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Mn—Fe-CALCITE CONCRETIONS FROM VARVED CLAYS OF ESTONIA AND THE GULF OF FINLAND: THE COMPOSITION AND GROWTH HISTORY

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Abstract. Carbonate concretions from varved ice-lake clays contain mineral calcite with a high content of manganese (3—9 mol %) and iron (2—4 mol %). The stable isotopic composition shows that the concretions grew in fresh-water conditions, during the early Holocene. Complex geological-geochemical data have allowed us to determine that the concretion growth took no more than 500—1000 years. The Mn/Ca molar ratio in sediment water at the growth time, reconstructed from calcite composition, was 0.0006—0.002. The values of $\delta^{18}O$ (PDB) are from −14 to −6‰, those of $\delta^{13}C$ (PDB) are from −18 to −3‰. The value of $\delta^{18}O$ (SMOW) of water at the growth time of concretions was between −17 and −9‰.

Key words: carbonate concretions, stable isotopes, minor elements, Pleistocene, Holocene, Gulf of Finland.

INTRODUCTION

The manganese and iron concentration in sedimentary calcites is ordinarily relatively low. The average content of manganese in carbonate rocks is 0.1%, in carbonate oceanic sediments 0.11% and in Palaeozoic limestones of Estonia 0.09%, rarely exceeding 0.5%. Interesting are therefore finds of manganese- and iron-rich diagenetic calcite concretions in ice-lake clay sediments of Estonia and the Gulf of Finland. The diagenetic environment is often characterized by a low content of oxygen favouring the existence of reduced forms of chemical elements (Barnaby & Rimstidt, 1989; Hendry, 1993). Reduced bivalent forms of iron and manganese have similar ionic radii to calcium ion, thus being capable of replacing calcium in the crystal lattice. The distribution of manganese and iron in concretions reflects environmental conditions during the concretion growth. Good results have been achieved in reconstructing the diagenetic history of rock by using complex minor element and stable isotope investigations (Astin & Scotchman, 1988; Scotchman, 1991). Theoretical models of the concretion growth were worked out by Berner (1968), Raiswell (1988), Wilkinson (1989), Wilkinson and Dampier (1990). Carbonate concretions in varved clays of Estonia have been investigated by Pirrus (Pirrus, 1962, 1966; Пиррус, 1964, 1968; Kiipli & Pirrus, 1986).

Roundish slightly flattened concretions with a size of 1—5 cm have been found at four sites of the southern part of the Gulf of Finland, ranging from 48 to 120 m in the water depth (Fig. 1). All concretions, except one, were found in homogeneous Baltic Ice Lake clays at a depth of 1.7—5.2 m from the sea bottom (Fig. 2). The lenticular structure of clays is very weak and becomes visible in drying clays. One carbonate concretion (site 38-14) was found on the sea bottom among iron—manganese concretions at a depth of 120 m, in the deepest depression of the Gulf of Finland eroded into late-glacial clays by strong bottom currents. Most likely the carbonate concretion was initially formed in sediments and became exposed later.

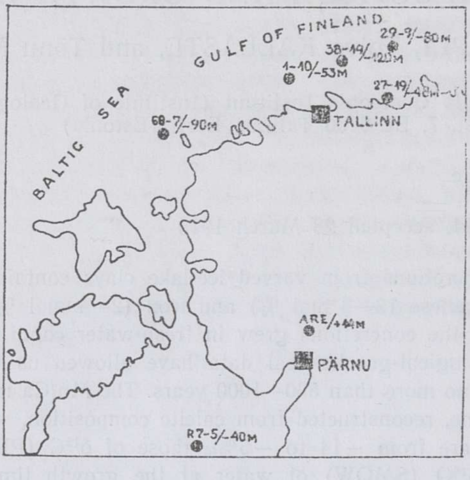


Fig. 1. Sketch map showing the location, number and absolute height of sampling stations.

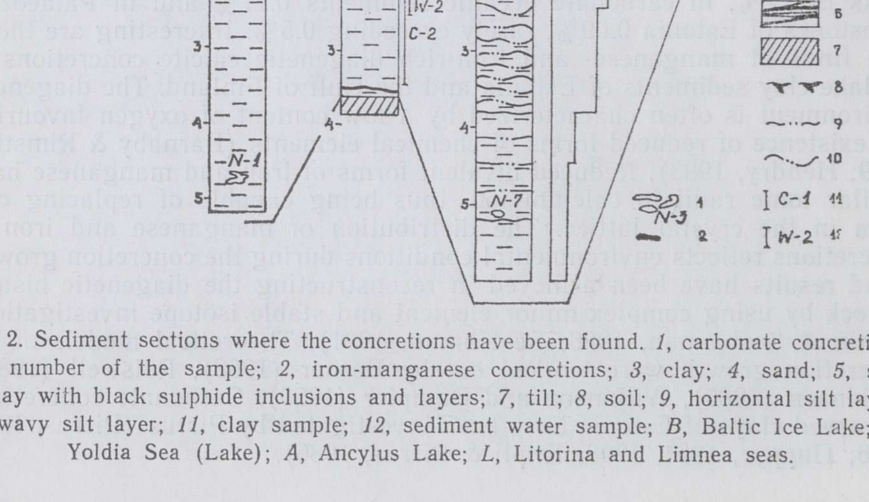
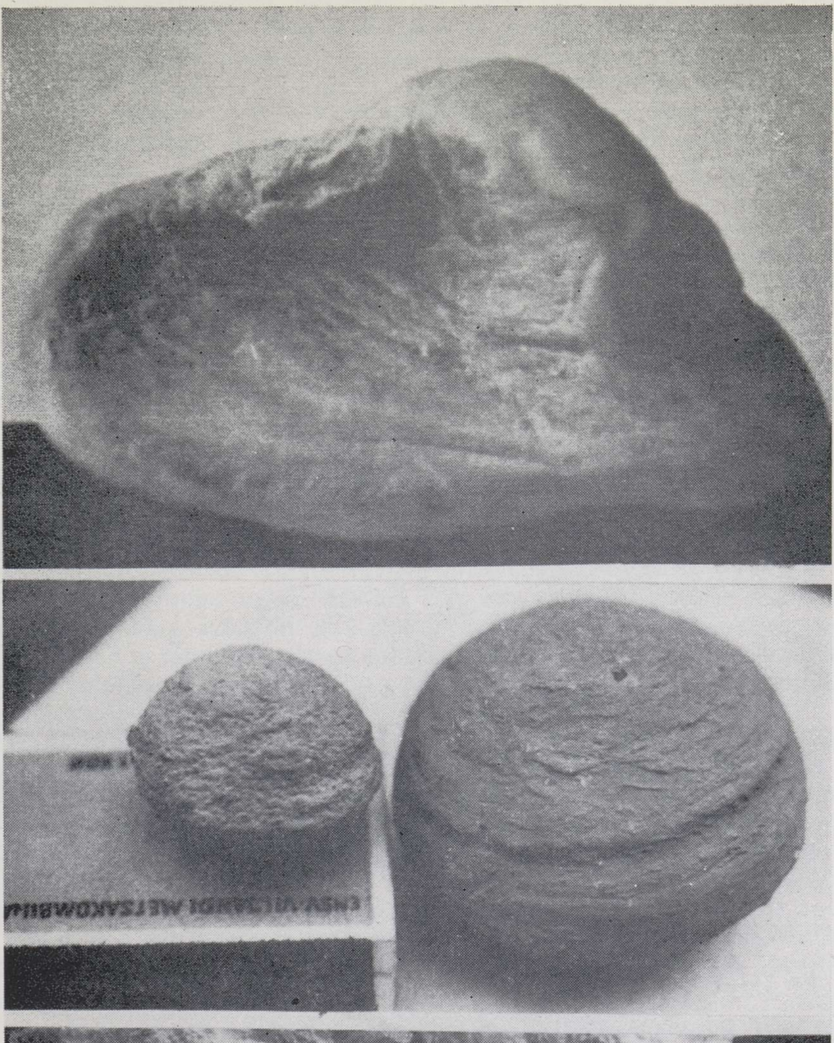


Fig. 2. Sediment sections where the concretions have been found. *1*, carbonate concretions and number of the sample; *2*, iron-manganese concretions; *3*, clay; *4*, sand; *5*, silt; *6*, clay with black sulphide inclusions and layers; *7*, till; *8*, soil; *9*, horizontal silt layer; *10*, wavy silt layer; *11*, clay sample; *12*, sediment water sample; *B*, Baltic Ice Lake; *Y*, Yoldia Sea (Lake); *A*, Ancylus Lake; *L*, Litorina and Limnea seas.



Carbonate concretions from late-glacial clays of the Gulf of Finland. *1*, deformed concretion from site 68-7 (N-1), ×1.7; *2*, concretions from site 1-10 (N-3 and N-2), ×1.2; *3*, surface of concretion N-2, ×100.

One of the concretions, found in the lower part of the slope of Osmussaar Island (site 68-7), is fold-like and evidently deformed (Plate), possibly due to slide processes after rapid sedimentation of clays on the slope. The deformed shape of the concretion seems to prove its early formation as unstable conditions were more characteristic of the time after ice-sheet melting, fast sedimentation and abrupt fall of ice lake water level. This conclusion was questioned by E. Pirrus (pers. comm.) as the growth of the concretion into a previous fold is possible.

Two samples analysed were found in varved clays of western Estonia, not far from Are, in a layer of concretions at a depth of 1.5 m. These concretions are more flattened compared to the marine ones: the diameter is 5—15 cm and thickness approximately 1.5 cm.

Scanning electron microscopic investigations have shown that the size of calcite crystals in the concretions is 1—2 μm. In concretion N-2 no distinct crystals could be seen near the surface, evidently they are smaller there than in the central part.

CRYSTALLOGRAPHY AND CHEMISTRY

X-ray diffractometric measurements have revealed crystallographic parameters unusual for calcite (Table 1). Reflection 104 is displaced compared to the common value (3.0355 Å). Therefore it is clear that calcite is actually a solid solution and the crystal lattice contains other components beside Ca. Crystallinity of calcite was low in all samples. Asymmetry of the crystallographic reflection proves nonhomogeneous distribution of minor elements in samples (Fig. 3).

The chemical composition of concretions shows (Table 1) three elements possibly inserted in the calcite structure: *Mn*, Fe, and *Mg*. All these have smaller ions than Ca and the substitution of any of them deforms the calcite structure in the same direction. The comparison of the *Mn* content of varved clays and carbonate concretions (0.07% and 1—4%) has revealed an unusually high *Mn* concentration in concretions. Therefore most of *Mn* is likely to occur in carbonate form. In the case of Fe and *Mg* this is not so clear, because their concentrations both in the concretion and in the surrounding sediment are similar and very common for varved clays.

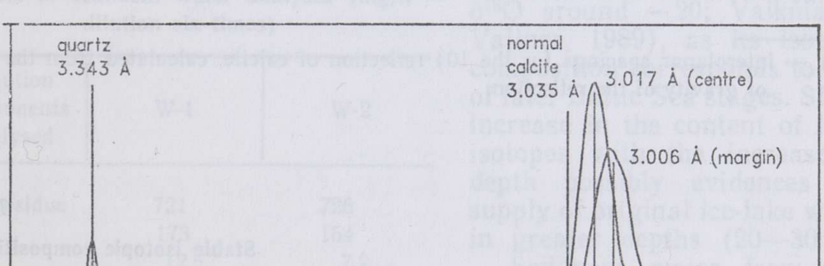


Fig. 3. X-ray diffraction patterns of two samples — from the centre and surface of concretion N-2, showing the shift of the 104 reflection of calcite caused by the substitution of *Mn* and Fe for Ca.

Table 1

Analytical data of investigated samples

Parameter analysed	N-1	N-2	N-3	N-4	N-5
		X-ray fluorescence analyses, %			
CaO	36.2	30.1	32	30.7	28.9
MnO	1.3	3.9	3.2	1.1	1.4
Fe_2O_3	2.6	3.3	2.7	3.4	3.6
SiO_2	20	21	19	26	25
Al_2O_3	5.5	6.1	5.1	6.7	5.7
Sr	0.009	0.012	0.013	0.012	0.012
Cl	0.045	0.05	0.063	0.032	0.032
S	0.042	0.015	0.027	0.067	0.059
		Chemical analyses 0.2 n HCl, %			
CaO	32.1	30.4	30	27.4	27.7
MnO	1.46	3.76	3.69	1.30	1.47
MgO	2.6	3.0	3.4	2.2	1.6
Insoluble residue	28.7	27.7	28.6	36.8	30.6
CO_2	28.6	27.1	26.7	25.0	23.9
		Atomic absorption analyses, %			
MnO	1.5	4.2	4.1	1.3	1.5
		X-ray diffractometry			
d (Å) average	3.024	3.008	3.010	3.022	3.018
d (Å) centre	3.025	3.017			
d (Å) surface	3.026	3.006			
		Stable isotopes			
$\delta^{13}C$ ‰	−18.1	−4.7	−4.2	−14.2	−13.5
$\delta^{18}O$ ‰	−13.9	−10.0	−10.2	−12.4	−12.2

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d (Å) — interplanar spacings for the 104 reflection of calcite, calculated from the centre of gravity of the reflection.

Table 2

Calculated calcite formulas

Sample	$CaCO_3$, mol %	$MnCO_3$, mol %	$FeCO_3$, mol %
N-1	95	3	2
N-2	87	9	4
N-3	88	9	3
N-4	94	3	3
N-5	92	4	4

Table 3

Stable isotopic composition of varved clay sediment waters, Gulf of Riga

Depth, m	$\delta^{18}O$ ‰, SMOW
0.1—0.2	−7.6
0.6—0.7	−8.2
1.3—1.4	−8.4
1.9—2.0	−8.7
2.5—2.6	−8.9
3.0—3.1	−9.4

Valuable information is obtained from microprobe analyses of the minor element distribution in concretions. There is a good correlation (coefficient +0.95) between *Mg* and Al, therefore most probably *Mg* is in the silicate phase. *Mn* and Fe are showing positive correlation with Ca (coefficients +0.59 and +0.84). The correlation is not strong and it is caused by uneven distribution of *Mn* and Fe in the carbonate phase.

As a result, formulas of calcite are calculated (Table 2). All of *Mn* is calculated to be in the calcite structure. X-ray diffractometric data show that more minor element than actually measured *Mn* is needed to cause the structure deformation recorded. Therefore a certain portion of Fe is calculated to be in the calcite structure.

POROSITY

The calculated from the measured density (2.57 g/cm^3) porosity in concretions N-2 and N-3 is 7% (Kiipli & Pirrus, 1986). The porosity of the Baltic Sea sediments, estimated on the basis of the water content, is 86% near the sediment surface and 64% at a depth of 9 m. The porosity of sediments at the time of the concretion growth can be estimated on the basis of the carbonate content in concretions (Raiswell, 1971; Dix & Mullins, 1987). The carbonate content is 63% in N-2 and 66% in N-1. Adding porosity 7%, we can conclude that the average sediment porosity at the growth time was 70—73%.

SEDIMENT WATERS

To determine the influence of diffusion from an open body of water into sediments, the stable isotopic composition of sediment waters from varved clays in the Gulf of Riga was analysed. Samples were taken from 3.1 m of core R7-5. The depth of the sea was 40 m. The sediment water was pressed out during 30 min, rising the pressure gradually up to 15 *M*Pa. The oxygen isotopic composition in water was measured (Table 3).

Table 4

Results of sediment water analyses (mg/l, dilution six times)

Solution components analysed	W-1	W-2
Dried residue	721	726
Na^+	173	154
K^+	12.5	7.2
NH_4^+	6	9.9
Ca^{2+}	13.4	23.7
Mg^{2+}	10	6.9
Cl^-	361	353
SO_4^{2-}	63.4	54.3
NO_3^-		1.3
NO_2^-	0.4	0.17
HCO_3^-	54.9	73.2
pH	7.4	7.75

As is seen from the results, the sediment water is not the original ice-lake water (having $\delta^{18}O$ around −20; Vaikmäe & Vallner, 1989), as its isotopic composition corresponds to that of later Baltic Sea stages. Slight increase in the content of light isotopes with the increase in depth possibly evidences the supply of original ice-lake water in greater depths (20—30 m).

Sediment water from core 1-10 (Fig. 1, Table 4) was separated by mixing 350 g of sediment with 750 g of distilled water. After the sedimentation of solid particles, the main solution components were analysed. The high sodium and chlorine content evidences that this sediment water is not the original Baltic Ice Lake water, but is modified by the diffusion of ions from seawater. The depth of the diffusion of sodium and chlorine into the sediments in the Baltic Sea is estimated to be 20 m (Шишкина et al., 1981).

From these data we can conclude that at a depth of a few metres concretions grew in an open or partly open system connected with a body of water by diffusion.

STABLE ISOTOPES

Carbon and oxygen isotopes were measured in average samples (Table 1) and profiles through concretions N-2 and N-5 (Table 5, Fig. 4). Measurements were done on Finnigan MAT "Delta E" mass spectrometer in carbon dioxide obtained by the decomposition of samples in 100% orthophosphoric acid at 50 °C. The results are given as a difference from the standard in parts per thousand (‰). For carbonate material the Peedee Belemnite (PDB) standard was used. The isotopic composition of water is presented relative to standard mean ocean water (SMOW). The difference between the PDB and SMOW scales is approximately 30‰ (details see in Фейцер, 1987).

A. Oxygen. The oxygen isotopic composition of carbonate minerals is mainly controlled by the isotopic composition and temperature of the crystallization environment water. The characteristic values of $\delta^{18}O$ are from —5 to —7(—9)‰ (SMOW) for the Baltic Sea water (Punning et al., 1988), —10.4‰ for annual average atmospheric precipitation in Estonia, from (—5)—8 to —10‰ for lakes and from —20 to —25‰ for continental ice-sheet meltwater of the last deglaciation (Tullborg & Larson, 1984; Vaikmäe & Vallner, 1989).

In the investigated samples of carbonate concretions the oxygen stable isotopic composition is highly variable, ranging from —6 to —14‰ (PDB). All variations were caused by the changes in the water composition, because the temperature was constant and close to +4 °C in sediments of a deep body of water. Therefore, to reconstruct the concretion growth environment, we must consider a constant temperature fractionation value. According to Veizer (Фейцер, 1987, fig. 5), the $\delta^{18}O$ of the calcite crystallization water environment (SMOW) at +4 °C can be derived from $\delta^{18}O$ of calcite (PDB) by adding approximately —3‰.

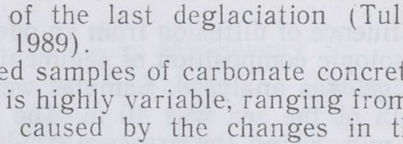

Fig. 4. Investigated profiles across concretion N-2. There is a feldspar fragment near the concretion centre. Dashed lines are showing growth stages suggested on the basis of stable isotopic data. *A*, *B*, *C*, *D*, profiles.

Table 5

Stable isotope profiles

Profile direction	Distance from margin, mm	δ13C, ‰ (PDB)	δ18O, ‰ (PDB)
	Concretion N-2		
vertical	0—2 margin	−3.7	−6.7
(*A* Fig. 3)	2—4	−3.5	−8.6
	3—5	−4.7	−10.0
	5—7	−5.6	−11.1
	7—9	−6.9	−11.7
	9—11	−7.6	−12.1
	11—13	−7.9	−12.4
	13—15 centre	−8.4	−11.9
horizontal	1—3 margin	−4.6	−6.4
(*C* Fig. 3)	5—7	−3.5	−9.0
	13—15 centre	−6.4	−11.5
diagonal	0—0.5 surface	−11.6	−5.9
(*D* Fig. 3)	1—3 margin	−8.7	−5.8
	6—8	−3.1	−7.0
	11—13	−3.6	−9.3
	16—18 centre	−5.8	−11.2
	Concretion N-5		
horizontal	2—4 margin	−14.2	−12.0
	6—8	−13.9	−12.2
	10—12	−14.5	−12.5
	14—16	−15.0	−12.6
	18—20	−15.2	−12.7
	22—24	−15.2	−12.8
	26—28	−15.0	−12.8
	30—32	−14.7	−12.2
	34—36	−14.0	−12.3
	42—44	−15.0	−12.8
	Concretion N-1		
near the	1—4 outer	−18.2	−14.3
deformed	6—8 centre	−17.1	−14.1
centre	9—11 inner	−16.5	−14.1

The $\delta^{18}O$ value is lowest (—14‰) in concretion N-1 (near Osmussaar). Therefore $\delta^{18}O$ of the mineral precipitation environment was about —17‰ (SMOW), being close to the ice-sheet meltwater value (<—20‰). Evidently, at the time of the concretion formation the continental ice sheet was not far and meltwater controlled the main isotopic composition. Therefore oxygen isotopes confirm the early formation of the concretion, which is concluded from its deformed shape. Although the concretions from Are (N-4, N-5) have small variations in $\delta^{18}O$, the values increase from centre (—12.9‰) to margin (—12‰). At the time of the concretion growth the sediment water had $\delta^{18}O$ values from —15 to —16‰. These values evidence smaller influence of glacier meltwater than in the case of concretion N-1. Obviously these concretions formed later. On the other hand, the growth of these concretions took place before the Ancylus Lake maximum transgression time, with the water oxygen isotopic composition ranging from —13 to —10‰ (Punning et al., 1988).

The value of $\delta^{18}O$ is approximately the same in the central part of concretion N-2 from the slope of Naissaar Island changing considerably from centre (–12‰) to margin (–6‰) (Fig. 5). Therefore at the concretion growth time, water had $\delta^{18}O$ values from –15 to –9‰, which corresponds to Ancylus Lake waters. The inflow of large amounts of ocean water into the Baltic basin took place at the beginning of the Litorina Sea time. The isotopic composition of the Litorina Sea water, derived from the oxygen isotopic composition of mollusc shells, was from —5 to —6‰ (Punning et al., 1988). The isotopic composition of water, where the outer layers of concretion N-2 grew, was —9‰ (—6‰ added —3$^{0}/_{00}$). Thus the concretion growth finished before the Litorina Sea time. The evolution of the isotopic composition from centre to margin can be explained by gradual replacement of glacier meltwater with water from atmospheric precipitation. Small influence of ocean waters was possible, but there is no evidence for it.

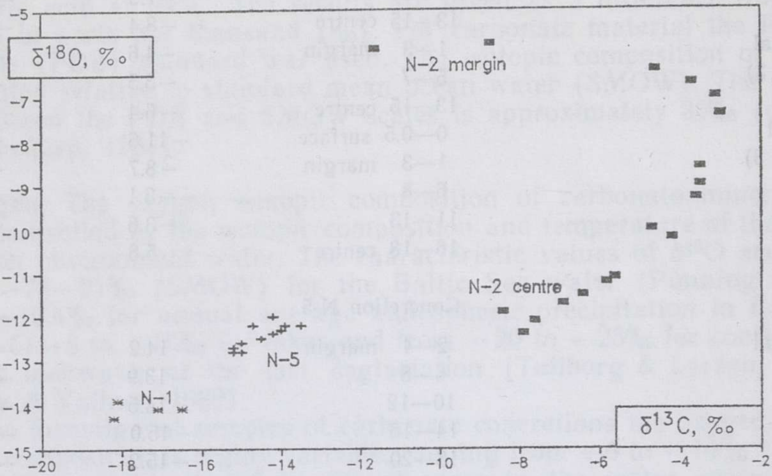

Fig. 5. Stable isotope ratios in investigated samples.

B. Carbon. The carbon isotopic composition in carbonate minerals is controlled by the carbon isotopic composition of HCO_3^- of the precipitation environment. HCO_3^- of ocean water, being in equilibrium with atmospheric CO_2, has $\delta^{13}C$ values near zero (PDB) — from +2 to —2‰. The same values were recorded for marine limestones. Organic matter and CO_2, produced from the decomposition of organic matter, have negative values about —25‰. Bacterial decomposition of organic matter in oxygen deficiency conditions, resulting in methane generation, produces residual CO_2 with positive $\delta^{13}C$ values (Фейцер, 1987).

In the investigated samples $\delta^{13}C$ varies widely from —3.1 to —18‰. Early stages of the concretion growth are characterized by negative $\delta^{13}C$ values ranging from —18 to —8‰. Different growth sites have different $\delta^{13}C$ levels: at Osmussaar from —16 to —18‰, at Are from —14 to –16‰ and at Naissaar from –3 to —8.4‰. The reason of these negative values in the varved clay sediment water is problematic, because there is no other source for so light carbon than decomposition of organic matter, but the content of organic matter in varved clays is very low. Therefore the negative $\delta^{13}C$ values could have two possible explanations: firstly, the water, originated from ice melting, contains very little carbon dioxide and the decomposition of the varved clay organic matter was able to change the averace $\delta^{13}C$; secondly, CO_2 generated from organic matter penetrated into varved clays from near-bottom water.

During the growth of concretion N-2 from the slope of Naissaar Island, $\delta^{13}C$ changes greatly from -8.4 to $-3.1‰$. Such an evolution from lighter carbon to heavier during growth is characteristic of many concretions (Dix & Mullins, 1987; Astin & Scotchman, 1988), but the cause of this is not very clear. The main explanation could be the evolving diagenetic environment. In the outer few millimetres of concretion N-2, especially on the surface, there is new depletion of $\delta^{13}C$ down to $-11.6‰$. Evidently the decomposition of large amounts of organic matter created CO_2 with light carbon. Supposedly the climate became warmer and favoured the life of planktonic organisms in the surface layer of the body of water producing a lot of organic matter. Decomposition of organic matter in younger sediments produced much of CO_2 that probably penetrated downward by diffusion, caused the lowering of pH and made calcite precipitation impossible. The concretion growth ended.

Mn AND Fe DISTRIBUTION IN CONCRETIONS

The internal distribution of Mn and Fe in the concretions was investigated by energy-dispersive LINK microanalyser combined with TESLA electron microscope and ROBOTRON computer. The measuring, fitting with chemical element standards, and calculation of integral intensities were performed by the software created by P. Rummi.

The distribution of Mn and Fe in concretions N-2 and N-5 (Fig. 6) shows a twofold increase in their concentration from centre to surface. The concentration of Fe is similar in both concretions, but the Mn concentration is clearly higher in N-2.

The content of minor elements in calcite depends on their concentration in the precipitation environment and on the distribution coefficient between solid and liquid phases. The distribution coefficient depends mainly on the precipitation rate (Lorens, 1981; Dromgoole & Walter, 1990a). In the first paper the Mn distribution coefficients are from 5 to 50, the other work gives Mn coefficients from 3.8 to 16 and Fe coefficients from 1.9 to 3.7. Higher values characterize lower rates (in near-equilibrium solutions). Calcite favours incorporation of both elements (distribution coefficients exceed 1).

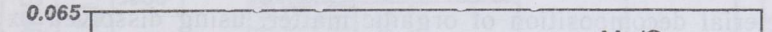

Fig. 6. Mn and Fe distribution in vertical profile across concretion N-2 (profiles *A* and *B* in Fig. 4).

There are two possible explanations for the growth of Mn and Fe concentrations from concretion centre to margin: firstly, the growth of Mn and Fe concentrations in the precipitation environment due to the lowering of EH and pH; secondly, the lowering of the precipitation rate at a late growth stage due to equilibration of the precipitation environment. It should be mentioned that Mn inhibits calcite growth (Dromgoole & Walter, 1990b) amplifying both effects. In reality all these factors may act at the same time.

RECONSTRUCTION OF THE SEDIMENT WATER COMPOSITION AT THE GROWTH TIME

Supposing that calcite has a slow precipitation rate during the concretion growth, we can use the maximum distribution coefficient (*D*) values to calculate element ratios in the sediment water at the growth time. The maximum *D* value for Mn/Ca between the solution and calcite is 50 (Lorens, 1981). The calculations show that the Mn/Ca molar ratio in sediment water at the growth time of concretion N-2 was 0.002, in the case of concretions N-1 and N-5 it was 0.0006—0.0008. For comparison: in the bottom of the Gotland Depression the molar ratio of dissolved Mn and Ca is 0.0009, in the Baltic Sea surface water it is 0.00004 (combined from the data in Черновская et al., 1965; Лисицын & Емельянов, 1981), and in the ocean water 0.000003.

The solubility of manganese depends on EH conditions. A high Mn/Ca ratio characterizes low EH conditions. In the bottom sediments of the Baltic Sea there are two stratigraphical levels with layers of black sulphide clay, indicating low EH conditions in deep water. The first level appears in Late Preboreal and the second in Late Boreal sediments. Basing on stable isotopic data and Mn/Ca ratio, we can correlate the outer layers of concretion N-2 with Late Boreal sulphide clays.

CONCRETION GROWTH MODEL

Bacterial decomposition of organic matter, using dissolved oxygen or oxygen from sulphates in the upper layer of sediments, creates HCO_3^-, lowers pH and favours dissolution of terrigenous calcite. This process was established in numerous sites in the Atlantic Ocean (Sayles, 1979). The problem is a low content of organic matter in the clays of the Baltic Ice Lake. Organic matter concentration after sedimentation was undoubtedly higher and it would have been lowered during diagenesis by bacterial and abiotic decay.

At a depth of 1.5—5 m, ice-lake sediments contain no free oxygen or sulphates for bacterial metabolism, therefore bacteria use oxygen from iron and manganese oxides. This process generates much OH^- and favours calcite precipitation (Hendry, 1993). Iron and manganese are transferred to a bivalent form and are then able to co-precipitate with calcite.

The concentration gradient between upper and lower sediments forces dissolved $Ca(HCO_3)_2$ to move into deeper layers and precipitate when saturation is achieved. Concretions formed in the conditions of the geochemical barrier stayed on the same level for a relatively long time, therefore disruption in sedimentation was needed.

The process ends when the supply of organic matter is consumed or the geochemical barrier is displaced. Then we must search for a hiatus in the sediment section to determine the time and duration of the concretion growth.

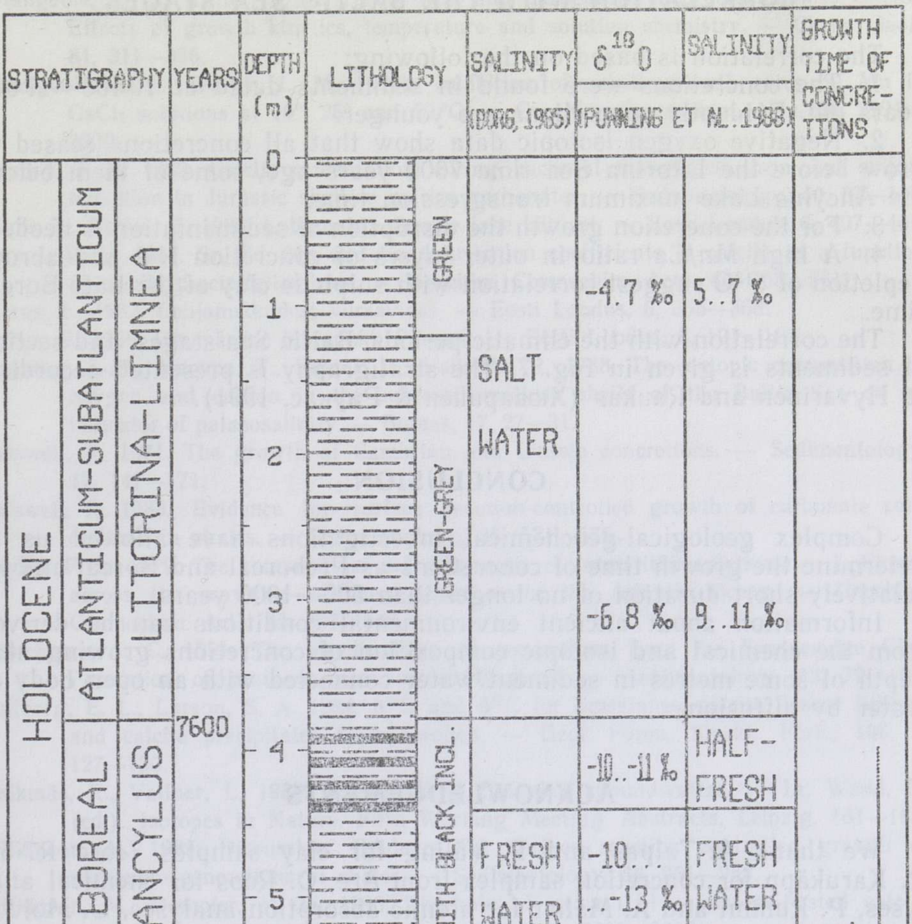

Fig. 7. Correlation of the concretion growth with the history of the Baltic Sea. The oxygen isotopic composition of Baltic Ice Lake water is given according to Tullborg & Larson (1984) and Vaikmäe & Vallner (1989). Lithological legend see Fig. 2.

CORRELATION WITH THE BALTIC SEA STAGES

The correlation is based on the following:

1. The concretions were found in sediments dated at 10 400—11 000 years old. Evidently concretions are younger.
2. Negative oxygen isotopic data show that all concretions ceased to grow before the Litorina Sea time 7600 years ago, some of them before the Ancylus Lake maximum transgression time.
3. For the concretion growth the disruption of sedimentation is needed.
4. A high Mn/Ca ratio in outer layers of concretion N-2 and abrupt depletion of $\delta^{13}C$ suggest correlation with sulphide clay of the Late Boreal time.

The correlation with the climatic periods, Baltic Sea stages, and section of sediments is given in Fig. 7. The stratigraphy is presented according to Hyvarinen and Raukas (Хюваринен & Раукас, 1991).

CONCLUSION

Complex geological-geochemical investigations have allowed us to determine the growth time of concretions as Preboreal and Boreal and its relatively short duration of no longer than 500—1000 years.

Information about ancient environmental conditions can be derived from the chemical and isotopic composition of concretions growing at a depth of some metres in sediment water connected with an open body of water by diffusion.

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Mn—Fe-KALTSIITSED KONKRETSIOONID EESTI JA SOOME LAHE VIIRSAVIDEST: KOOSTIS JA KASV

Tarmo KIIPLI, Toivo KALLASTE, Tõnu MARTMA

Karbonaatsed konkretsioonid (lubjanukud) koosnevad suure mangaani- (3—9 mol %) ja rauasisaldusega (2—4 mol %) kaltsiidist. Hapniku ja süsiniku stabiilsed isotoobid kaltsiidis tõendavad konkretsioonide kasvu varases holotseenis magevee tingimustes. Kompleksed geoloogilis-geokeemilised andmed võimaldasid määrata kasvu lühikese kestuse (mitte üle 500—1000 aasta). Kaltsiidi koostisest tuletatud Mn/Ca molaarsuhe kasvuaja settevees on 0,0006—0,002. $\delta^{18}O$ konkretsioonide kaltsiidis on −14 kuni −6‰ (PDB), $\delta^{13}C$ väärtus on −18 kuni −3‰ (PDB). $\delta^{18}O$ konkretsioonide kasvuaegses settevees oli −17 kuni −9‰ (SMOW).

Mn—Fe-КАЛЬЦИТОВЫЕ КОНКРЕЦИИ В ЛЕНТОЧНЫХ ГЛИНАХ ЭСТОНИИ И ФИНСКОГО ЗАЛИВА: СОСТАВ И ИСТОРИЯ ОБРАЗОВАНИЯ

Тармо КИЙПЛИ, Тойво КАЛЛАСТЕ, Тыну МАРТМА

Карбонатные конкреции состоят из кальцита с высоким содержанием марганца (3—9 мол. %) и железа (2—4 мол. %). Стабильные изотопы кислорода и углерода указывают на формирование конкреций в пресноводных условиях раннего голоцена, причем, согласно геолого-геохимическим данным, их рост был кратковременным (не более 500—1000 лет). Во время роста конкреций молярное соотношение марганца и кальция в поровых водах ленточных глин (вычисленное по составу кальцита) было 0,0006—0,002, $\delta^{18}O$ воды составляло от —17 до —9‰ (SMOW), $\delta^{18}O$ кальцита определено от —14 до —6‰ (PDB), $\delta^{13}C$ кальцита — от —18 до —3‰ (PDB).