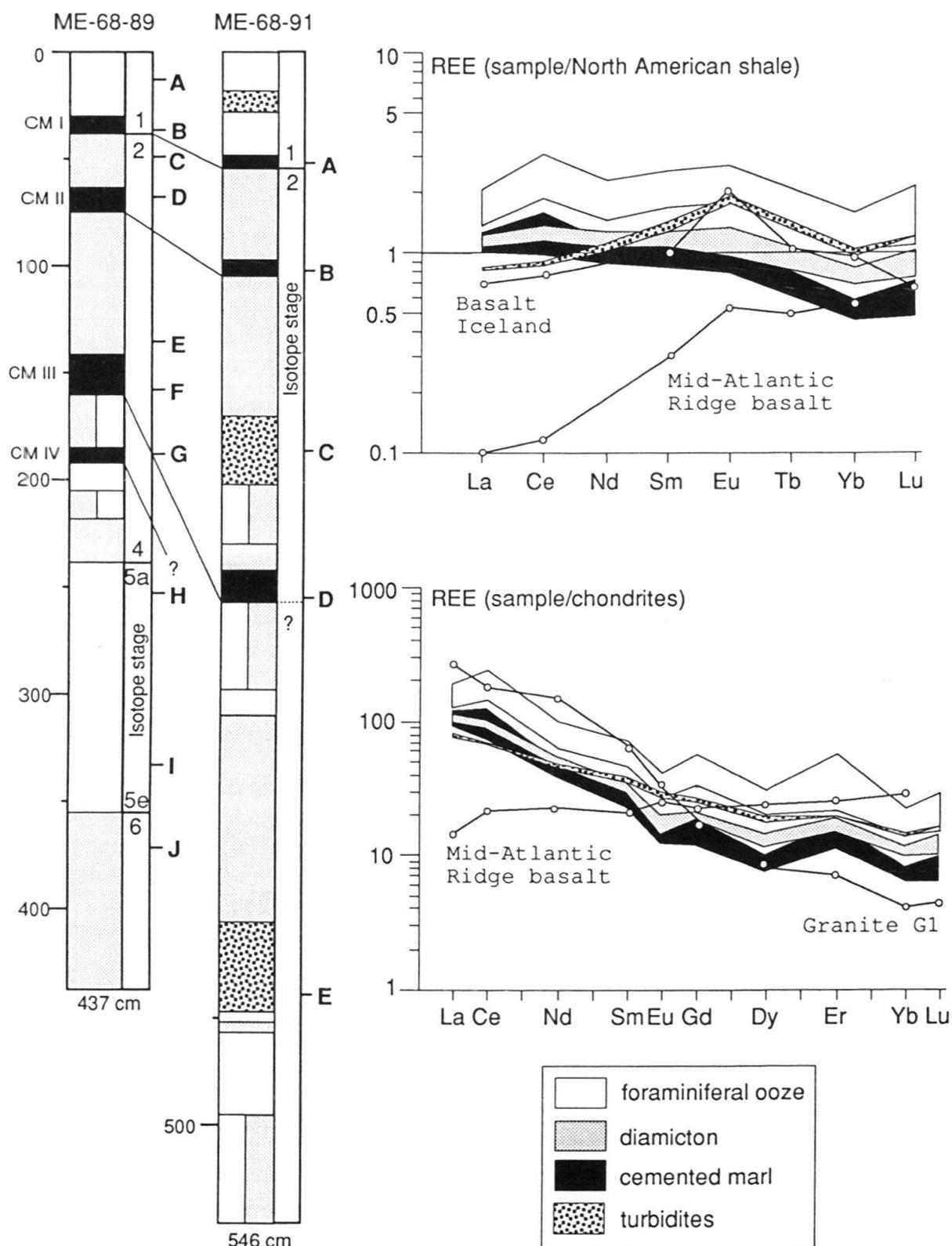


Fig. 5. Lithological variations of cores ME-68-89 and ME-68-91 with corresponding isotope stages and sampling position (A–J) for REE analysis. N-American shale and chondrite normalized distribution patterns are given for the different sediment types.

Chondrite normalized samples generally display very similar patterns for all sediment types. Light REE are enriched compared to the heavier elements. Such distribution patterns are typical of highly fractionated rocks such as granites (Mason & Moore 1982), but are also characteristic of the average REE content of marine sediments (Haskin & Haskin 1966; White et al. 1985). However, the slope of the distribution profile of FO, DI and CM samples is less than expected from a comparison with the G₁ granitic composition. It is most likely that less fractionated basaltic components occur within the sediment. Similar REE patterns were reported in sediments from the Mid-Atlantic Ridge region at 45°N by Grousset et al. (1988). These patterns were interpreted as binary mixtures of material originating from the acidic North American province and the volcanic region of Iceland. The TU sample also displays an intermediate REE pattern but much closer to that of the Mid-Atlantic Ridge basalt than the other sediment types. Normalization of the REE data to the North-American shale composition (fig. 5) provides FO, DI and CM patterns close to that of the shale. A slight decrease is only noticed for the heavy elements (Yb, Lu). A small positive Ce-anomaly is given by the FO curve, most likely induced by scavenging of Ce⁴⁺ to biogenic sediment particles from sea-water (Thompson et al. 1984). A marked Eu-anomaly, typical of basaltic rocks, is only present in the turbidite (TU) samples. Its REE pattern is more consistent with Tertiary-Quaternary basalts from Iceland than with those of the Mid-Atlantic Ridge and is in good agreement with the Islandic provenance of the turbidites, transported southward in the Maury Channel system (Lonsdale et al. 1981; Heinrich 1986a; Jantschik & Lohoff 1987; Gabel 1989).

Rb-Sr isotopic data

1) Dropstones

The K-Ar whole-rock ages of 4 ice-rafted dropstones recovered within DI and CM sediments types (2460 ± 28 , 1985 ± 25 , 1406 ± 21 and 3.7 ± 0.1 Ma, Jantschik & Huon 1992) suggest derivation from the Precambrian basements of Greenland and/or North America, as well as from the Tertiary-Quaternary volcanic region of Iceland. The basaltic dropstone yields a low $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.7046 consistent with an average oceanic basalt composition of 0.7040 ± 0.002 (Faure 1986). This rock fragment is also depleted in Rb (12 ppm, table 1) and in Sr (204 ppm), which suggests a loss by pedogenic processes or sea-water alteration (Clauer 1976; Hoffert 1980; Parra et al. 1985). However, the Rb/Sr ratio (≈ 0.058) remains in the range of the average basaltic composition (≈ 0.065 ; Turekian & Wedepohl 1961). One of the most common product of these alteration processes is smectite which provides a mineralogical trace of the supply of basalt-derived material into deep-sea sediments of the NE Atlantic (Grousset & Chesselet 1986). The granodiorite dropstone, which yields a K-Ar apparent age of 2460 Ma, shows a relatively low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.71500, in comparison to differentiated continental rocks. The calculated initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, using the K-Ar age value, drops to about 0.7037. This ratio is consistent with the composition of old mantle-derived rocks found in the Precambrian metamorphic belts of Canada or Greenland (Faure 1986). The diorite and monzonite dropstones display high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.73536, 0.85036, respectively) and low

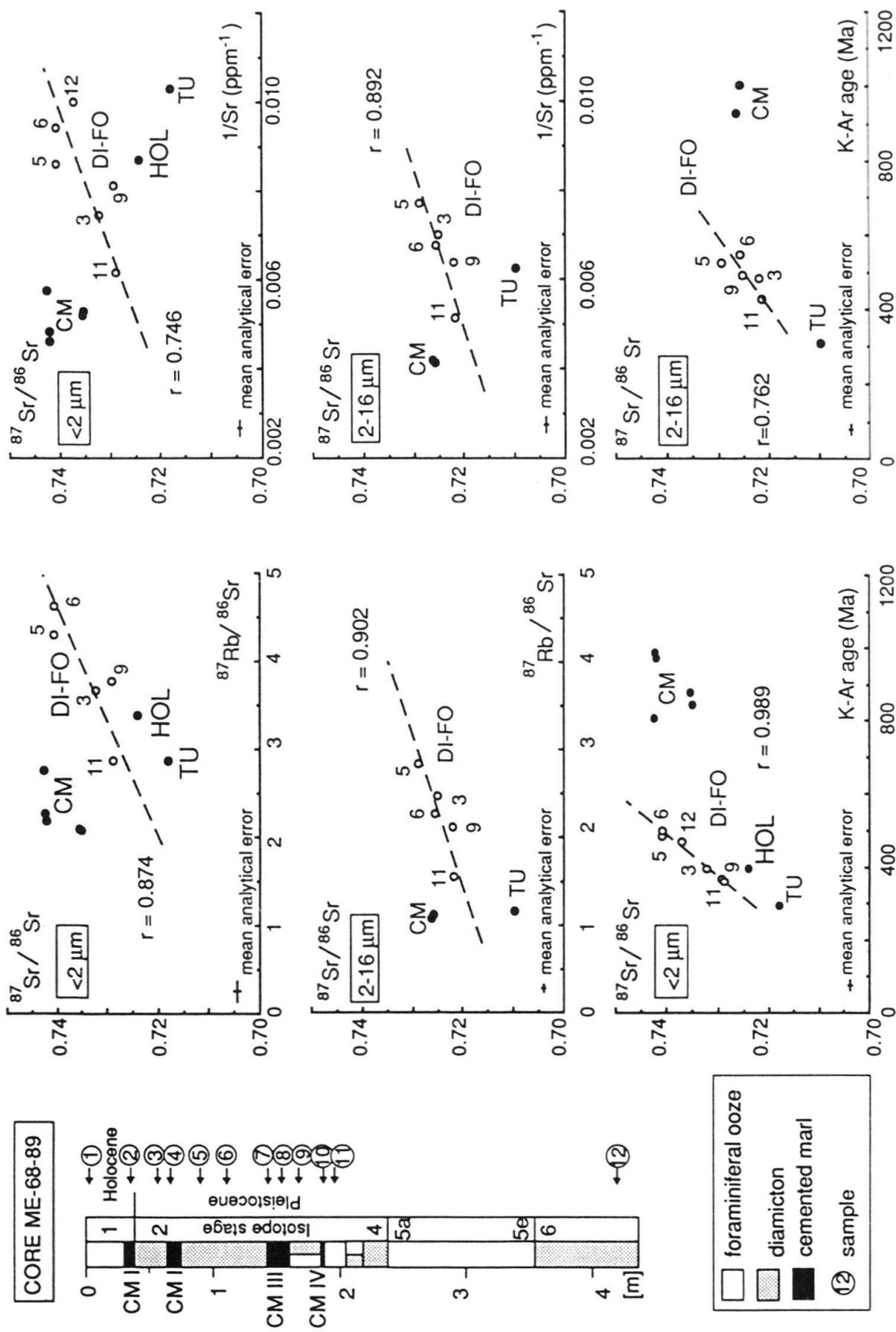
to high $^{87}\text{Rb}/^{86}\text{Sr}$ ratios (0.83, 5.03, respectively), according to the petrographic nature of these rocks.

2) Fine-grained silicate fractions

The $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$ ratios of the clay-size and the 2–16 μm fractions do not directly match the Rb-Sr isotopic compositions of the dropstones (table 1). These deviations can be explained by the occurrence of mixtures of particles from several different origins, including that of the dropstones, and/or by the relative enrichment of the fine-grained fractions in specific minerals (e.g. mica in the clay-size fractions), which then no longer reflect the bulk-rock composition of the source material.

Figure 6 shows the Rb-Sr isotopic compositions of the two size fractions, plotted in the conventional isochron diagram. The $^{87}\text{Sr}/^{86}\text{Sr}$ values of the clay-size fractions are scattered between 0.7180 and 0.7425, whereas the $^{87}\text{Rb}/^{86}\text{Sr}$ ratios range between 2.09 and 4.63. Only the silicate fractions of the DI-FO sediment types show a rough alignment along a straight line ($r = 0.874$), with an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of about 0.7045. The TU and Holocene FO clay fractions fall far from a linear relationship. An equivalent pattern is displayed by the 2–16 μm fractions of the same samples, with systematically lower isotopic ratios, ranging from 0.7099 to 0.7290 and 1.08 to 2.83 for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{87}\text{Rb}/^{86}\text{Sr}$, respectively. The coarse fractions of the DI-FO samples deviate less from the best straight line ($r = 0.902$) than the clay-size fractions and display a higher initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of about 0.7118. The size fractions of the CM samples do not show an alignment in the isotope diagram. The clay-size minerals display lower $^{87}\text{Rb}/^{86}\text{Sr}$ ratios (2.09–2.75) than those of the DI-FO sediment types (2.86–4.63). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, however, lie within the scatter of the other sediment types (0.720–0.740). The lower Rb/Sr ratios can be explained by a change in the mineralogical composition, as the CM horizons contain more amphibole and feldspar than the DI-FO sediments (Jantschik & Huon 1992). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the CM remain comparable to those of the DI-FO as the lower ^{87}Sr contribution, due to lower mica (^{87}Rb -rich phase) content, is counterbalanced by a higher radiogenic ^{87}Sr contribution due to occurrence of Precambrian minerals. The decrease of the isotopic ratios between the two size fractions of each sediment type can also be related to a change of the mineralogical balance. For example, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of CM VI sample roughly decrease with increasing grain size, from 0.7445 to 0.7282 (fig. 7). This variation corresponds to a diminution of the mica content and a relative increase of amphibole, feldspars and quartz in the coarser grain sizes.

The plots of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios against inverse Sr contents of DI-FO sediment types are also roughly linear, although scattering is still important ($r = 0.746$, $< 2 \mu\text{m}$ and $r = 0.892$, 2–16 μm , fig. 5). As already shown by Boger & Faure (1974), these patterns are characteristic of binary mixtures between two components with different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and strontium contents. In such cases, straight lines in the $^{87}\text{Sr}/^{86}\text{Sr}$ - $^{87}\text{Rb}/^{86}\text{Sr}$ diagram cannot be interpreted as isochrons. In the NE Atlantic Ocean, binary mixtures of detrital minerals have already been identified for Holocene sediments (Grousset & Chesselet 1986). The decrease of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with 1/Sr content is then interpreted as due to a mixing of basaltic detritus from the province of Iceland with sialic material from the Paleozoic-Precambrian basements of Greenland and North America. The K-Ar age values measured on the same samples rise with increasing $^{87}\text{Sr}/^{86}\text{Sr}$ and 1/Sr ratios



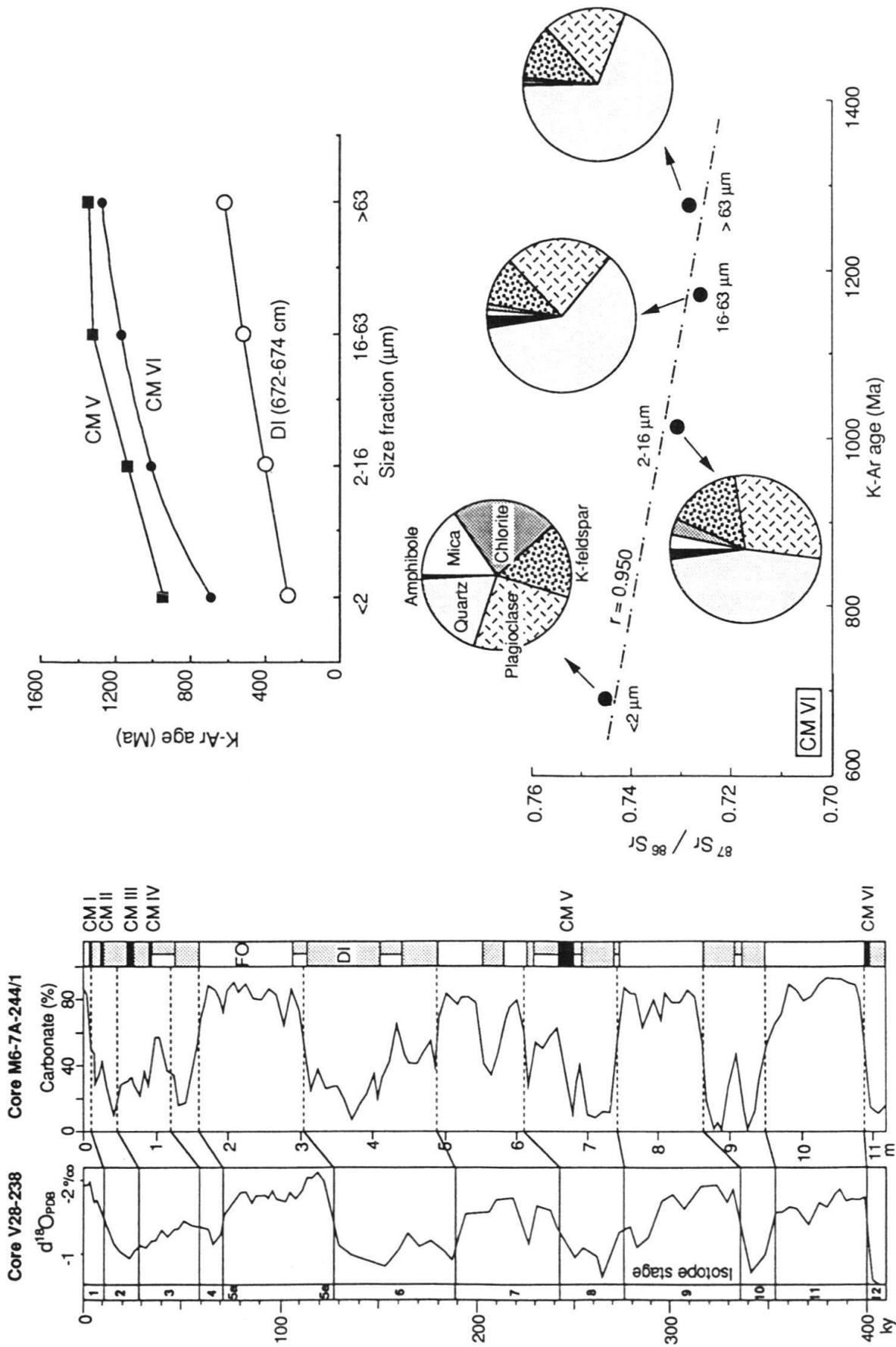
(fig. 6). Therefore, the older component of the silicate mixture is characterized by detrital grains with high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and low Sr contents, provided by granitic source rocks. The Sr-rich and low $^{87}\text{Sr}/^{86}\text{Sr}$ component would then be consistent with a detrital supply of basalt-derived material from the Tertiary-Quaternary province of Iceland. However, the detrital mixtures could also account for a minor contribution of silicate grains with a broader range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, reflecting other acidic-basic continental sources, and so deviate from the assumed primary mixture. Such occurrences are probably involved in the scattering of the data.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured for the clay-size fractions from core ME-68-89 are displayed in figure 8. The Holocene FO sample, recovered near the surface (-3 cm), yields a value of 0.72407, consistent with other values reported from this region (Dasch 1969; Grousset & Chesselet 1986; Huon & Ruch 1992). During the Late Pleistocene (marine isotope stages 2–4), the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the clay-size fractions increase to 0.7425 (DI-CM). These values are higher than those measured for the FO (0.7241–0.7291), sampled at several depths (-3 , -168 , -196 cm , Fig. 8). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios rise again (0.73706) for the DI sample, collected at the bottom of the core (-420 cm , stage 6). A high value is also obtained for a CM horizon (0.74454) of an older glacial period, recorded in the lithological sequence of core M6-7A-244/1 (-1084 cm , marine isotope stage 12). Therefore, determination of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios provides an effective tool for the study of lithological variations, occurring during alternating warm (FO) and cold (DI-CM) climatic periods of the NE Atlantic. However, no significant difference is evident between DI and CM layers. In contrast, the K-Ar age values measured on the same samples (Jantschik & Huon 1992), are more or less equivalent in DI and FO sediment types (350–495 Ma), but systematically higher (690–990 Ma) in the CM layers. The variations of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and K-Ar apparent ages measured for the coarser fractions (2 – $16\text{ }\mu\text{m}$) follow that of the clay-size fractions (Fig. 8). The Sr isotopic values (0.7217–0.7291, tab. 1) are systematically lower than those of the fine-grained concentrates, according to the variations in the mineral balance already mentioned. The differences observed between FO (0.7217–0.7221) and DI-CM (0.7251–0.7291) sediment types are still significant although the deviations are smaller. The K-Ar apparent ages increase with grain size, from about 290 up to 625 Ma for a DI layer and from about 690 up to 1340 Ma within CM V and VI (tab. 2, fig. 7). These values do not overlap. Equivalent conclusions to those for the clay-size fractions can be drawn.

Discussion

The major-element data indicate that the silicate fractions are composed of mixtures from several different sources of detrital minerals and therefore that they do not match the bulk-rock compositions determined for ice-rafted dropstones. During the Late Pleistocene (marine isotope stages 2–4), at least the two end-members of the potential sources are identified: the basic province of Iceland which supplies detrital material through bottom currents or fine nepheloid clouds associated with turbidity currents and the Northwestern and Northern continents (North America, Greenland) through aeolian,

Fig. 6. Plots of Rb-Sr and K-Ar isotopic data for FO, DI and CM samples of core ME-68-89. A turbidite sample from core ME-68-91 is also included. HOL = Holocene.



bottom-surface currents and ice-rafting input. All REE-patterns, except for turbidites, are also best explained by binary mixtures of detrital material from an acidic continental source (Greenland, North-America) and a basaltic source from the region of Iceland. No significant differences between the DI, FO and CM samples are found. Detailed analysis of fine-grained size fractions rather than bulk sediment might be required to improve the resolution of REE distribution patterns.

The Rb-Sr isotopic data are also consistent with a dominant basaltic-granitic mixture. The basaltic material is characterized by rather low $^{87}\text{Sr}/^{86}\text{Sr}$ and high Sr content bearing components. The Tertiary-Quaternary regions of Iceland and of the Faraoe Islands are potential sources of the detrital supply. This conclusion is also supported by the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio measured for the clay-size fraction of turbiditic sediments from core ME-68-91 (0.71796, -418 cm, tab. 1). The amount of basalt-derived material significantly increases due to direct turbiditic input from the Icelandic shelf. The highest smectite content (49% of K-bearing phases) and the lowest K-Ar age value (295 ± 6 Ma) are ascribed to this sample (Jantschik & Huon 1992). The continental areas supply more variable Sr isotopic compositions, depending on the magmatic and metamorphic histories of the source rocks. Nevertheless, the average $^{87}\text{Sr}/^{86}\text{Sr}$ value should be greater than for the volcanogenic component (Faure 1986).

The two isotopic signatures, K-Ar apparent ages and Rb-Sr ratios, yield complementary information on the source, the transport mechanism and the composition of the mixtures of fine-grained detrital silicates recovered in deep-sea sediments. These parameters are directly related to the different sediment types (FO, DI, CM) and therefore to the prevailing climatic conditions. During alternating warm (FO) and cold (DI) climatic periods of the last glacial period (marine isotope stages 2–4), the K-Ar signature is reasonably constant and does not record the discrete variations of acidic continental and basaltic materials. The radiogenic ^{40}Ar content of low K-bearing phases such as smectite or zeolite, is negligible compared to that of Paleozoic-Precambrian mica or feldspar grains which generally represent 80–90% of the potassic minerals. In contrast, the Sr isotopic compositions allow an accurate separation of these variations and this is best seen in the clay-size fractions. It is most likely that the sources, as well as the transport mechanisms, are roughly constant. Only the proportions of each major constituent vary with an increasing supply of continental terrigenous material during the colder periods. A significant shift of the K-Ar ages is only noticed within the CM and corresponds to a drastic change of the mineralogical supply. During several phases of enhanced ice-rafting, the rock sources are mainly composed of Precambrian rocks from high latitudes (Greenland, North-America) whereas a breakdown or at least a strong decrease of basalt-derived supply by bottom currents from Iceland, and eventually also of other transport mechanisms is displayed. This change is not recorded by the Sr isotopic compositions but is indicated by lower Rb/Sr ratios. In this case the comparable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for both DI and CM clay fractions do not imply a common origin but rather a different mineralogical balance, averaging at about the same value. Therefore, these two isotopic methods cannot be used without a detailed mineralogical study.

Fig. 7. Detailed lithological variations of core M6-7A-244/1 and cross-correlation with reference core V28-238 (Shackleton & Opdyke 1973) and corresponding isotope stages. The carbonate curve is taken from Jantschik (1991). Scattering plots of K-Ar ages and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios are represented for different non-carbonate size fractions of 3 DI and CM samples. The mineralogical composition of the size fractions of CM VI is also displayed.

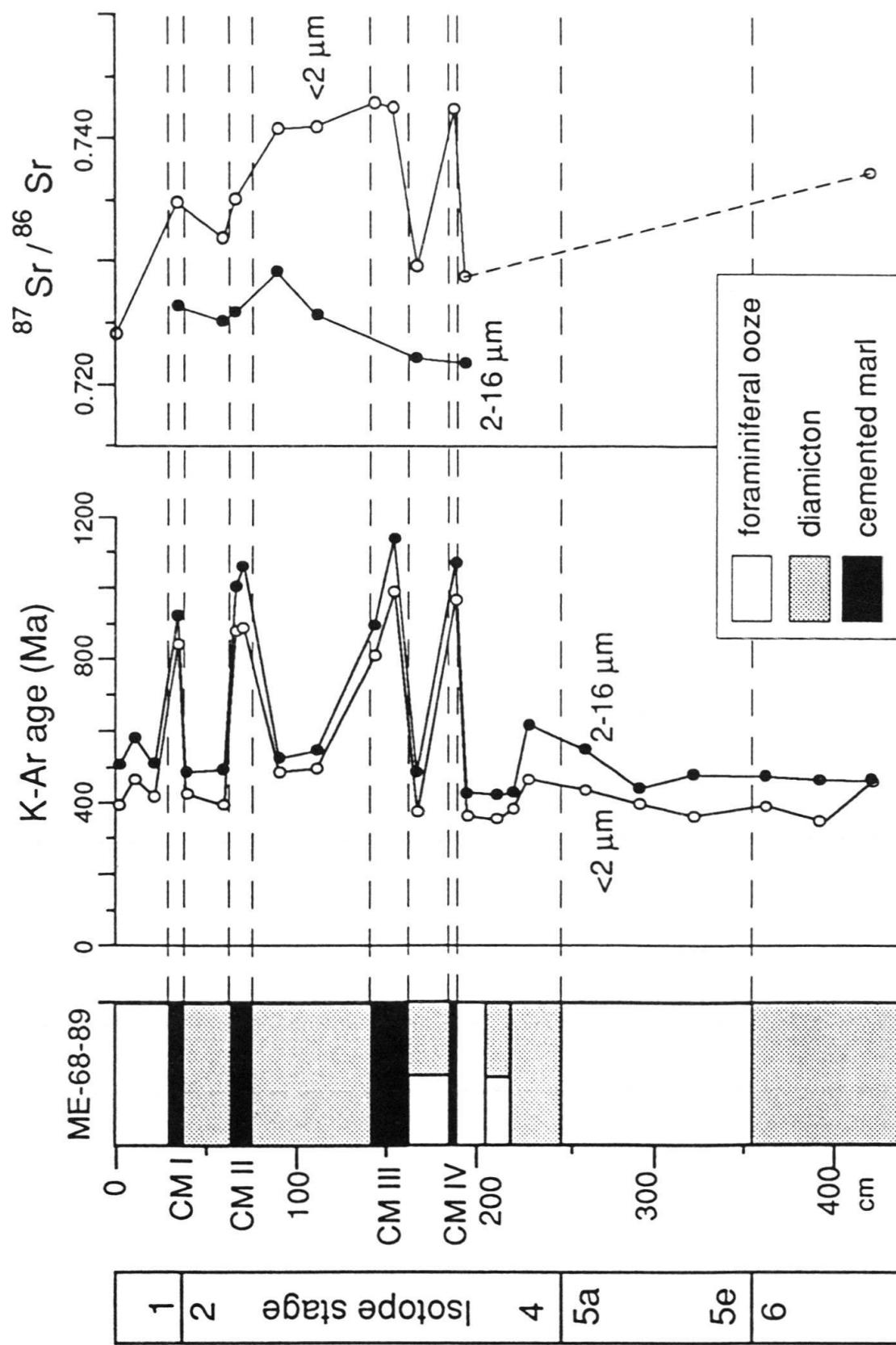


Fig. 8. Downcore distribution of K-Ar ages (Jantschik & Huon 1992) and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios for clay-size and 2–16 μm fractions of sediments from core ME-68-89.

Conclusions

In the NE Atlantic at $47^{\circ}30'N$, $19^{\circ}30'W$ the chemical compositions of detrital clay fractions of deep sea sediments support the hypothesis of mixtures of several different mineral sources, according to the prevailing transport mechanisms. The TiO_2 - FeO -smectite-oligoclase group is related to the basic province of Iceland through bottom current circulation or fine turbidite nepheloid clouds whereas, the Al_2O_3 - K_2O -Rb-mica-chlorite group represents the continental sialic input occurring through wind, surface and bottom currents. During the Late Pleistocene (marine stages 2–4) the CaO - Na_2O - MgO -Sr-amphibole-feldspar-chlorite group mainly records several phases of enhanced ice-rafting transport from the NW continental regions of Greenland and North-America. Consequently these geochemical data do not match single bulk rock compositions. The REE distribution patterns also reflect binary mixtures of highly fractionated (granitic) and less fractionated (basaltic) detrital material, dominated by the acidic composition. Based on REE-patterns, the origin of the turbidite sediment can clearly be located in the region of Iceland.

The K-Ar and Rb-Sr isotopic methods provide complementary geochemical tracers of deep-sea sedimentation, recording the prevailing potential mineral sources, transport mechanisms and climatic conditions. During the warm climatic periods (FO) of the last 140 ky, the $^{87}Sr/^{86}Sr$ ratios of the clay-size fractions are lower (0.7241–0.7291) than during the cold climatic periods (DI, 0.7321–0.7407). This isotopic signature records the discrete variations of the relative content in basalt-derived material within a mixture of at least two main petrological components, a basic component derived from the province of Iceland and an acidic supply from the Northern and Northwestern land masses, most likely North America and Greenland. The amount of acidic continental material is higher during cold climatic periods and therefore increases the $^{87}Sr/^{86}Sr$ ratios. The same conclusions can be drawn for the coarser 2–16 μm size fractions, although the differences between FO (0.7217–0.7221) and DI (0.7251–0.7291) sediment types are smaller. This indication is not supported by the K-Ar apparent ages, which mainly reflect the high radiogenic ^{40}Ar content of the continental supply (Jantschik & Huon 1992). During four of the 6 phases of enhanced ice-rafting (CM) of the Late Pleistocene (Heinrich 1988) and during previous glaciations (≈ 250 and 400 ky; Jantschik 1991), the K-Ar age values shift up to 989 ± 16 Ma for the clay-size fractions and up to 1338 ± 22 Ma for the coarser size fractions. These ages are significantly higher than within the FO-DI-TU sediment types and are related to a drastic change of mineralogical supply. The source material is then mainly restricted to Precambrian rocks from high latitudes (Greenland, North-America). During these phases a breakdown or at least an important decrease in the bottom water supply (NADW) and may be also of some other transport mechanisms (possibly aeolian) is assumed. This variation, however, is not recorded by the Sr isotopic compositions (0.7351–0.7445) but is indicated by lower Rb/Sr ratios. Combining these two isotopic signatures provides supporting information on paleoceanographic and paleoclimatic conditions in the NE Atlantic ocean during the Late Pleistocene.

Acknowledgements

The authors are very thankful and indebted to Prof. Dr. B. Kübler (Neuchâtel), Dr. H. Heinrich (Hamburg), Dr. D. Fontignie (Genève), Dr. I. Hedley (Genève), M. Senn (Genève), D. Yu (Genève). We are also grateful to

Dr. F. Oberli (Zürich) and Dr. S. Chambers (La Jolla) for critical reviewing of a former draft of this manuscript and to Prof. Dr. D. Meischner (Göttingen) and Prof Dr. C. Hemleben (Tübingen) for providing all the samples and for helpful discussions. Previous litho-stratigraphic work on the cores was carried out together with R. Lohoff and Prof. Dr. D. Meischner (Göttingen). We thank the crews of RV "Meteor" (old and new) and RV "Polarstern" and specially H. Rumpel (Göttingen) for technical shipboard assistance. The cores were recovered as part of the activities of the NOAMP project (Bundesministerium für Forschung und Technologie, Germany, No. KWA 5310) and the "Deutsche Forschungsgemeinschaft" (He 697/4). This study was supported by Swiss FNRS grants n°20.26'243.89 (RJ) and n°2.338-0.86 (SH). This paper and the article by Jantschik & Huon (1992) contain parts of one of the author's (RJ) doctoral thesis.

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Manuscript received 3 January 1992

Revision accepted 2 November 1992