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The kaolinite/chlorite clay mineral ratio in surface sediments of the southern Baltic Sea as an indicator for long distance transport of fine-grained material

Thomas Leipe, Franz Xaver Gingele

The ratio of kaolinite to chlorite in the clay mineral fraction of surface sediments (0-2 cm) of the Baltic Sea and of the transition area to the North Sea was used to describe the pathways of the material from the sources to the sinks. The spatial gradient of this ratio reflects a mixing (dilution) row of a two end-member system, which is mainly caused by sediment resuspension, and lateral transport processes from the coastal zone (incl. river estuaries) and gateways (Danish straits) towards the depositional basins of the Baltic Sea. The loads of major rivers of the southern and eastern catchments of the Baltic can be traced, as well as the import of material from the North Sea via the Kattegat and Belt Sea, to the different basins of the Baltic Sea. The knowledge about these pathways is relevant to a number of related problems as the transport of particle bound nutrients and pollutants, the explanation of sedimentation (accumulation) rates in the basins and probably for the reconstruction of historical (climatic) changes in the past.

☐ Baltic Sea, recent sediments, clay minerals, kaolinite, chlorite, pathways, rivers, North Sea.

☐ *Thomas Leipe [thomas.leipe@io-warnemuende.de], Institute of Baltic Sea Research, Seestrasse 15, D-18119 Warnemünde, Germany.*

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INTRODUCTION

Recent sedimentation in the Baltic Sea is mainly determined by the basement topography, the delivery of material from rivers, coastal and submarine erosion of old sediments, plankton production, and by the hydrography (waves and currents) as the driving forces of sediment transport. Thus, the spatial distribution of the bottom sediment types reflects the temporal integration (average) of the various environmental influences. Finally, the fine-grained and light material (silt, clay, organic matter) will be deposited under low energy conditions, which are present in larger extension in the major basins of the Baltic Sea. This context is well known and can be confirmed by a look at the available sediment maps of the Baltic Sea (e.g. Ignatius et al. 1981; Nielsen 1992; Emelyanov et al. 1994; Repečka & Cato 1998). Detailed studies of material transport from the nearshore to the basinal environment in the southern Baltic Sea were published by Christiansen et al. (2002) and Emeis et al. (2002). But still, it is an important and interesting question from where to where and how far the material actually can be transported. Clay minerals and other "stable markers" (isotopes, biomarkers) can help to solve such problems and there are a few examples in the literature for reconstruction of origin or pathways of material in Baltic Sea sediments (Voss & Struck 1997; Voss et al. 2000; Schulz et al. 2000; Miltner & Emeis 2000, 2001).

The publications by Zöllmer & Irion (1993, 1996) and Irion & Zöllmer (1999) for the North Sea and our own results about kaolinite/chlorite ratios in sediments from the western Baltic Sea/Oder river estuary (Gingele & Leipe 1997) and later on from the North Sea-Baltic Sea transition area (Gingele & Leipe 2001) showed already that this parameter is a suitable tool for identification of transport pathways. In the meantime, we extended and completed our study towards the central and eastern parts of the Baltic Sea and now we are able to present and discuss a large scale overview of the results.

STUDY AREA

The investigated area reaches from the eastern part of the Skagerrak in the west, throughout the Kattegat, Belt Sea, western and central Baltic Sea, to the Gulf of Finland in the east. The Gulf of Riga is represented only by a few stations and a lack of stations has to be stated for the northern Baltic (Gulf of Bothnia) and for an area off the Lithuanian and Latvian coasts. In the future, we intend to obtain and to investigate material from these areas as well. The presented results are based on data from more than 400 stations with the highest density in the area of the western Baltic Sea (Mecklenurg Bay, Arkona Basin, Pomeranian Bay). Between 1995 and 2000 several cruises, mainly with r.v. "Prof. A. Penck", were carried out to obtain these samples.

MATERIAL AND METHODS

Sediment samples were obtained with help of a 15x15 cm box-corer, normally 2-3 holes per station. Only the surface (0-2 cm) of the sediment was removed, homogenized and freeze-dried. The dry sediment samples were treated with 10% hydrogen peroxide solution and 10% acetic acid for disaggregation and removal of organic carbon and carbonate. The <2µm fraction was separated by repeated centrifugation. XRD measurements were performed on a Philips PW 1830 device using CoK? radiation and scans were run over the preferentially oriented clay sample preparations. For separation of the 3.54 Å / 3.57 Å chlorite/kaolinite doublets a slow scan with a step size of 0.005° was run between 28° and 30.5° 2?. More details of sample preparation, analyses, and spectra evaluation are described by Petschik et al. (1996) and Gingele & Leipe (1997).

RESULTS AND DISCUSSION

The kaolinite/chlorite ratios of the surface sediment samples of the investigated area are displayed as filled circles in a graded colour scale from 0.5 to 1.4 in steps of 0.3 from green to red (Fig. 1). Red means kaolinite dominates and green chlorite dominates this ratio in the clay fraction of the sediments. Before going into more details we want to point out that the general distribution pattern of this ratio is remarkably regular or smooth in the gradients. It means that we have nearly no crude outliers or inexplicably high spatial variations within the sub-areas. This is an important point, because local kaolinite sources inside the

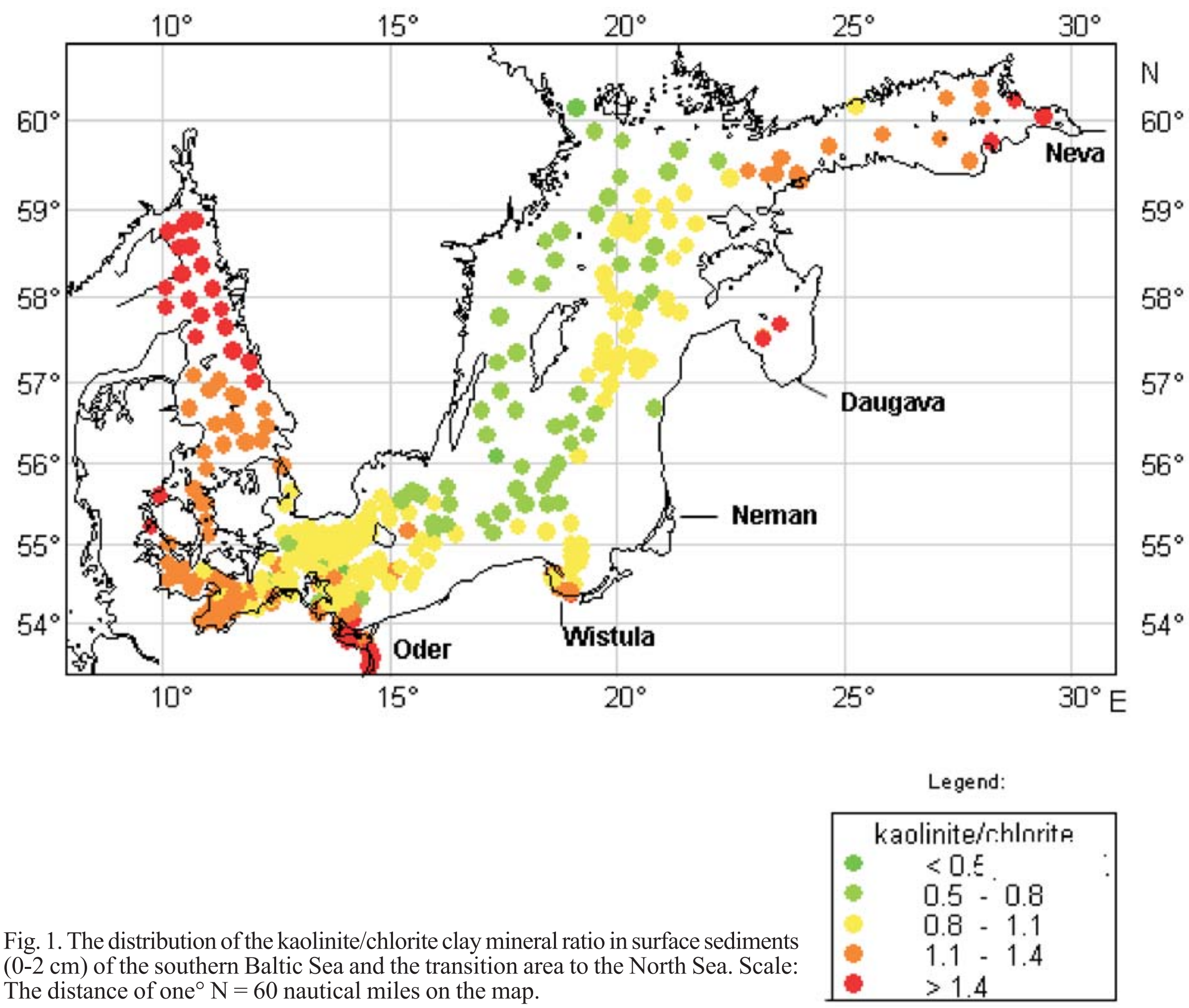

Fig. 1. The distribution of the kaolinite/chlorite clay mineral ratio in surface sediments (0-2 cm) of the southern Baltic Sea and the transition area to the North Sea. Scale: The distance of one° N = 60 nautical miles on the map.

Baltic Sea would disturb the large scale distribution pattern of the ratio. And, on the other hand, the signals of the "outside" sources are separate and strong enough and sediment transport and mixing processes do not lead to a complete homogenization of the clay mineral ratios over the entire region. It seems that size, morphology, and hydrography of the area as well as properties, sources and sinks of the fine-grained material are just in favourable "proportions" to each other to use the kaolinite/chlorite ratio for reconstruction of long distance transport in the Baltic Sea.

Kaolinite and chlorite, properties and origin

Besides of the three layer silicates (e.g. mica, illite, smectite, montmorillonite) kaolinite (two layer silicate) and chlorite (four layer silicate) belong to the major components of the clay mineral associations of sediments and sedimentary rocks. Most of the kaolinite rich sedimentary rocks are formed by humid chemical weathering of silicate magmatic rocks (granite), which are primarily rich in feldspars and micas. This process is very slow, needs geological time scales of millions of years and warm and humid climates. In middle Europe, such kaolinite rich sedimentary rocks are mainly found in or close to the Paleozoic formations of Variscian age. These areas are at least partly in the catchments of major rivers entering the Baltic Sea (Oder, Vistula). Furthermore, the English North Sea coast consists of Paleozoic and Mesozoic rocks, which are rich in kaolinite and cliff erosion in this area is the most important source for kaolinite in the sediments of the North Sea (Zöllmer & Irion 1996).

Chlorite, on the other hand, is a clay mineral that mainly derives from metamorphic rocks with high contents of Fe- and Mg- rich silicate minerals (biotite, garnet, pyroxene, amphibole and others). The formation and/or stability of chlorite in near surface sediments are more connected to colder climates. A typical chlorite rich sediment is the glacial till of Pleistocene age in northern Europe (Gingele & Leipe 1997) and the glacial till and its weathering products are the dominating stratigraphical units of the basis of Holocene sedimentation within the Baltic Sea.

For the discussion of the distribution pattern of the kaolinite/chlorite ratio in the surface sediments of the Baltic Sea we can assume that this ratio reflects a mixing row (gradient) of two "end members" or "proxies". The lower end of this row is represented by the original glacial till of the initial Baltic Sea, which has values of 0.3 to 0.5. The upper end of this row is represented by the allochthonous material, discharged by the southern streams (rivers) into the Baltic Sea and the material, which arrives from the North Sea. Maximum values were found in sediments of the Oder river mouth (2.8) and in the eastern Skagerrak (1.8).

A further precondition is the temporal stability of both minerals. At least for the relevant time scales of Holocene transport and sedimentation it is justified to assume that early diagenetic processes do not affect these ratios.

The pathways of the material in the Baltic Sea

The river loads

Table 1 includes a compilation of the 10 largest rivers of the Baltic Sea catchments with some available or estimated values of the flow and the suspended matter discharge. Among these rivers, the most important five (Neva, Vistula, Daugava, Neman, Oder), entering the Baltic from the southeast, are responsible for at least the half of the total river freight into the Baltic Sea. Unfortunately, only for the Oder River we have extensive information about the kaolinite/chlorite ratio in sediments of the whole estuary (Gingele & Leipe 1997). But, we can use these results as a representative example, and there is no doubt, that the situation in the other four of the named rivers is very similar. The Oder freight is clearly to be followed to the north into the Arkona Basin, and partly towards the southern Bornholm Basin, which can be confirmed by the results of Christiansen et al. (2002) and Emeis et al. (2002). For the Arkona Basin, we have to consider the material transport from the west as well, which will be discussed later in more detail. For the Vistula river, we can see that the river signal disappears relatively fast in the near Gdansk Basin. There is no hint, that larger amounts of Vistula material reach the Bornholm or Gotland Basins. Neman River discharges into the Curonian Lagoon at first, but, similar to the Oder Lagoon, the material should arrive in the Baltic sooner or later. The lack of sampling sites in the area in front of the Neman River estuary in our study is a disadvantage, of course. But, the low kaolinite/chlorite ratios in the southern part of the Gotland Basin indicate that no larger amounts of material from the Neman River end up there. Probably, the main direction of transport is to the north, towards the eastern Gotland Basin. Daugava river material is caught mainly in the Gulf of Riga, but a part of it should reach the eastern and northern Gotland Basin as well. Neva river material is well detectable throughout the whole Gulf of Finland. Further on, the medium kaolinite/chlorite ratio in the Northern Central Basin might be also attributed to material import from the Neva River.

The Scandinavian rivers are different to the south-eastern catchment of the Baltic Sea, as well as the geology of both areas. As discussed before, there are no important kaolinite rich sources in the crystallinic basement rocks of the Scandinavian shield. Thus, the ratio is low and there is no way to separate the river material e.g. from the older reworked Baltic Sea sediments in recent deposits by the kaolinite/chlorite signal. In this case the method is not suitable to describe the material transport. But, we have to establish at least, that the western Gotland Basin, the area south of Gotland as well as the north-eastern part of the Bornholm Basin have constant low kaolinite/chlorite ratios. It means that these areas are certainly the last or most far away ones, in which material from the named kaolinite rich sources arrive!

The transition area between the North Sea and the Baltic Sea

To this area special attention has to be paid because this is the main gateway for the water (and suspended sediment) exchange between the North Sea and the Baltic Sea. The average annual water exchange at the permanent Darss-Sill hydrographical station (IOW) situated in a key area of this process was measured to be 1500 km^3 a^{-1} inflow and 2000 km^3 a^{-1} outflow (Lass et al. 1997, see Table 1). Taking into account a general "estuarine circulation" of the Baltic water exchange (Fennel 1996), the higher saline (heavier) inflowing water transports much more sediment, than the outflowing (lighter) lower saline water. We know from our own ship borne measurements, that this difference can be up to ten times and more which was confirmed by Danish colleagues (Valeur et al. 1996; Lund-Hansen, pers. comm.). At least, this difference is big enough to postulate a net import of fine-grained sediment material

Table 1. Estimation of river load (suspended particulate matter = SPM) in to the Baltic Sea as well as the water and particulate matter exchange at the "Darss Sill".

River	**Flow**	**Flow**	**SPM**	**SPM**
	m^3 s^{-1}	**km^3 a^{-1}**	**t km^{-3}**	**t a^{-1}**
Neva	**2,460**	**78**	16,000	1,241,257
Vistula	**1,065**	**34**	**16,882**	**567,000**
Daugava	**659**	**21**	**3,464**	**72,000**
Neman	**632**	**20**	**13,146**	**262,000**
Oder	**573**	**18**	**17,377**	**314,000**
Kemijoki	**562**	**18**	8,000	141,786
Göta älv	**574**	**18**	8,000	144,813
Ångermanälv	**489**	**15**	8,000	123,369
Luleälven	**486**	**15**	8,000	122,612
Indalsälven	**443**	**14**	8,000	111,764
Sum	**7,943**	**250**		3,100,601
Total Baltic Sea rivers		483	≈11,000	5,313,000
			(average)	
Water exchange "Darss Sill"				
Inflow		**1,500**	5,000	7,500,000
Outflow		**2,000**	1,000	2,000,000

Fat numbers = measured values after HELCOM - PLC-3, and other sources.
Normal numbers = estimated values. The Daugava river suspended load seems to be underestimated. SPM at the Darss Sill based on averages of our own measurements.

(SPM) from the North Sea (via Kattegat) to the western Baltic Sea (Gingele & Leipe 2001). It is interesting to note that this material import is estimated to be in the same order of magnitude as the total river material discharge of the whole Baltic Sea (Table 1). In this sense, the Danish straits might be called the most important "rivers" of the Baltic Sea with respect to water and particulate matter transport.

The gradient of the kaolinite/chlorite ratio in surface sediments of this area in fact follows (duplicates) the pattern of saline water inflow (Fig. 2). In completion (or extension) of the investigation results of Irion & Zöllmer (1999) and Kuijpers et al. (1993) we now can track the way of the material from the southern North Sea around Skagen (DK) through the Kattegat and Belt Sea to the basins of the western Baltic Sea (Mecklenburg Bay, Arkona Basin). In Bornholmsgat and in the northern part of the Bornholm Basin the signal disappears. Of course, we know that strong saline water inflows can reach the Gotland Basin (e.g. Matthäus & Franck 1992), but the episodic character of such events and sediment mixing processes leads to a gradually dilution of the signal and we are not able to trace the material further to the east.

CONCLUSIONS

The knowledge about the pathways of clay minerals and therefore the reconstruction of long distance transport of fine-grained material in the Baltic Sea can contribute to the solution of a number of related problems. A few examples should be mentioned here. One of the most interesting consequences of the particulate matter transport in the North Sea – Baltic Sea transition area is the hypothesis that the basins of the western Baltic Sea, especially the Mecklenburg Bay and the Arkona Basin act as a trap for the material from the North Sea and from the Kattegat (Gingele & Leipe 2001). Further investigations about the interrelation of suspended matter load and water exchange in the Belt Sea could result in new statements of mass balances and accumulation rates of the adjacent basins.

Furthermore, we know that transport and deposition of fine-grained minerals and organic matter is always connected to the transport and deposition of particulate bound nutrients and pollutants. Investigation results about the function of the so-called "fluffy layer" as a carrier for e.g. heavy metals and organic substances in the Oder estuary – Arkona Basin area (Löffler et al. 2000; Staniszewski et al. 2000; Pazdro et al. 2001; Witt et al. 2001) should be transferable to other regions.

Finally, the amounts and pathways of river- and North Sea derived material in the Baltic Sea depends (among others) on the climatic and hydrological situations in northern Europe and reconstruction of climatic changes in Holocene time scales are just in

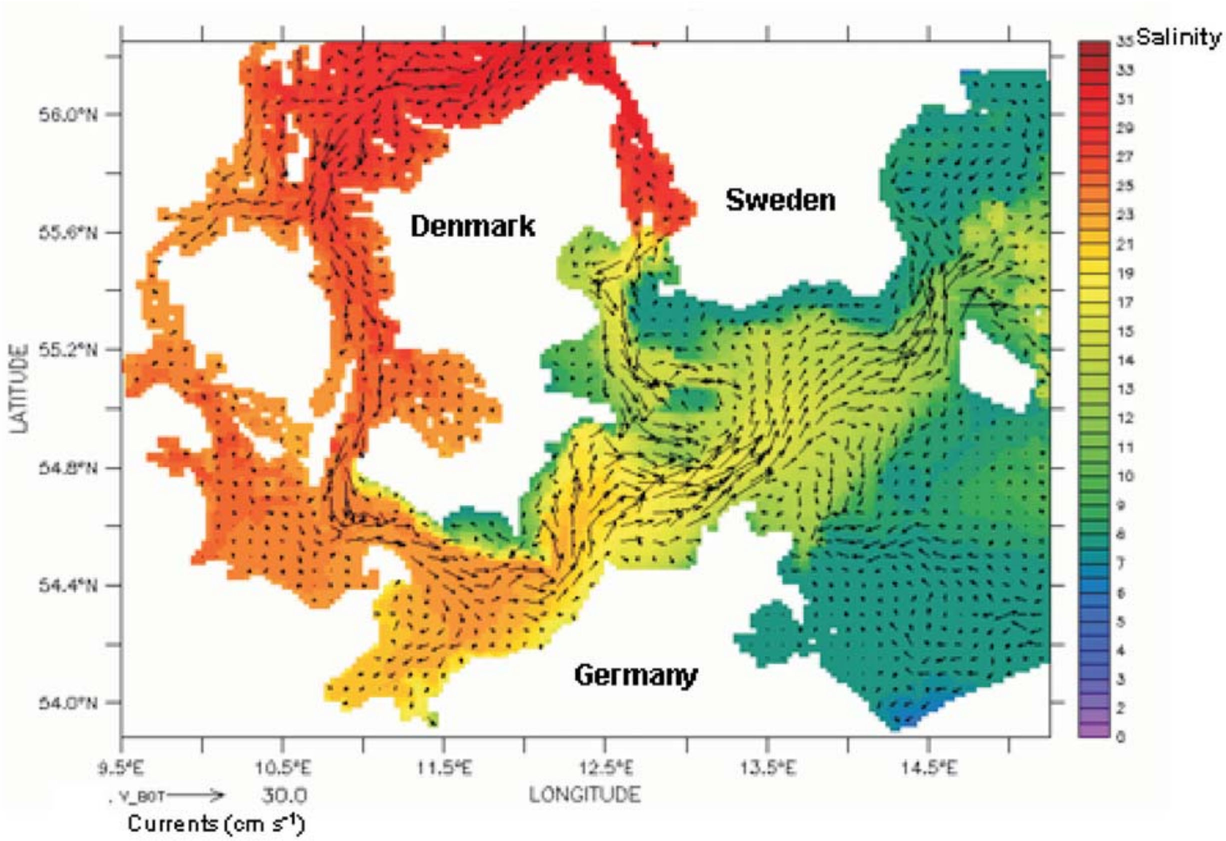

Fig. 2. Computer model of salinity (scale on the right side) and currents in the near-bottom layer of the Belt Sea – Arkona Sea area during a salt water inflow on hand of an example of the 22. January 1997. Current direction and speed (cm s^{-1}) is displayed by arrows. The model run and the figure were provided by U. Lass, V. Mohrholz & T. Seifert (IOW).

the focus of national and international research programmes. Thus, variations in salt water intrusions (Matthäus & Schinke 1994) and/or fresh water supply to the Baltic may be also detectable in laminated sedimentary records of the central Baltic Sea basins. In comparison to the geochemical investigations by Neumann et al. (1997) and Emeis et al. (1998), and with a much higher vertical resolution in the upper sediment column than it was used by Gingele & Leipe (1997), variations in clay mineral ratios could contribute to the solution of these problems.

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