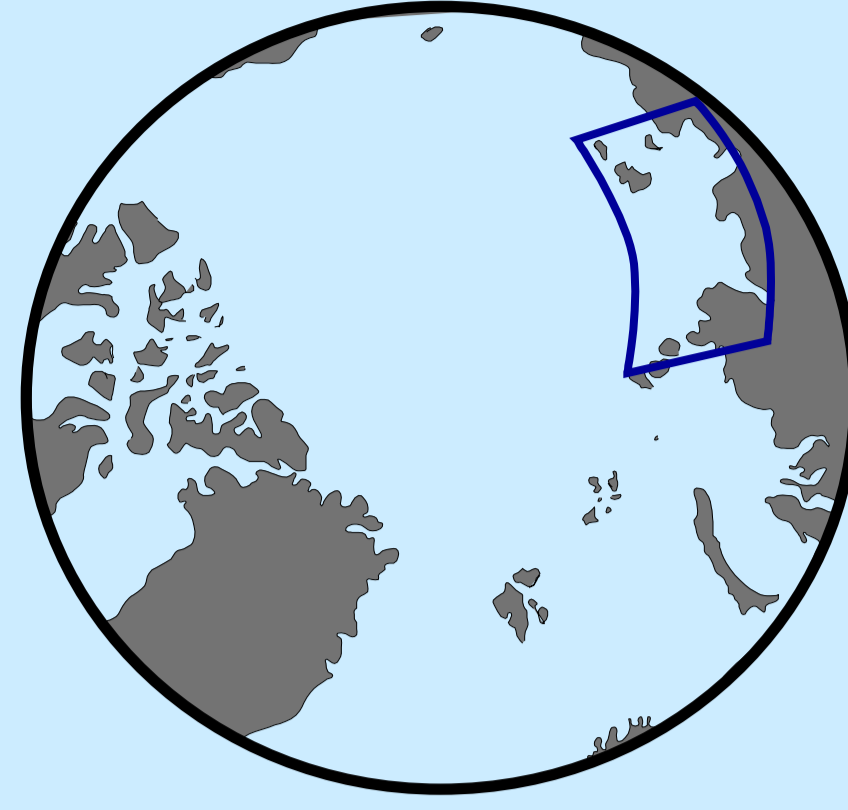


# Carbon Isotopic and Molecular Characterization of Sedimentary Organic Matter in the Late Quaternary Arctic Ocean

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**Introduction:** The Arctic Ocean is a unique area of environmental conditions because of its ice cover, limited water exchange with the surrounding oceans, the dominance of marginal seas and the influence of large river discharge. Although known as an area of low primary productivity, recent calculations on the organic carbon budget of the Arctic Ocean indicate its importance for the global organic carbon cycle (Macdonald et al., 1998; Anderson et al., 1998; Stein and Fahl, 1998). From a compositional point of view, bulk parameters and biomarker studies clearly revealed that most of the organic carbon buried in the sediments of the Arctic Ocean and its marginal seas is of terrestrial origin (Stein et al., 1994; Schubert and Stein, 1997; Fahl and Stein 1997, 1998; Knies and Stein, 1998). By far the greatest part of sedimentary organic matter (>95% by weight, Durand and Nicaise, 1980) is represented by kerogens. The high molecular weight and the polymeric nature of the kerogens excludes a chemical characterization by „classical“ methods, e.g. gaschromatography and gaschromatography-mass spectrometry. Despite its quantitative importance, reports on the chemical composition from a molecular point of view and thus information on the sources of macromolecular organic constituents are scarce for the Arctic environment. In this study, we report on the macromolecular inventory of organic compounds as revealed by pyrolysis-gaschromatography/mass spectrometry (Py-GC/MS) on kerogen isolates from the Laptev Sea and the adjacent continental slope area. Surface sediments as well as core samples (PS 2458, PS2725) have been analyzed. Furthermore, the carbon isotopic composition and C/N ratios of the sedimentary organic matter in core PS2725 were used to characterize the origin of the organic carbon.



**Samples and Methods:** A set of surface samples and two sediment cores (PS2458, PS 2725), obtained during the Transdrift I Expedition (Kassens and Karpov, 1994), the RV "Polarstern" Expeditions ARK-IX/4 (Fütterer, 1994) and ARK-XI/1 (Rachor, 1997), were investigated. The locations of the samples are given in Fig. 1. Kerogen isolates, admixed with an internal standard where weighed directly into small quartz tubes. The quartz tubes were then inserted into the platinum coil of the pyrolytator head (CDS 2000 Pyroprobe). Sample pyrolysates effluent with the carrier gas (He) were directly refocused on the capillary column at -20°C by a nitrogen-cooled cryofocusing unit prior to GC separation. Identification of the pyrolysis products was based on their mass spectra compared to synthetic references and literature data. Quantification of compounds was done by integrating peak areas of appropriate ion chromatograms selected for the most prominent compound classes. Product distributions on this poster are presented relative to the sum of identified compounds or normalized to the most abundant component of the respective compound class.

## GENERAL OVERVIEW: PYROLYSIS PRODUCTS AND THEIR SUGGESTED ORIGIN

Table 1 summarizes the compound classes identified in the pyrolysis products and indicates the carbon atom number range and the range of relative abundance in which these compounds have been observed in the investigated samples. A short overview of possible sources for the most prominent compounds is given below.

Tab. 1	Compound class	relative abundance (%)
	<i>n</i> -Alkenes + <i>n</i> -alkanes (C9-C32)	28 - 54
	<i>n</i> -Alkan-2-ones (C7-C29)	2 - 6
	<i>n</i> -Alkyl-nitriles (C12-C30)	2 - 16
	Fatty acids (C7-C22) incl. <i>ω</i> - <i>ω</i> -1-branched acids	0 - 40
	<i>n</i> -Alkylbenzenes (C3-C25)	1 - 11
	Phenolic compounds (CO-C3)	8 - 25
	Furanes/Furaldehydes	2 - 14
	Naphthalenes / Methyl-naphthalenes	3 - 9

The dominant species identified in most kerogen pyrolysates are *n*-alkenes and *n*-alkanes, which thus are ubiquitous constituents of kerogens. However, the carbon atom number distribution of these aliphatic hydrocarbons as well as the alkene/alkane ratio seem to reflect the organic matter type. Terrestrial (higher plant) derived kerogens are known to produce mainly odd-dominated alkenes and even-dominated alkenes with carbon atom numbers >C<sub>20</sub> whereas kerogens derived from marine organisms yield mainly aliphatic hydrocarbons below C<sub>20</sub> (van de Meent et al., 1980). *n*-Alkan-2-ones and *n*-alkyl-nitriles are reported to occur preferentially in pyrolysates of kerogens that are composed primarily of algae-derived from both, freshwater and marine microalgae (Largeau et al., 1986; Derenne et al., 1991; Gelin, 1996). Although *n*-alkyl-nitriles might be formed via secondary reactions of fatty acids with ammonia upon heating (Evans et al., 1985), for the samples investigated such an origin is less likely, as the relative amounts of nitriles and fatty acids as well as their carbon atom number distributions differ within the samples. Pevlúv et al. (1996) reported on the occurrence of alkyl-nitriles in pyrolysates of suspended and sedimentary organic matter in the Lena delta and also ascribed them to autochthonous (algal) sources. Fatty acids in pyrolysates are usually observed with a strong predominance of even-numbered straight chain compounds with multiple origins, e.g. terrestrial and marine plants (algae), zooplankton and bacteria. However, fatty acids dominated by C<sub>14</sub>-, C<sub>16</sub>- and C<sub>18</sub>-compounds are considered to indicate autochthonous input of microalgae-derived organic matter (e.g. Taylor et al., 1984) and their preservation in algaeans has been shown (Derenne et al., 1991; Gelin, 1996). Contrary, even dominated, long chain (C<sub>24</sub>-C<sub>30</sub>) fatty acids are related to terrigenous inputs and considered to be derived from the epicuticular waxes of higher plants. Phenols, including their C<sub>1</sub>- to C<sub>3</sub>-methylated homologues in kerogen pyrolysates can be related to manifold sources, e.g. proteins, seed-coats of higher plants, modified lignin (Pevlúv et al., 1996, and ref. therein) and spore walls from angiosperms and gymnosperms (van Bergen et al., 1993). Usually, phenolic compounds in kerogen pyrolysates are ascribed to originate from terrestrial derived material.



Fig. 1: Locations of the investigated samples

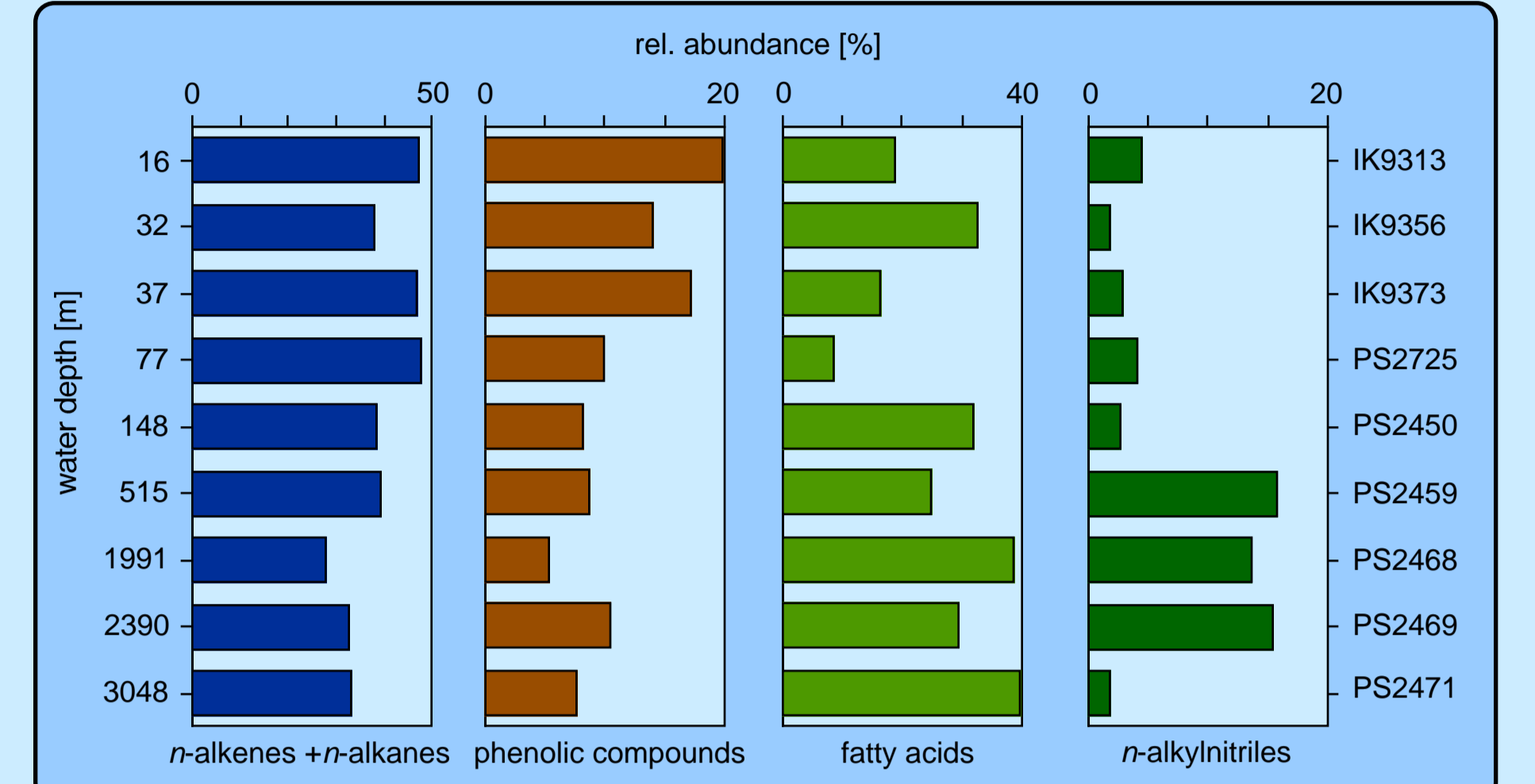


Fig. 3: Distribution of selected pyrolysis products in surface sediments ordered according to the water depth

The carbon atom number distribution of the fatty acids (data not given here) shows that they most probably are related to marine autochthonous sources, as even-numbered homologues in the carbon atom number range from C<sub>12</sub> to C<sub>18</sub> predominate. Varying proportions of marine vs. terrigenous organic matter preserved in the kerogens can also be observed with respect to the carbon atom number distribution of the hydrocarbons (Fig. 4a), representing the most abundant fraction of pyrolysis products. Whereas the aliphatic hydrocarbon moieties derived from surface kerogens of PS2725 are dominated by compounds <C<sub>20</sub>, the contrary is found for sample IK9313, showing a strong predominance of odd numbered homologues >C<sub>20</sub>. This indicates a relatively enhanced proportion of terrestrial derived organic matter in the kerogens of IK9313 compared to PS2725. To further classify the surface kerogens, the ratios of C<sub>10</sub>-C<sub>20</sub>/C<sub>21</sub>-C<sub>31</sub> hydrocarbons and the CPI, which is a measure of the relative abundance of odd-numbered homologues in the >C<sub>20</sub> carbon atom number range, were calculated (Fig. 4b). This plot reveals that the hydrocarbon compositions of PS2725 and PS2450 are different from the other surface samples and seems to be controlled by the sample position. Thus, samples receiving their terrestrial proportion of organic matter from discharge of the same rivers (Lena, Khatanga) plot in a narrow range. The terrestrial proportion in the kerogen of PS2725, although less abundant,

## DISTRIBUTION OF PYROLYSIS PRODUCTS IN SURFACE SEDIMENTS

The composition and distribution of compounds identified in the pyrolysates of surface sediments from the Laptev Sea and its adjacent areas is shown in Fig. 2 - Fig. 4. The by far most abundant pyrolysis products are *n*-alkenes + *n*-alkanes which, together with fatty acids, account for over 50% of the components in all of the investigated surface samples (Fig. 2). Phenolic compounds and *n*-alkyl-nitriles account for an additional ca. 20% of the pyrolysis products, whereas the remaining proportion of the pyrolysis products are made up by minor amounts of *n*-alk-2-ones, *n*-alkylbenzenes, naphthalenes (including methyl-naphthalenes) and furanes. Concerning the variations in the relative proportions of the most abundant compound classes, significant differences are observed for the analyzed set of surface samples. In Fig. 3, the relative abundances of these compound classes are shown in dependence of the water depth in which these sediments have been deposited. The water depth can be taken as a rough proxy for the distance of the sample location to the coast (cf. also Fig. 1). It is well documented that most of the inorganic and organic sedimentary matter on the Laptev Sea continental shelf is terrestrial in origin and supplied by the Lena river (Stein et al., 1996). Thus, it should be expected that shallow water/near coastal samples receive an enhanced proportion of terrestrial derived pyrolysis products, even though this riverine input also results in a high fluvial nutrient supply, possibly leading to an enhanced marine primary production. However, regarding the relative amounts of phenolic compounds in the pyrolysates, a systematic decrease with increasing water depth is obvious. Contemporary to the relative decrease of phenolic compounds an increase in the relative proportions of fatty acids as well as of *n*-alkyl-nitriles is clearly evident from Fig. 3.

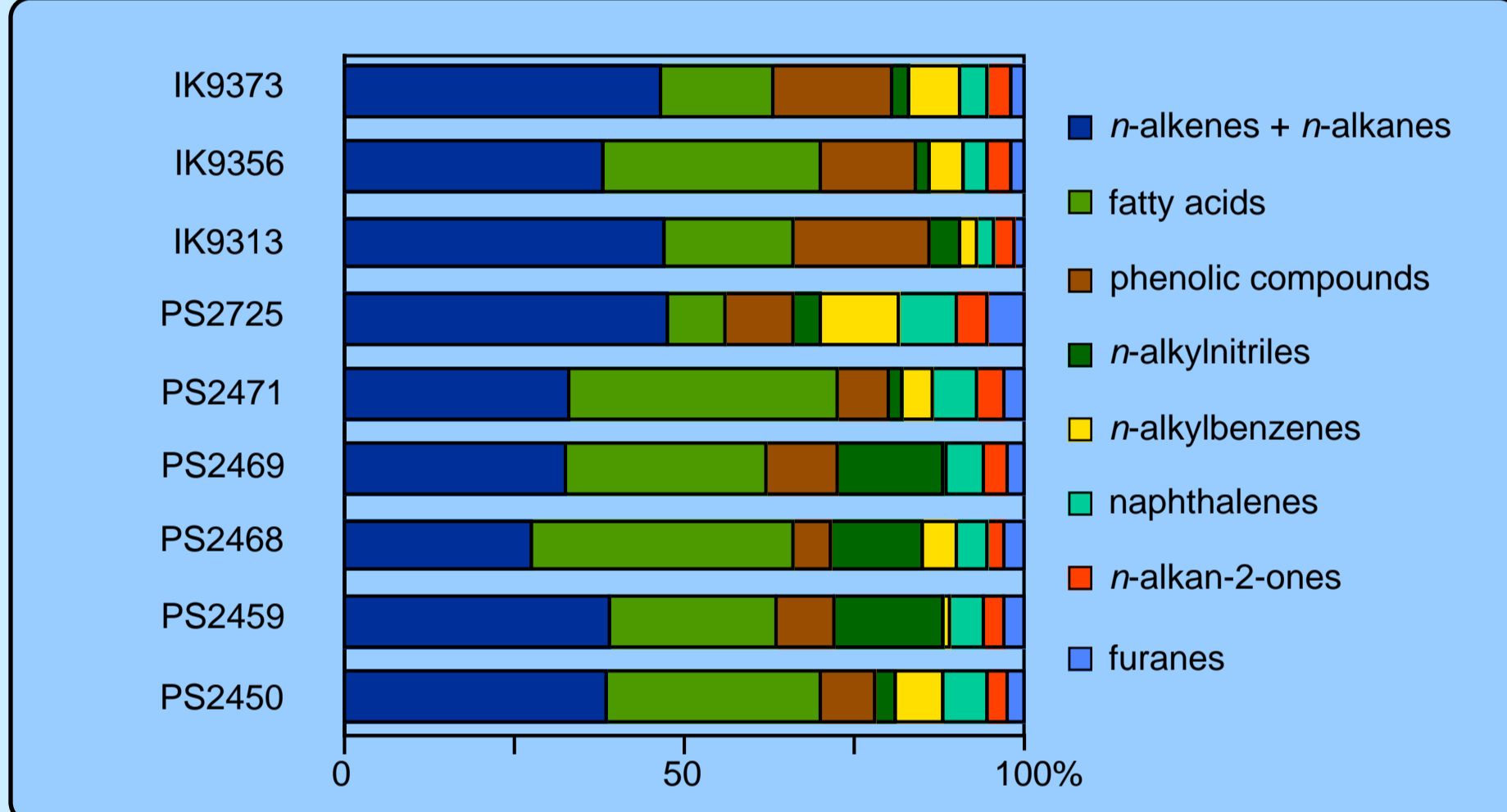


Fig. 2: Relative distribution of identified pyrolysis products in surface sediments of the Laptev Sea and adjacent areas

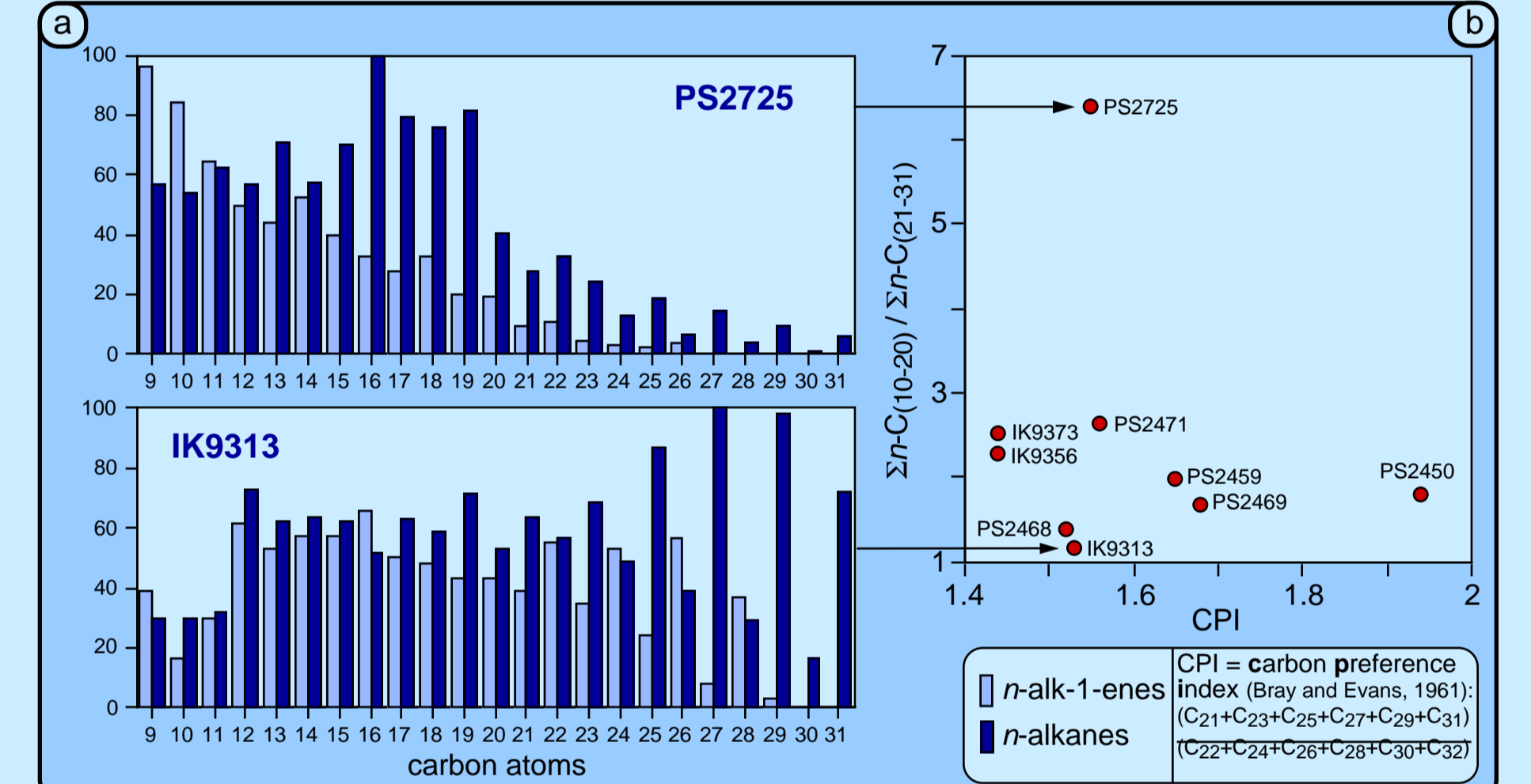


Fig. 4: Variations of the internal distribution of *n*-alkenes and *n*-alkanes (a) and classification of the surface sediments based on the ratio of short to long chain hydrocarbons and the CPI (b)

## PS 2725

Combined informations derived from  $\delta^{13}C_{org}$ -values, C/N-ratios and the composition of selected kerogens as revealed by Py-GC/MS were used to characterize the organic matter preserved in core PS2725-5. This core, located on the eastern outer Laptev Sea shelf, represents the last about 10 Cal ka (Stein and Fahl, 1998). The sedimentary organic carbon isotopic composition displays a high uniformity for most of the samples (Fig. 5), and the average of -25.4‰ indicates a terrestrial dominated origin of the organic carbon for the majority of the samples. This also becomes obvious in a cross-plot of carbon-isotope values vs. the C/N-ratios (Fig. 6). However, samples from the uppermost (recent) and samples of about 10 Cal ka show a change in the organic matter composition which, according to the C/N-ratios and stable carbon isotopes, is related to an enhanced contribution of marine derived organic carbon. Py-GC/MS of the surface sediment kerogen of core PS2725 (cf. Fig. 4 and related discussion) also revealed a dominating proportion of pyrolysis products from a marine organic carbon source, as documented for example by the high relative proportion of hydrocarbons <*n*-C<sub>20</sub>. A similar distribution of hydrocarbons was detected in the pyrolysates of the PS2725 kerogen sample from 450cm core depth.

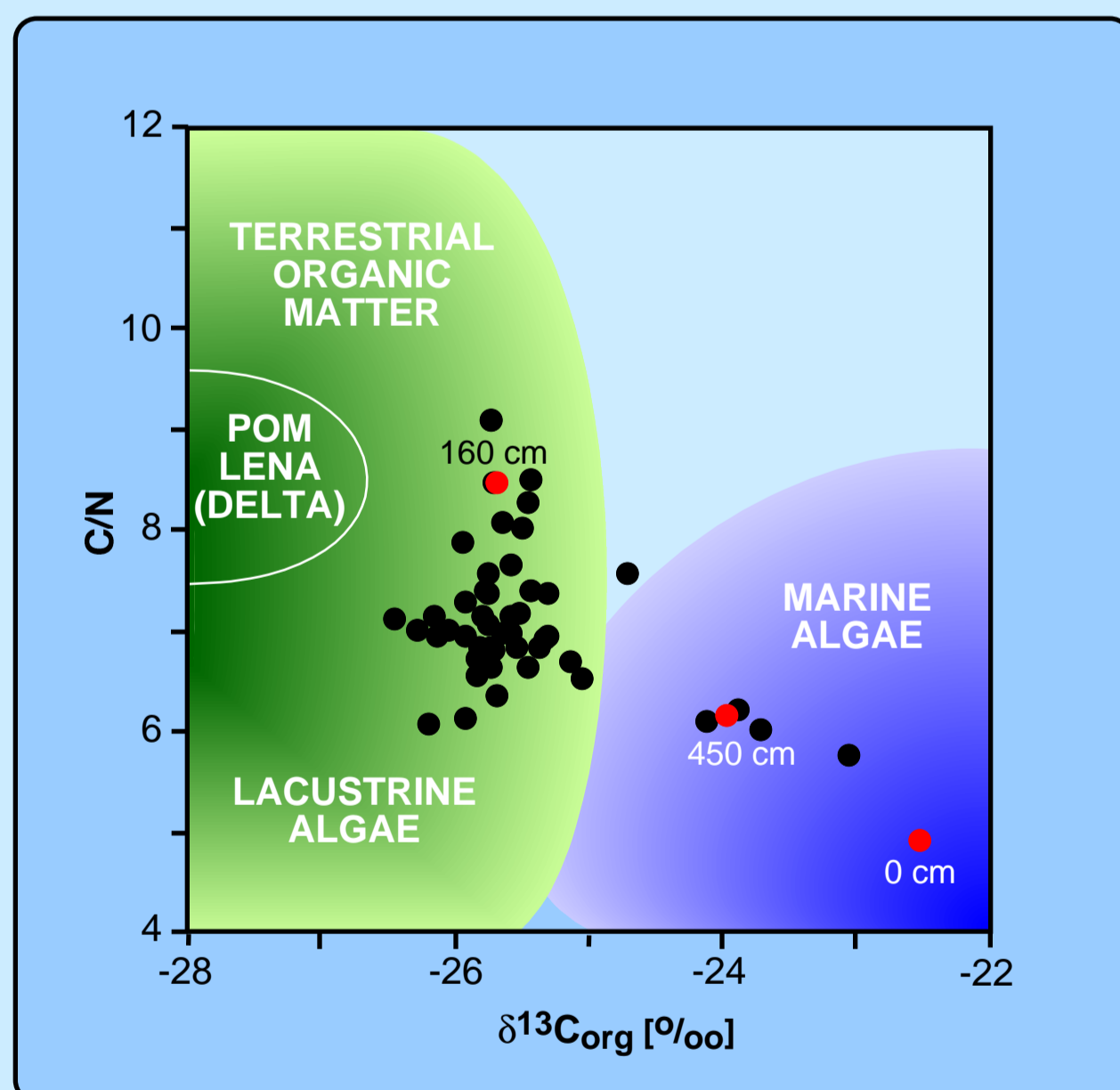


Fig. 6: Position of PS2725 core samples in a scatter plot of  $\delta^{13}C_{org}$ -values vs. C/N ratios. Values given for the Lena delta POM from Rachold and Hubberten, 1998.

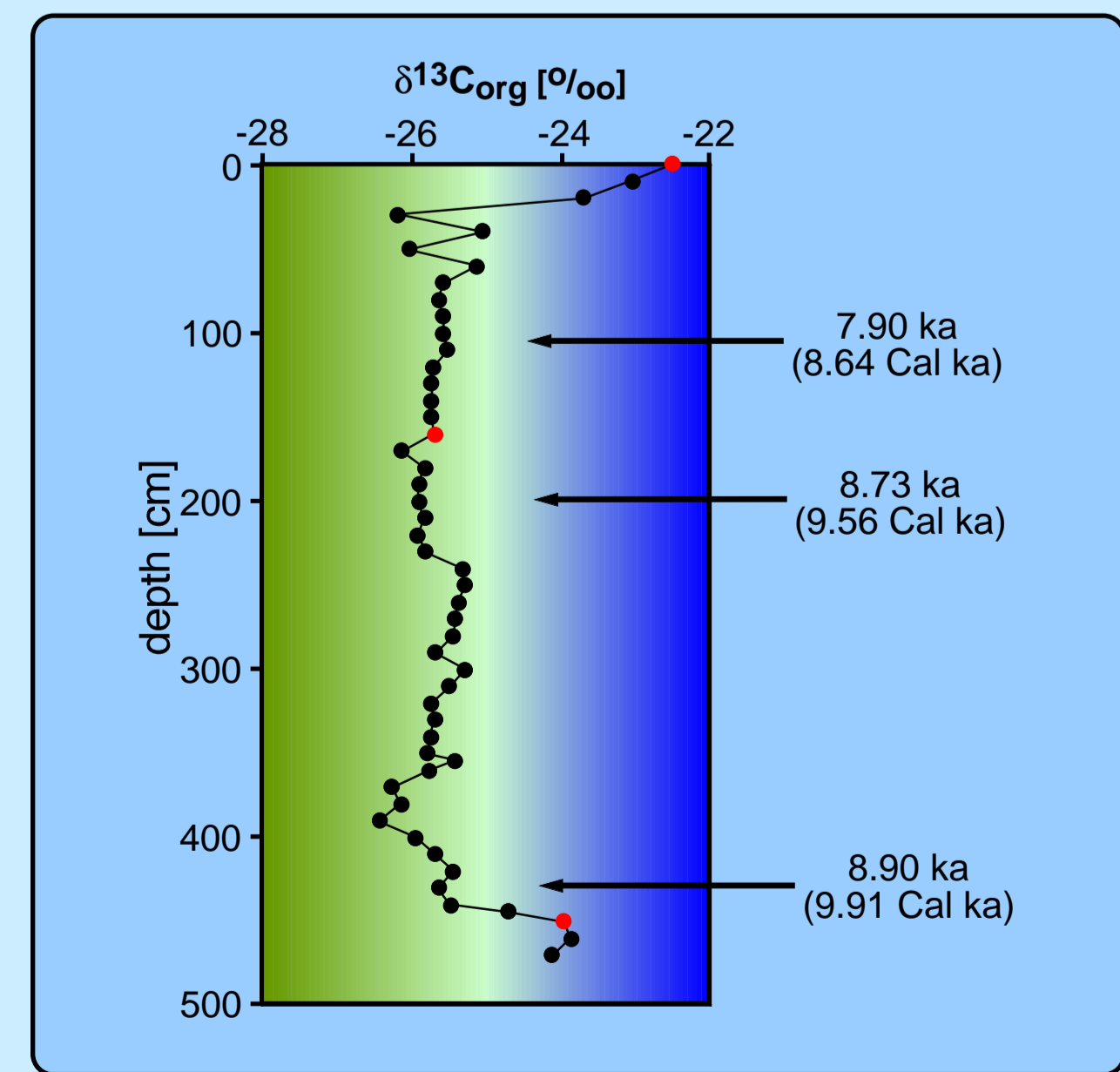


Fig. 5:  $\delta^{13}C_{org}$  vs. depth, core PS2725. Red dots indicate kerogen samples analyzed by Py-GC/MS.

In contrast, the kerogen sample (150cm, see Figs. 5, 6) chosen to be representative for the "terrestrial"-dominated part of core PS2725 revealed increased relative amounts of odd-dominated hydrocarbons >C<sub>20</sub> upon pyrolysis. Results obtained on the extractable biomarker composition (see AGU-Poster Fahl et al., 1998; Fahl and Stein, 1998) fully support the above findings. With respect to the paleoenvironmental situation, the prominent terrestrial signal in core PS2725 started to establish around 10 Cal ka BP, documented by the transition from carbon-13 enriched (-24‰) sedimentary organic matter towards lighter (-26‰) carbon isotopic values (Fig. 5). At this time, the postglacial sea-level rise flooded the shelf and contemporary, a distinct increase in coastal erosion and/or river discharge, well documented in maximum sedimentation rates (cf. AGU-Poster Stein et al., 1998) resulted in an enhanced accumulation of terrestrial derived organic material. This period of increased terrestrial derived organic matter supply lasted about 2000 years, and than the "modern" situation began to establish and the terrestrial proportion of organic carbon decreased.

## PS 2458

Core 2458-4 contains a sequence of sediments originating from the continental slope and represents the last ~15.000 Cal. yrs. BP (Spielhagen et al., 1996). The relative proportions of compounds identified in the kerogen pyrolysates are shown in Fig. 7. As in the surface samples, hydrocarbons comprise ~50% of the pyrolysis products, followed by ~20% of phenolic compounds. Contrary to the surface samples, only low relative amounts of fatty acids could be detected. The variance in the macromolecular matter composition becomes obvious in the depth profiles of selected compound classes (Fig. 8) and reveals major fluctuations and changes in relative abundance around 10 Cal ka BP. Prior to this time, higher relative amounts of hydrocarbons are preserved in the kerogens, whereas from 10 Cal ka towards the youngest sample, lower amounts are detected. The chain lengths distribution of the hydrocarbons (Fig. 9) also shows a major change around 10 Cal ka from a preference of long chain compounds towards increasing amounts of *n*-alkenes and alkanes <C<sub>20</sub>. This indicates that the contribution of marine organisms in the upper (0-350cm) core section is higher compared to the deeper part, which also is documented in the extractable biomarker distribution, the maceral composition and by micropaleontological investigations (AGU-Poster Fahl et al., 1998). Thus, comparable to the situation found in the shelf core PS2725, increasing proportions of marine organic matter contemporary to the last major postglacial sea level rise, are documented for the Laptev Sea continental slope. However, the relative amounts of the other compound classes (e.g. phenolic compounds) indicate a more complicated situation for core PS2458, as they also show an increase in the upper core section. This might, at least partly, be explained by a contribution of phenolic compounds derived from other than terrestrial sources and therefore, further investigations are in progress.

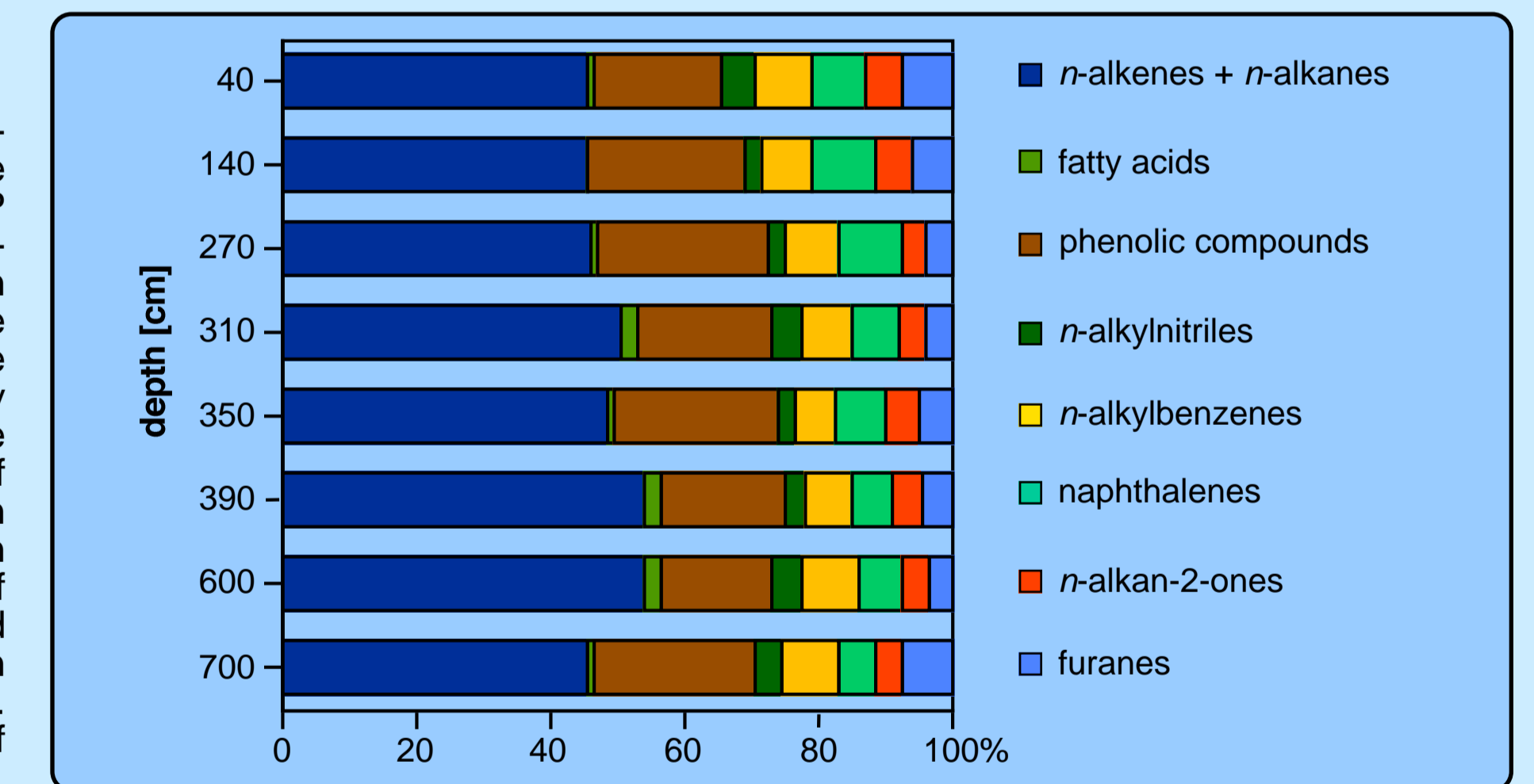


Fig. 7: Relative distribution of identified pyrolysis products in kerogens from core PS2458

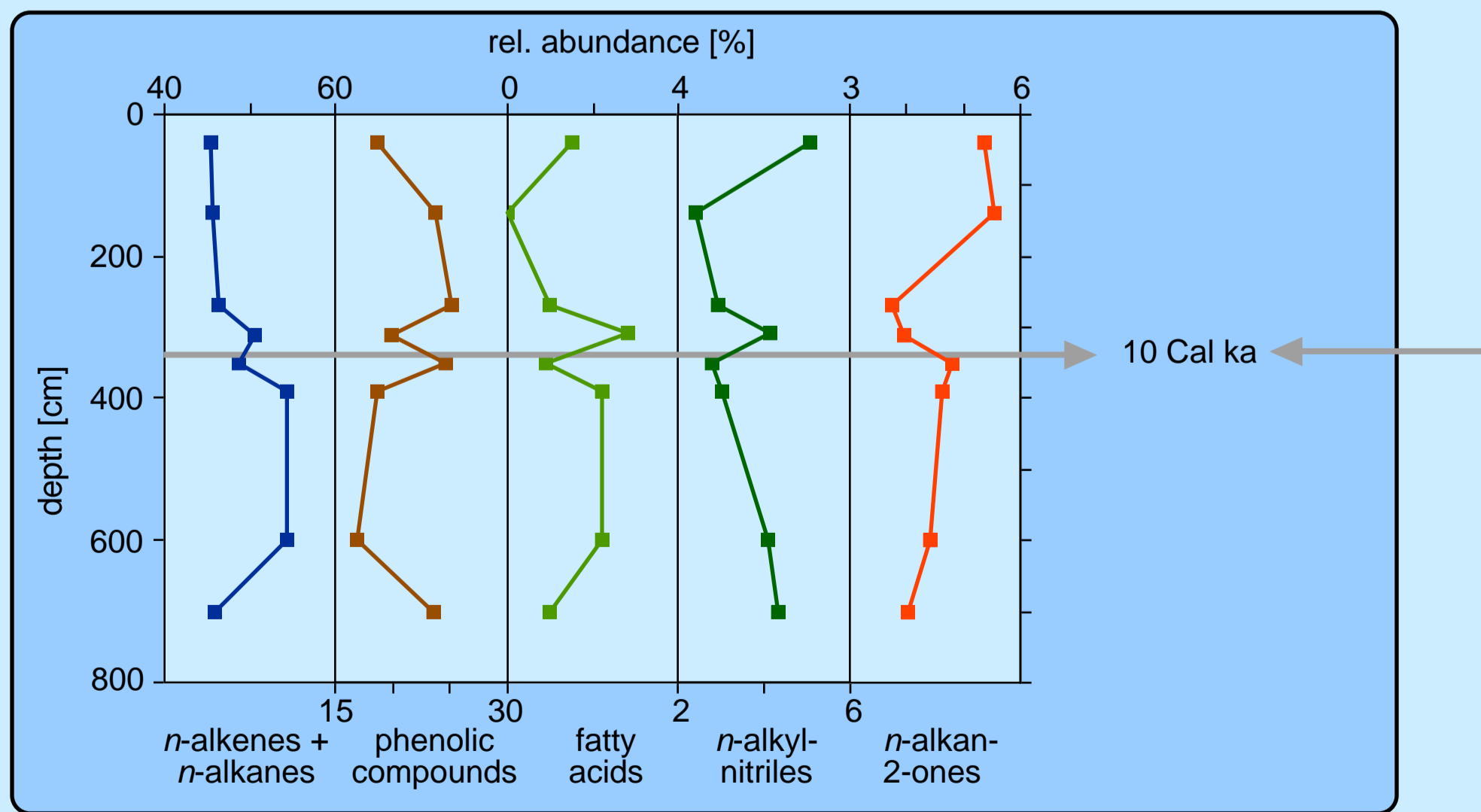


Fig. 8: Relative abundance of selected pyrolysis products from kerogens of core PS2458

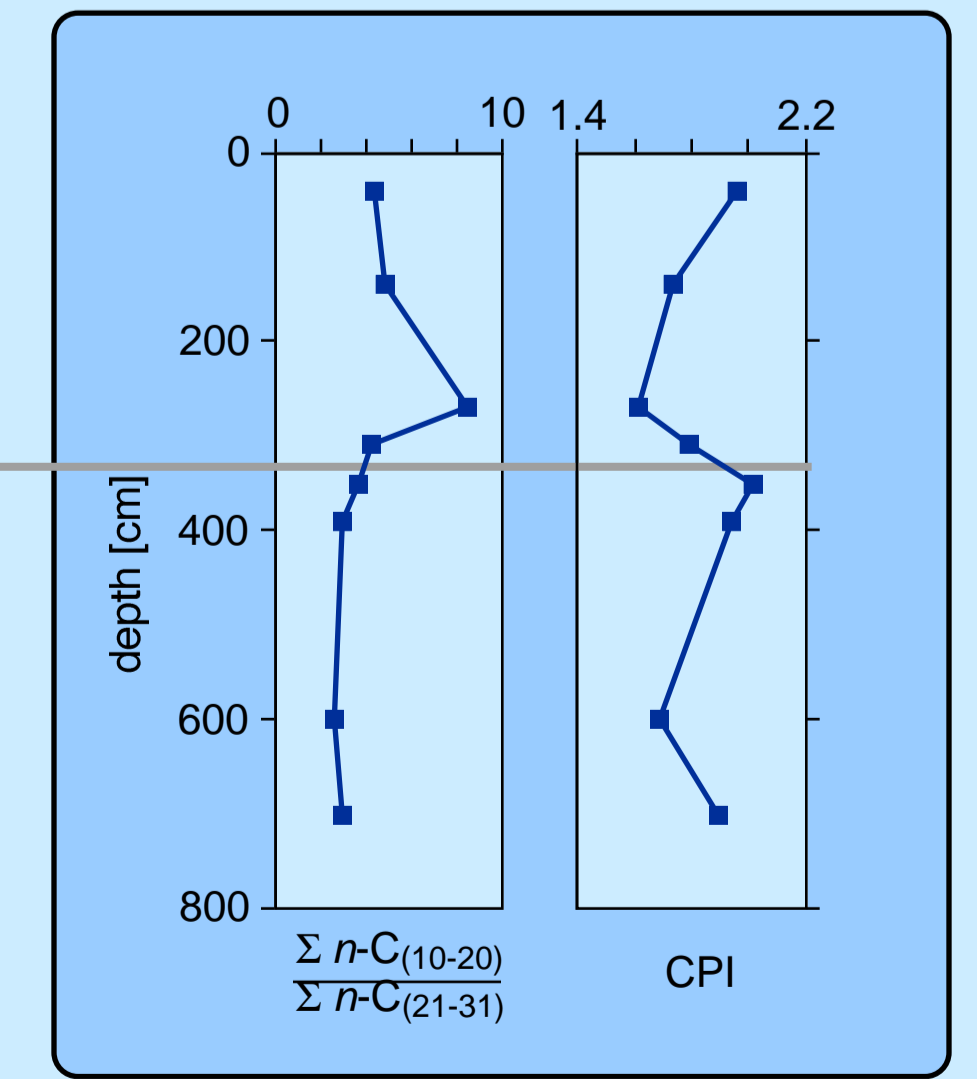


Fig. 9: Molecular parameters for the carbon atom number distribution of hydrocarbons in pyrolysates of core PS2458

**REFERENCES** Anderson LG, Olsson K and Chierici M (1998) A carbon budget for the Arctic Ocean. *Global Biogeochem. Cycles* 12, 465-465. Bray EE and Evans ED (1961) Distribution of *n*-paraffins as a clue to recognition of source beds. *Geochim. Cosmochim. Acta* 22, 2-15. Derenne S, Largeau C, Casadevall E, Berkalo C and Rousseau B (1991) Chemical evidence of kerogen formation in source rocks and oil shales via selective preservation of thin resistant outer walls of microalgae: Origin of ultralaminae. *Geochim. Cosmochim. Acta* 55, 1041-1050. Durand B and Nicaise G (1980) Procedures for kerogen isolation. In: Durand B (ed.), *Kerogen: Insoluble Organic Matter from Sedimentary Rocks*. Paris (Editions Technip), 35-53. Fahl K and Stein R (1997) Modern organic-carbon-deposition in the Laptev Sea and the adjacent continental slope. *Surface-water productivity vs. terrigenous input*. *Org. Geochem.* 26, 379-390. Fahl K and Stein R (1998) Biomarkers as organic-carbon-source and environmental indicators in the Late Quaternary Arctic Ocean: "Problems and perspectives". *Mar. Chem.* 63, 293-309. Fütterer DK (1994) The Expedition ARK-IX/4 of RV "Polarstern" 1993. Reports on Polar Res. 149, 244 pp. Gelin F (1996) Isolation and chemical characterization of resistant macromolecular constituents in microalgae and marine sediments. PhD thesis, University of Utrecht, *Geologica Ultraiectina* 133, 147 pp. Kassens H and Karpov Y (1994) Russian-German Cooperation: The Transdrift I Expedition to the Laptev Sea. Reports on Polar Res. 151, 188 pp. Knies J and Stein R (1998) New aspects of organic carbon deposition and its palaeoceanographic implications along the Barents Sea margin over the last 30,000 years. *Paleoceanography* 13, 384-394. Largeau C, Derenne S, Casadevall E, Kadouri A and Salier L (1996) Pyrolysis of immature torbanite and of the resistant biopolymer (PRB A) isolated from extant alga *Botryococcus braunii*. In: *Advances in Organic Geochemistry 1995* (ed. Leythaeuser D and Rulkötter J). *Org. Geochem.* 10, 1023-1032. Macdonald RW, Solomon SM, Cranston RE, Welch HE, Yunker MB and Goboll C (1998) A sediment and organic carbon budget for the Canadian Beaufort Shelf. *Mar. Geol.* 144, 255-273. Pevlúv S, de Leeuw JW, Sicre M-A, Baas M and Salta A (1996) Characterization of organic matter in sediment traps from the northwestern Mediterranean Sea. *Geochim. Cosmochim. Acta* 60 (7), 1239-1259. Pevlúv S, Sicre M-A, Salta A, de Leeuw JW and Baas M (1996) Molecular characterization of suspended and sedimentary organic matter in an Arctic delta. *Limnol. Oceanogr.* 41(3), 488-497. Rachold V and Hubberten HW (1998) Carbon isotope composition of particulate organic material in East Siberian rivers. In: *Land-Ocean Systems in the Siberian. Dynamics and History* (eds. Kassens H et al.). Springer-Verlag, Berlin, 223-236. Rachor E (1997) Scientific cruise report of the Arctic expedition ARK-XI/1 of RV "Polarstern" in 1995. Reports on Polar Res. 226, 157 pp. Schubert CJ and Stein R (1997) Lipid distribution in surface sediments from the central Arctic Ocean. *Mar. Geol.* 138, 11-26. Spielhagen RF, Erlenkeuser H and Heinemeier J (1996) Decadal changes of freshwater export from the Laptev Sea to the Arctic Ocean. *Quaternary Environment of the North (QUEEN)*. First Annual Workshop, Strasbourg. Abstract Volume. Stein R and Fahl K (1998) Holocene accumulation of organic carbon at the Laptev Sea continental margin (Arctic Ocean): Sources, pathways and sinks. *Geo-Mar. Letters*, subm. Stein R, Grobe H and Wahnsner M (1994) Organic carbon, carbonates, and clay mineral distributions in Eastern Central Arctic Ocean surface sediments. *Mar. Geol.* 119, 269-285. Stein R, Ivanov GI, Levitan MA and Fahl K (1996) Surface-sediment composition and sedimentary processes in the central Arctic Ocean and along the Eurasian continental margin. *Reports on Polar Res.* 212, 324pp. Taylor J, Young C, Parkes RJ, Eglinton T and Douglas AG (1984) Structural relationships in protoketogens and other geopolymers from oxic and anoxic sediments. In: *Advances in Organic Geochemistry 1983* (eds. Schenck P et al.). *Org. Geochem.* 6, 279-286. van Bergen PF, Collinson ME and de Leeuw JW (1993) Chemical composition and ultrastructure of fossil and extant salivalean microspore massulae and megasporae. *Grana* Suppl. 1, 18-30. van de Meent B, Brown SC, Philp RP and Simonet B (1980) Pyrolysis-high resolution gas chromatography-mass spectrometry of kerogens and kerogen precursors. *Geochim. Cosmochim. Acta* 44, 999-1013.



