

7.8 New findings of ikaite in the Kara Sea during R/V "Akademik Boris Petrov" Cruise 36, September 2001

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Introduction

Only few findings of ikaite are known in the Arctic shelf seas up to the present (Schubert et al. 1997). Numerous findings of calcite pseudomorphs were described in Jurassic and L.Cretaceous sedimentary deposits in the large area (0,7 million km²) between river Pjasina and Vilyui, Lena basin and in the Laptev Sea shoreline area from Taymyr to the Lena delta (Kaplan 1978). Well-shaped crystals of different sizes, single or clustered were shown to be widespread in marine clayey or silty and sandy deposits (ball-shaped conglomerates of 0,5-8 cm in diameter, single crystals 1-8 cm in length). On the author's opinion, ikaite was the parent mineral of the carbonate pseudomorphs. This speculation fits well the geological situation and pseudomorph composition and was supported later (Suess et al. 1982).

In the joint German-Russian expeditions carried out onboard R/V "Akademik Boris Petrov" during the period of 1997-2001 ikaite and related authigenic carbonate inclusions in sediments have been repeatedly found in sediments (Kodina et al. 1998 2001; Geological core description, 2001). Most of them were observed along the Yenisei main channel, which is characterized by a high sedimentation rate (Stein 2001). Depositional environments, where ikaite occurs, are generally within silty clay or sandy silty clay, and often organic rich. Crystals occurred in the sediments at subbottom depths from 5-20 cm to 260 cm. During the last expedition (BP 2001) ikaite crystals were found at St. 26 and 55 and a carbonate crust ($\delta^{13}\text{C} = -14,4\text{‰}$) was detected on the sediment surface at St. 45 and raised onboard (Fig 7.16.)

Results and discussion

Core description.

The lithology of the ikaite bearing cores is presented in Figure 7.17. The detailed visual core description was made on board. The preliminary lithological description was supplemented by our onboard analytical data on the water content and the specific density of the raw sediments and comments of Drs R. Stein and M. Levitan. Geologists have made good use of the physical properties to study lithology and stratigraphy of sedimentary sections (Dunaev et al. 1995; Dittmers 2001). Both core sections exhibit a rather variable lithology. Within the sedimentary section St. 26, three lithological units could be distinguished. The upper part (0-195cm) of the core consisted of clayey sediments with a wet specific density (WSD) from 1,36 to 1,58 cm³. A sharp lithology and density boundary at 195-200cm marks the top of the second unit (195-385cm) comprising alternating sequences of very dense fine-grained silt, silty clay and more coarse-grained clayey silty sand and thin sandy (WSD=1,52-1,86 cm³) sediment intervals of variable thickness. The bottom part of the core (385-506 cm) was represented by dense silt and silty clay with diatoms (WSD= 1,56-1,64 cm³). Shell debris and intact bivalve

shells were abundant in the first unit and at the top interval of the second units (0-50 cm, 190-210 cm). The sediment was moderately reduced as observed by its grey, dark-grey, black color and slight H_2S smell in the interval from 200-270 cm. At a depth of 226-230 cm, a weakly radiated spherical cluster (diameter of about 5 cm), of tightly connected, small (0,7-1 cm in length) yellowish to light-brown ikaite crystals was found.

The sedimentary sequence at St. 55 consisted mainly of sandy clay (WSD up to $1,80\text{ cm}^3$) in the uppermost part (0-70 cm) and partially of silty clay (WSD = $1,53\text{--}1,72\text{ cm}^3$). The interval from 70 to 230 cm was represented by soft silty clay (WSD= $1,48\text{--}1,58\text{ cm}^3$), with sand grains (sandy silty clay) below 170cm (WSD = $1,58\text{--}1,62\text{ cm}^3$) being abundant. The bottom part of the section ($230\text{--}310\text{ cm}^3$) consisted of highly reduced black sandy sediment (silty sand of WSD= $1,78\text{--}1,90\text{ cm}^3$). Intact bivalves (*Saxicava arctica*) and shell debris were present in the intervals from 10-20cm, 35-40cm, 120-130 cm. The sediments of the whole section were highly reduced, and strong H_2S smell was present throughout the complete core.

Two ikaite crystal accumulations occurred close to each other in the silty clay core sections at depths from 135 - 145cm and 159 and 165 cm, respectively. The first one consisted of about 30 individual or doubled well-developed crystals of different sizes from less than 1 cm to 6,5 cm in length (Fig. 7.17). The weight of the crystal accumulation was about 300g. Within the second accumulation three small crystals and one giant, massive (169g), euhedral, magnificent crystal with a perfectly shaped front pyramidal termination (11,5 cm in length and 4,5 cm in diameter) occurred. To our knowledge, this is the largest known ikaite crystal up to now. All crystal specimens were translucent, dark amber in color. Few white points, consisting of calcite inclusions within the ikaite crystal are already visible by bare eye.

For the preservation of the ikaite crystals the crystals were kept onboard in a freezer and could successfully be transported to the home laboratory.

X-Ray study of the crystals

X-ray study of the crystals was carried out on diffractometer DRON-3,0 using $Co_{K\alpha}$ radiation. The study included phase identification and specification of the elementary cell parameters based on the random powder X-ray diffractometry data using silicon as an internal standard. Because of crystal metastability at room temperature, a rather high scanning rate of 1cm/min was used.

The following crystal specimens were investigated: small (0,8 – 1 cm in length) crystals of the crystal cluster from St. 26, a single crystal of about 5 cm in length and fragments from different parts of the giant crystal (St. 55). No compositional difference between the specimens has been detected; they all showed the typical reflections of stable ikaite and were accordingly identified as the natural, monoclinic mineral ikaite with a very low degree of replacement by calcite.

The transformation from ikaite to calcite at room temperature over a period of 12 to 24 hours was well documented by XRD on the ikaite sample from station BP00-37 (Kodina et al. 2001). However, some fragments of the crystals were found to be rather stable. After staying at room temperature for one day, some crystal fragments remained intact and X-ray diffractometry showed the typical ikaite structure.

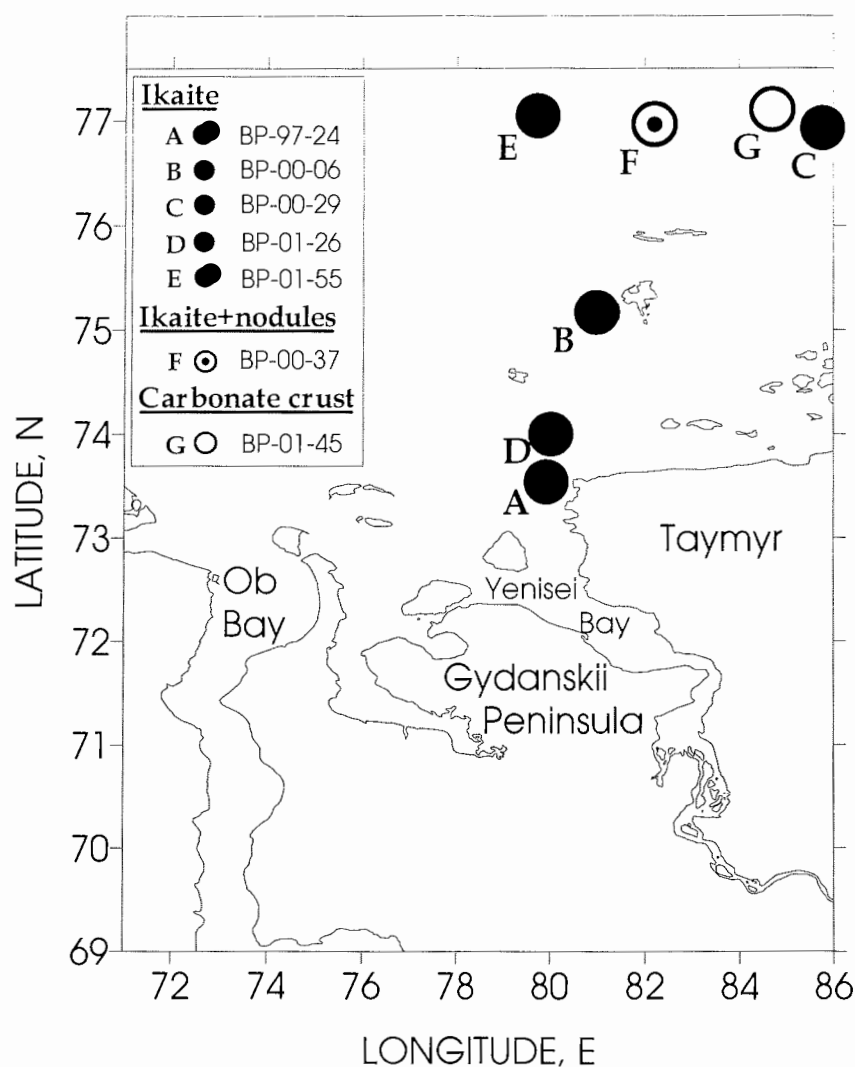


Fig. 7.16. Ikaite sampling stations in the Kara Sea German- Russian expeditions on board R/V "Akademik Boris Petrov", 1997-2001.

Determination of the elementary cell parameters was undertaken to get an additional efficient proof of the mineral nature. The data obtained were the following: $a = 8,85$ (1); $b = 8,25$ (1); $c = 11,0(2)$ Å; $\beta = 110,50(9)$; $V = 7533(1,9)$ Å³. They are similar to the published data (Brown and Dickens 1970; Marland 1975; Schubert et al. 1997) for artificial and natural ikaite minerals.

Carbon isotope composition

Inorganic carbon isotope compositions of the ikaite samples from st. 55 and 26 are different (Table 7.10). This is evidence for different carbon sources, namely sedimentary organic carbon at St. 26 and a partial contribution of methane-derived CO₂ at St. 55.

Table 7.10: Carbon isotope composition of the ikaite crystals

Station	Specimen		$\delta^{13}\text{C}_{\text{‰}}$
BP01-26	Crystal № 1		-24.01
	Crystal №2		-23.82
	Crystal №3		-24.52
	Crystal № 4	Random powder	-23.32
		Rest after sieving	-24.18
BP01-55	Giant crystal	Front pyramid termination	-41.64
		External part	-42.33
		Internal part	-42.26
	Crystal №1		-41.74
	Crystal №2		-42.71
	Crystal №3		-40.94
	Crystal № 4	Random powder	-41.99
		Rest after sieving	-43.01

The stable carbon isotopic composition is variable between different crystals within one station as well as within different parts of the giant crystal. The magnitude of variations may be as large as 1.8‰ between different crystals and about 1‰ for different fragments inside single crystal. Isotopic variations are indicative of a complexity of isotope effects during formation of mineral phase and/or during the initial stage of the ikaite crystal pseudomorphism. Inclusion of organic or inorganic particles of the host sediment into the growing crystal can not be ruled out. Ikaite is generally believed to form near the sediment-water interface, and environmental conditions were favourable for this process (Larsen 1994).

Pore water hydrochemistry

The data on hydrochemistry of pore waters, pH, Eh of sediments and carbon isotope composition of dissolved inorganic carbon (DIC) throughout the sedimentary sequences at St. 55 and St. 26 are presented in Figures 7.18 A+B and 7.19). Both sedimentary sequences are characterized by a reducing regime. At St. 55 the most reduced interval occurs at a core depth of 135-165 cm as seen by the lowest Eh value of -320mV (Fig. 7.18A). St. 26 was found to be less reduced (Fig. 7.19). Development of anaerobic organic matter (OM) diagenesis in sediments with depth was noted by visual core description and a difference between the both cores was revealed.

Fig. 7.18A demonstrates a typical picture of anaerobic diagenetic OM decomposition in sediments, with increasing phosphate and silicate concentrations from the core top towards ~160 cm. Fig. 7.18B shows the distributions of the key parameters of organic matter diagenesis throughout the vertical section at St. 55. Common to earlier descriptions (Kodina et al. 2001), alkalinity increases as sulphate concentration decreases within the core section where ikaite precipitation occurs (135-165 cm). A change in the gradient of increasing alkalinity is notable. It corresponds to a synchronous drop of the $\delta^{13}\text{C}_{\text{DIC}}$ due to the rapidly depleting DIC became constrained by the precipitation of isotopically depleted carbonate mineral ikaite ($\delta^{13}\text{C}$ of about - 42‰). Methane is suggested as an additional

source of carbon dioxide depleted in the ^{13}C -isotope. We have not yet all needed data, however the preliminary data evidence that methane concentrations as high as 11,2 ml/l were present in sediment interval of 200-226cm, sharply decreasing towards the overlying horizons. In other words, we suppose that St. 55 gives a typical example of ikaite precipitation resulting from methane cycle operation coupled with sulphate reduction in a highly reduced sediment (Kodina et al. 2001).

Isotope composition of the ikaite sample from St. 26 (about -24‰) suggests a different geochemical situation in the sediment, resulting from a different lithology and environment of sedimentation. This study is under progress. The vertical profiles for the geochemical parameters presented in Fig. 7.18 and 7.19 have much in common with the wet specific density curves for the corresponding sediment cores and might be an additional useful tool to determine environmental changes in the geological past, including the position of stratigraphic bounding in sedimentary sequences.

Acknowledgements

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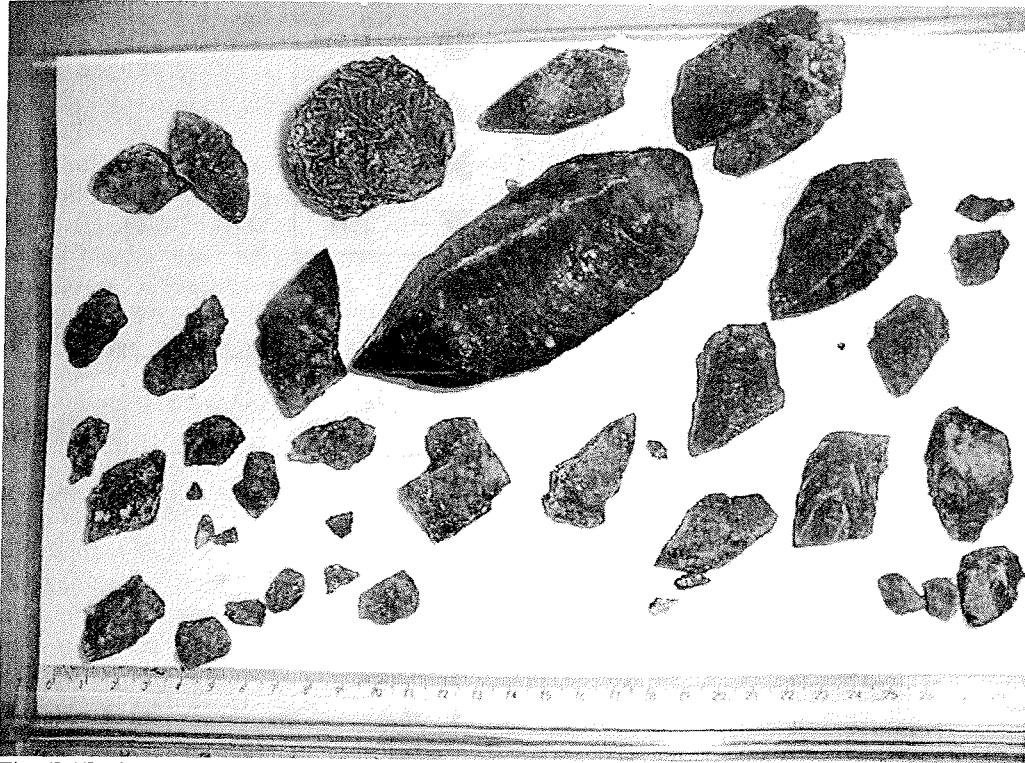


Fig. 7.17. Ikaite crystals from St. 26 (cluster spherical in shape , to the right of the giant crystal), from St. 55- giant crystal centrally positioned, single or doubled pyramidal and small bad-shaped crystals.

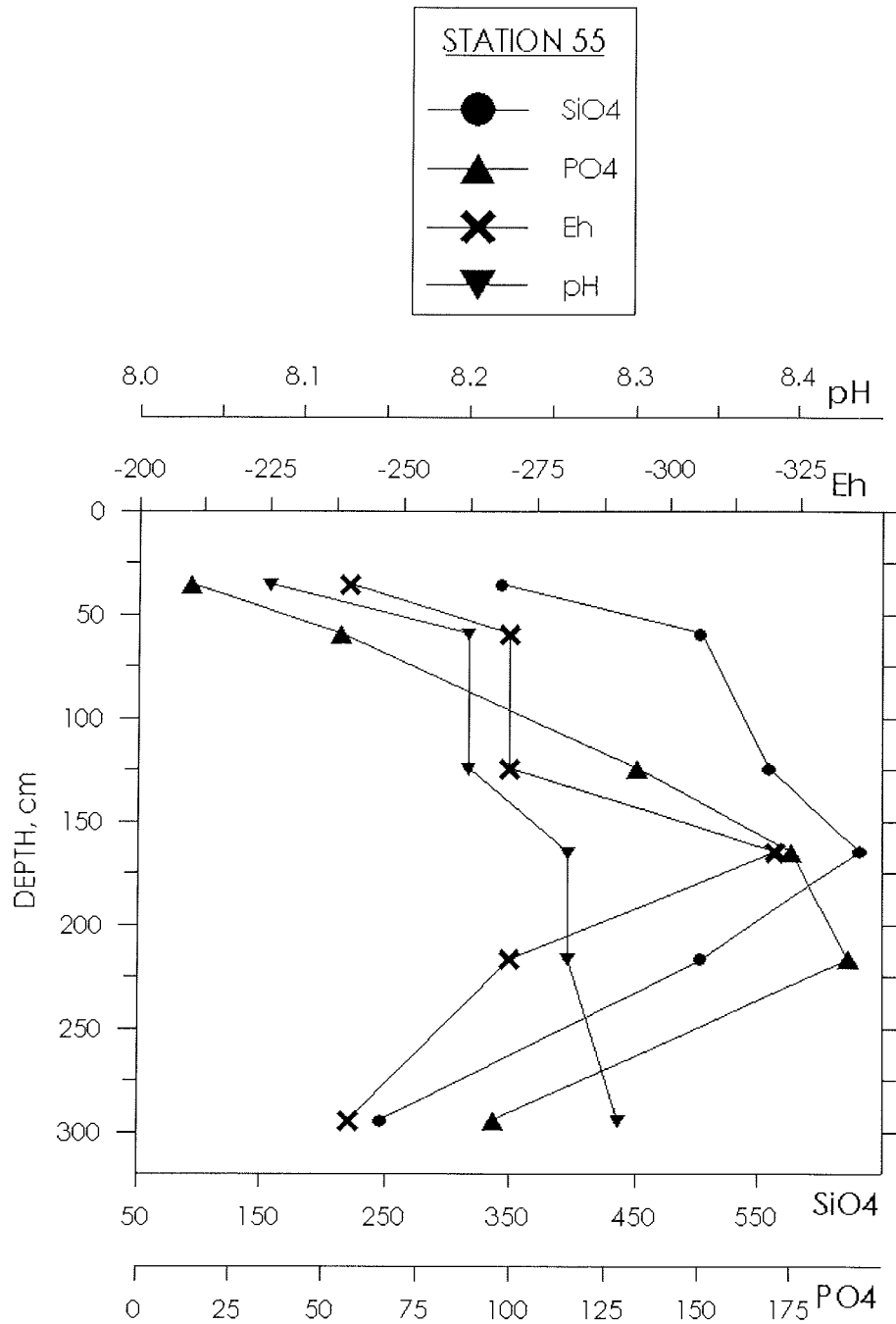


Fig. 7.18A.. Phosphate and silicate concentrations in pore water throughout the sedimentary sequence at St. 55.

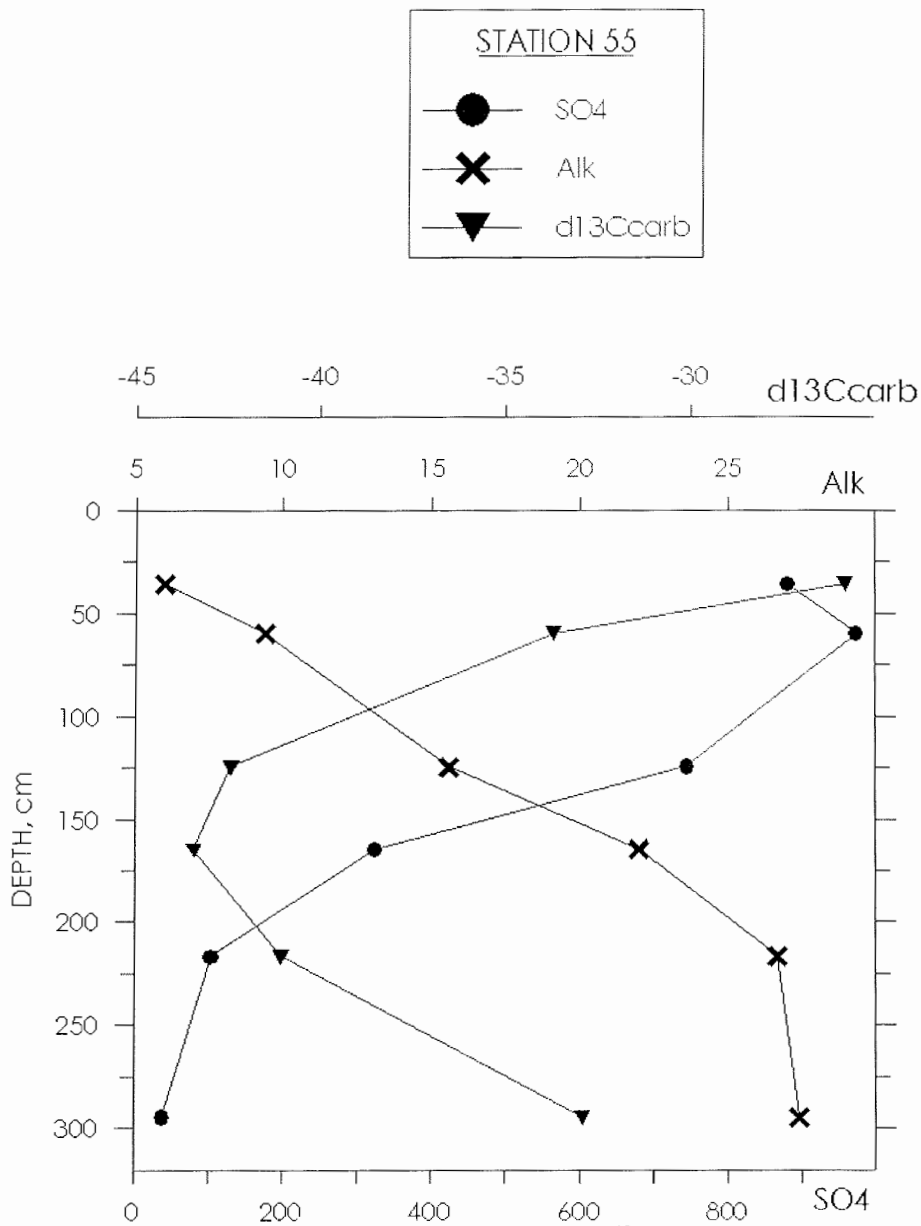


Fig. 7.18B. Alkalinity, sulphate concentration and $\delta^{13}\text{C}_{\text{carb}}$ -values throughout the sedimentary sequence.

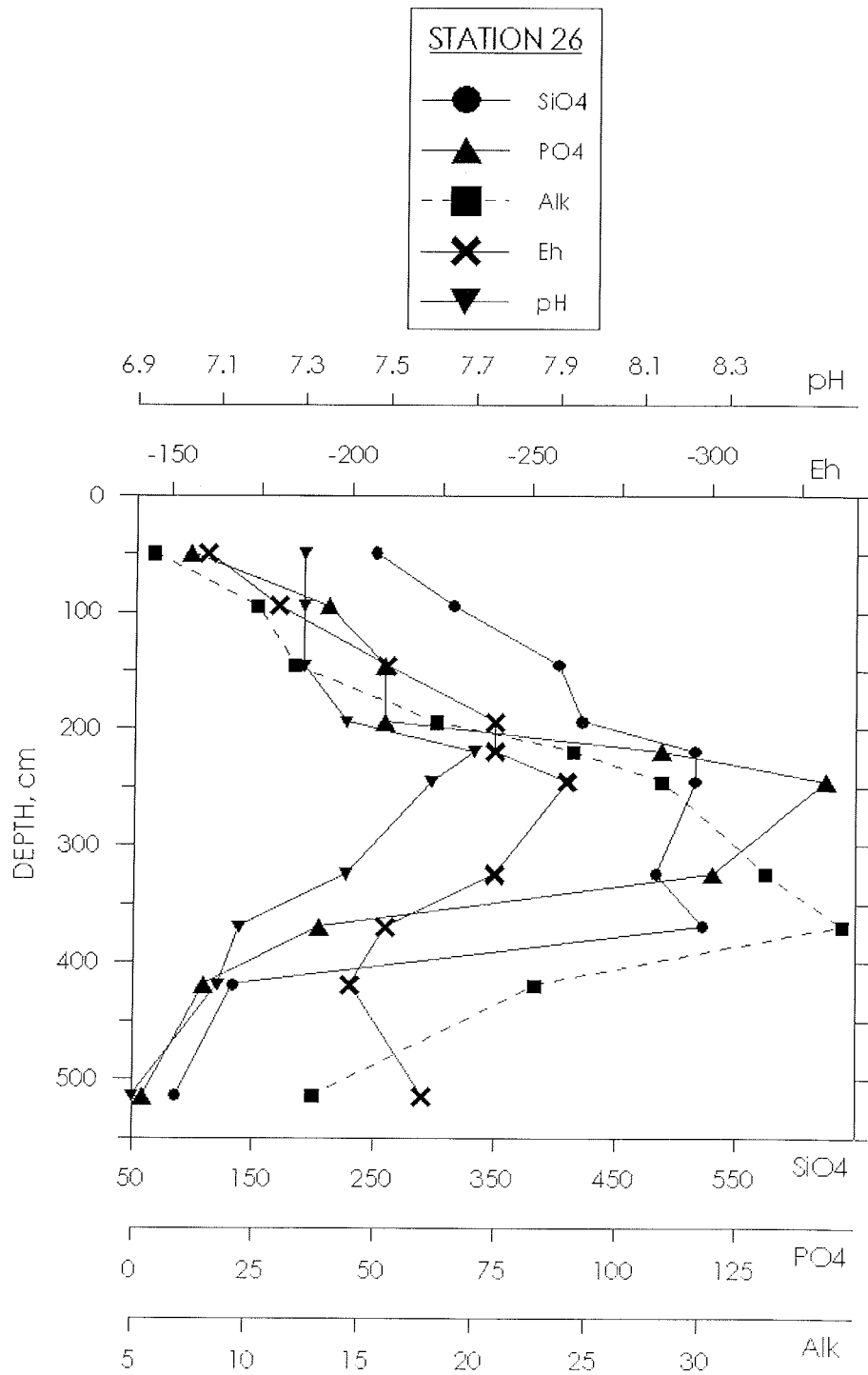


Fig. 7.19. Vertical profiles of Eh, pH and hydrochemical parameters of pore water throughout the sedimentary sequence at St. 26.