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The Ponto-Caspian basin as a final trap for southeastern Scandinavian Ice-Sheet meltwater

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1. Introduction

Climate change in Europe during the Last Glacial Maximum (LGM; ca. 26–19 kyr BP) and the subsequent deglaciation have been intensively investigated through various archives leading to recently published compilations that focus on both the extent and timing of the last European Ice Sheet (EIS) (Hughes et al., 2015; Stroeven et al., 2015; Toucanne et al., 2015). During the LGM and until the complete melting of the ice sheet after 9.7 cal kyr BP (Stroeven et al., 2015), the EIS affected environmental conditions not only locally but also on a much wider scale. As a prominent example of this, glacigenic sediments were deposited as far away as the Eastern North Atlantic and the Bay of Biscay through meltwater...
pulses originating at the southern margin of the Scandinavian Ice Sheet (SIS, itself part of the EIS system). The meltwater was funneled from Baltic lowlands by ice-marginal valleys and by the so-called Channel River (Toucanne et al., 2009, 2010). Part of the meltwater from the southeastern side of the SIS could have been evacuated into the Caspian and Black Seas via the Volga and Dniepr Rivers respectively, as it has been postulated by many authors (e.g. Mangerud et al., 2004; Soulet et al., 2013). Indeed, both rivers drain the East European Plain that constitutes partly their catchment area, and their northern extent is close to, or on the limit of the southeastern SIS margin during the LGM and the deglaciation.

In the Western Black Sea, the so-called Red Layers form part of the Late Quaternary sedimentary sequence (Major et al., 2002; Strechie-Sliwinski, 2007; Soulet et al., 2013). Their formation has been attributed to the transport of sediments into the Black Sea by meltwaters from the southern SIS margin during the last deglaciation (Soulet et al., 2011a). On the river terraces in the lower Volga, the so-called Chocolate Clays are present. They constitute part of sediments deposited during the Early Khvalynian transgression of the Caspian Sea in the Late Pleistocene (e.g. Varuschenko et al., 1987). Nevertheless the precise timing of this transgression, as well as the origin of Chocolate Clays (even if considered as being deposited during the Last Glacial Maximum and time of their deposition are not clearly established, and still debated (e.g. Leonov et al., 2002; Badyukova, 2010; Yanina, 2012; Tudryn et al., 2013a; Sorokin et al., 2014; Arslanov et al., 2015; Bezrodnikh et al., 2015; Makshaev and Svitoch, 2015 and papers cited therein)). As Kronenberger et al. (1997) pointed out, accurate dating of the Early Khvalynian transgression, and determination of the origin of the Chocolate Clays, would aid in clarifying the relationship between global climate (the primary driving mechanism), Caspian Sea level and the evolution of hydrological systems on the East European Plain, and provide major arguments for causal mechanisms.

In this context we propose a detailed sedimentological, palynological and geochemical study based on sediments from the western part of the Black Sea, from the river terraces in the lower Volga and from the middle basin of the Caspian Sea. Based on our results and on recent findings concerning the Caspian and Black Seas as well as SIS evolution, the aim of this study is to ascertain the source areas of clay minerals deposited in the Ponto-Caspian basin during the last deglaciation. Further to this, we intend to identify the origin of Chocolate Clays deposited in the Caspian Sea during the Early Khvalynian transgression to improve the chronological framework for this transgression and to establish its causal mechanisms.

2. Setting

2.1. SIS southern margin at the LGM

Studies of sediments along the southern and eastern SIS margin reveal the complexity of the spatiotemporal evolution of the SIS. The ice margin was marked by end moraines and hummocky landscapes with frequent ice-dammed lakes spanning from Lake Onega in Russia to northern Germany (Swendsen et al., 2004; Stroeven et al., 2015).

The precise timing for SIS fluctuations is still debated; nevertheless the timing for westward meltwater routing via ice-marginal valleys from the Baltic lowlands is quite well known. Indeed, based on glaciogenic sediments from the southern SIS margin deposited in the Bay of Biscay, Toucanne et al. (2015) proposed a revised chronology for the LGM and post-glacial ice sheet evolution in this area. According to these authors, the main Channel River meltwater releases occurred before the LGM and during the deglaciation. They were produced by five phases of the large-scale ice-margin retreats: (i) during Heinrich Stadial 3 (HS3: between ~31 and 29 cal kyr BP), (ii) during HS2 (between ~26 and 23 cal kyr BP), (iii) at ~22.5–21.3 cal kyr BP, (iv) at ~20.3–18.7 cal kyr BP and finally (v) from ~18.2 to 16.7 cal kyr BP (first part of HS1; between 18 and 15 cal kyr BP). At around 17 cal kyr BP, the Channel River stopped its activity; according to Toucanne et al. (2010), meltwater then flowed towards the Nordic Seas.

In the southern part of the SIS (i.e. Baltic lowlands of Poland and Germany), a succession of three moraine belts, the Brandenburg-Leszno, Frankfurt-Poznan and Pomeranian (Pomorska), was identified from the LGM and dated (Rinterknecht et al., 2006, 2008; 2012, 2013; Dzierzek and Zreda, 2007; Marks, 2015). The new chronology proposed by Toucanne et al. (2015) identifies the Brandenburg-Leszno ice advance between ~23.4 and ~20.3 cal kyr BP. The Brandenburg-Leszno phase ended with a significant ice retreat dated at ~20.3–18.7 cal kyr BP. The Frankfurt-Poznan ice advance occurred between ~18.7 and ~18.2 cal kyr BP, while the Pomeranian one was between ~16.7 and ~15.7 cal kyr BP.

In the southeastern part of the SIS, recent reconstructions of its deglaciation that include the recalibration of previously published dates (Rinterknecht et al., 2008), indicate that the south Baltic coast was already ice free at 15–14 kyr (Stroeven et al., 2015; Hughes et al., 2015). Stroeven et al. (2015) proposed that the last LGM was reached at ~19 cal kyr BP in Belarus (Orsha phase), Lithuania (Gruda phase), Latvia and Estonia. This local LGM has been correlated with the Frankfurt-Poznan phase to the west, while in the northeastern sector in Russia, it was reached at 17 cal kyr BP, and broadly correlates with Pomeranian ice advance. According to Swendsen et al. (2004) and Hughes et al. (2015), the maximum position of the ice sheet advance was reached there at ~20–18 kyr. The outermost ice sheet limit during its maximum formed three major lobes in the Russian sector (Hughes et al., 2015; Stroeven et al., 2015). But the exact extent in the area of the Rybinsk basin is still not clearly established. As pointed out by Marks (2015), the deglaciation steps in the Russian sector are not well known; nevertheless, at least the Vepsian (probably corresponding to the Pomeranian phase in central Europe), Sebezhia, Luga and Neva phases of ice sheet advance have been identified. The Luga phase was derived from the last ice sheet margin that extended to the south of Lake Onega, and it was considered as having occurred at ~14.2 cal kyr BP. Afterwards, the Neva phase was dated at ~13 cal kyr BP (Marks, 2015). This is in good agreement with data from the eastern shore of Lake Onega, which indicate that this area was deglaciated between 14.4 and 12.0 kyr BP (Saarnisto and Saarinen, 2001), and with recent compilation of Hughes et al. (2015).

During the LGM, the East European Plain belonged to the zone of continuous permafrost including the middle basins of Dniestr, Dniepr and Don (Bogutskiy et al., 1975; Velichko et al., 1996) as well as the Volga catchment area and the northern shoreline of the Caspian Sea from that time (Yanina, 2012). According to Vandenberghe et al. (2014), permafrost degradation started as early as 17–15 kyr BP.

2.2. The Ponto-Caspian basin - study area

The Black and Caspian Seas (Fig. 1) belong to the Ponto-Caspian region. They are relicts of the East Paratethys, and became individualized during the Pliocene (Varuschenko et al., 1987; Forte and Cowgill, 2013; Yanina, 2014; Van Baak, 2015). Caspian and Black Seas are intracontinental, effectively closed and semi-closed reservoirs of waters and thus very sensitive to climatic changes. They have important part of their catchment areas in the East European Plain and, during the Quaternary, were subjected to large amplitude water-level fluctuations (more than 100 m) (e.g. Serebryanny, 1982; Varuschenko et al., 1987).
2.2.1. Caspian Sea

The Caspian Sea, which today lies at 27 m below sea-level, is the world’s largest inland water body (390,000 km²; 66,100 km³) without connection to the world ocean (Fig. 1). It is a reservoir of brackish waters, with a catchment area of 3.5 million km², which extends northwards over 15° of latitude to the East European Plain. The salinity of the Caspian Sea varies from the north to the south within the range of 1–13.5‰; this variation is particularly strong in the north due to the large freshwater supply by the Volga River, in other areas average water salinity is ~12.5‰ (Dumont, 1998). The Volga River contributes >80% of the Sea’s total inflow (237 km³ yr⁻¹ on average), drains the eastern part of the East European Plain and has a catchment area of 1.4 million km² (Kroonenberg et al., 1997; Dumont, 1998).

According to many authors (Varuschenko et al., 1987; Kroonenberg et al., 1997; Dumont, 1998; Svitoch, 1997; Dolukhanov et al., 2009), the Late Khazarian and Khvalynian transgressions occurred during the Late Pleistocene, from about 130 kyr. The Atelian regression (~120 to ~140 m asl) occurred after the Late Khazarian (~100 to ~5 m asl), whereas the Enotayevian regression (~80 to ~100 m asl) separated the Early (maximum +50 m asl) and Late Khvalynian (maximum 0 m asl) transgressions. In the Holocene, the Mangyshlak regression and finally the Neocaspian transgression were evidenced. This general pattern of successive transgressions and regressions was complicated by second order variations of Caspian water level with various time constants and by change in the hydrographic network. Today the Caspian Sea is divided into three basins, each of about the same area, but differing in depth and volume. These are the South (water depth <1020 m), middle (~900 m) and North (~15 m) basins that represent ca. two-thirds, one-third and 1% of the total volume of water, respectively (Chaliè et al., 1997). During the Late Pleistocene transgressions, when water level reached 0 and even +50 m asl, the area to the north of the Caspian Sea, which is not currently submerged, formed an additional shallow water basin (Fig. 1).

2.2.2. Black Sea

The Black Sea is one of the largest anoxic basins in the world, with an area of 432,000 km², a water volume of 534,000 km³, a mean depth of 1240 m, and a maximal depth of 2206 m (Ross et al., 1974) (Fig. 1). It is nowadays connected to the Mediterranean Sea through the Bosporus Strait, the Marmara Sea and the Dardanelle Strait. The Black Sea is characterized by the presence of a halocline between 100 and 200 m depth separating near-surface water...
having salinity of -18‰, from a deep, more saline water of -22.5‰. This lower body of water is of Mediterranean origin that induces anoxic conditions below 150 m bsl (Bahr et al., 2005; Stroehle-Sliwinski, 2007). The north-western part of the basin drains European rivers, the largest being the Danube (catchment area of 817,000 km²) and the Dniepr (catchment area of 504,000 km²). To the South, Anatolian rivers supply today more than 33% of the total sediment input into the Black Sea (Popenescu, 2002); but they represent only 8% of the total freshwater discharge.

The connection with the Mediterranean Sea has been interrupted frequently over the history of the Black Sea (Deuser, 1974) and the Black Sea’s status oscillated between lacustrine (during glacial low stands of the ocean) and marine (during interglacial high stands) (Badertscher et al., 2011). The connection was previously located on the Sakarya Strait (Gürbüz and Leroy, 2010). For the last glacial–postglacial transition, two hypotheses have been proposed to explain the Mediterranean-Black Sea re-connection: a catastrophic (Ryan et al., 1997) or a gradual event, with the “Black Lake” freshwater inflow into the Mediterranean Sea at either ~17 kyr BP or ~9.5 cal kyr BP, with, after ~9.8 kyr BP possible oscillating manner allowing a periodic migration of Mediterranean organisms into the Black basin, and finally the marine water arrival into the “Black Lake” at ~7.6 cal kyr BP (Aksu et al., 2002; Hiscott et al., 2007a,b; Nicholas et al., 2011; Yanko-Hombach et al., 2007, 2013, 2015a; Yanina, 2012; Arslanov et al., 2015). Large-scale changes of the Black Sea level occurred in the late Quaternary: the ﬂow of Caspian Sea water over 

3.1. Caspian Sea

The 995 cm long Kullenberg sediment core SR-9418 GS20 (named GS20 thereafter, but called GS18 in Leroy et al., 2014), was collected from the middle basin of the Caspian Sea (41°32′53″N; 51°06′04″E; water depth of 479 m) (Fig. 1). It has already been analyzed for chronology, magnetic mineralogy, carbonate content and micropaleoontology (ostacods and palynology) (Boomer et al., 2005; Leroy et al., 2014; Tudryn et al., 2014), and presents a Late Pleistocene and Holocene record (Fig. 2a,b,c). Sediments from river terraces in the lower Volga were sampled directly from accessible outcrops in Srednaya Akhtuba (~20 m a.s.l., 48°43′00.37″N, 44°51′59.72″E), in Kolobovka (~10 m a.s.l., 48°39′21.06″N, 45°28′29.34″E) and in Tsagan-Aman (~0 m a.s.l., 47°33′02.69″N, 46°40′49.99″E) (Fig. 1, Photo 1b,c,d). The details of sampling (about 150 samples of 8 cm² perspex cubes were obtained) and results of magnetic and clay minerals, palynological studies, as well as ¹⁴C dating of this sequence representing part of Early Khvalynian transgression of the Caspian Sea during the Late Pleistocene, are reported in Tudryn et al. (2013a) and in Leonov et al. (2002). The core from the middle basin of the Caspian Sea was collected during a cruise that took place in 1994. Sampling of Early Khvalynian sedimentary sequences accessible from river terraces in the lower Volga in Srednaya Akhtuba, Kolobovka and Tsagan-Aman, was achieved during a French-Russian field trip in September 1997. Both were obtained as part of the multidisciplinary study of the paleo-olimnology of the Caspian Sea “Understanding the Caspian Sea Erratic Fluctuations” (an EU-INCO-Copernicus collaboration), conducted by a team that included five authors of this paper.
3.1.2. Black Sea

The 757 cm long Kullenberg sediment core BLKS 98-11 was collected from the slope of the NW Black Sea (44°03.02′N, 30°53.12′E; water depth 500 m), in the axis of the Danube River during a cruise as part of the French-Romanian program Blason1 in 1998 (Fig. 1). The 32 m long Calypso core MD04-2754 (41°59.23′N, 28°40.99′E; water depth 453 m) was obtained from the slope of the SW Black Sea, during the ASSEMBLAGE 1 cruise and as part of the European program ASSEMBLAGE (Fig. 1). Sediments from core BLKS 98-11 and seven upper meters from core MD04-2754 were previously studied for chronology, magnetic mineralogy, carbonate content, organic carbon and nitrogen contents and their isotopic signatures (Strechie et al., 2002; Strechie-Sliwinski, 2007) (Fig. 2d–h).

3.2. Methods

Clay minerals and grain-size analysis. Clay minerals from the Black and Caspian Seas were identified by XRD on oriented mounts of non-calcareous clay-sized (<2 mm) particles with PANalytical diffractometer, following the laboratory routine at the GEOPS laboratory, Université de Paris Sud (Liu et al., 2007, 2008). The oriented mounts were obtained according to a method described by Liu et al. (2004). Three XRD runs were made, following air-drying, ethylene glycol solute treatment for 24 h, and heating at 490 °C for 2 h. The identification of clay minerals was mainly made according to the position of the (001) series of basal reflections on the three XRD diagrams. Semi-quantitative estimates of peak areas of the basal reflections for the main clay mineral groups of smectite (including mixed-layers) (15–17 Å), illite (10 Å) and kaolinite/chlorite (7 Å) were carried out on the glycolated curve (Holtzapfel, 1985) using the MacDiff software (Petschick, 2000). Relative proportions of kaolinite and chlorite were determined based on the ratio of 3.57:3.54 Å peak areas. Based on the XRD method, the semi-quantitative evaluation of each clay mineral has an accuracy of ±5%. Grain-size distribution measurements of carbonate-free sediment from core GS20, Caspian Sea, were carried out on a Malvern Mastersizer 2000 device, at the GEOPS laboratory, Université de Paris Sud.

Palynological analyses. Ninety-two samples for the top 666 cm of core GS20 were palynologically studied for palaeoenvironmental reconstructions, both terrestrial and aquatic (Leroy et al., 2014). Twenty-two of them were treated at Université Catholique de Louvain (Belgium) by the heavy liquid method (Thoulet solution at a density of 2.1). The remaining seventy samples were treated at Brunel University (UK) by the HF method. On average the sample volume was 1.1 ml. Initial processing of samples involved the addition of sodium pyrophosphate to deflocculate the sediment. Samples were then treated with cold hydrochloric acid (from 10% to pure) and cold hydrofluoric acid (60%), and HCl (10%) again. The residual organic fraction was screened through 125 and 10 μm mesh sieves. Final residues were mounted on slides in glycerol and sealed with varnish. An additional 22 samples, below 666 cm depth (treated with the HF method), were treated but not published in Leroy et al. (2014) because of a suspected different taphonomy. The Pinus percentages are calculated on the sum of terrestrial pollen grains (that includes Pinus, but not reworked grains). The reworked percentages are calculated on the same sum, that does not include them and hence values higher than 100% can be reached. In the Lower Volga from the Srednaya Achtuba outcrop, six samples were chosen from fine-grained levels. The processing of 1.9–2.7 ml of sediment, following the HF method described for the...
GS20 core, did not yield any palynomorphs.

Neodymium. We measured Nd isotope ratios of fine-grained detrital fractions extracted from a series of the Caspian Sea sediments from three key locations. Sample selection was based on recorded changes in clay mineralogy. One measurement was made on the Early Khvalynian Chocolate Clays sample from Srednaya Akhtuba. Two others were made on samples from core GS20, at 970 cm and 770 cm depth. Additional analyses were performed on recent sediments from the Kuban, Don and Ropotamo rivers, all tributaries of the Black Sea, as well as from River Sefid Rud that drains the southern Caspian Basin and River Amu Darya (Fig. 1). The neodymium isotopic composition of terrigenous sediment is a powerful tracer for geographical provenance; it reflects to a large extent the mean age of the corresponding source region and is preserved during erosion and transport processes (Goldstein and Jacobsen, 1988). In this study we analyzed the fine clay-silt detrital fraction (~63 μm) of the sediment, for comparison with the Nd isotopic compositions of sediments recently reported by Soulet et al. (2013) and Toucanne et al. (2015). Dried fine-grained fractions (typically ~ 0.5 g) were crushed using an agate mortar and pestle. The terrigenous fraction of each sediment sample was digested by alkaline fusion (Bayon et al., 2009) after removal of carbonates, Fe–Mn oxide and organic components using a sequential leaching procedure (Bayon et al., 2002). Prior to analyses, Nd was separated by ion exchange chromatography (see details in Bayon et al., 2012). Isotopic measurements were performed at the Pôle Spectrométrie Océan, Brest (France), using a Thermo Scientific Neptune multi-collector ICPMS. Mass bias corrections on Nd were made with the exponential law, using (146Nd/144Nd) = 0.7219. Nd isotopic compositions were determined using sample-standard bracketing, by analysing JNd-1 standard solutions every two samples. Mass-bias corrected values for (143Nd/144Nd) were normalized to a JNd-1 value of 0.51215 (Tanaka et al., 2000). In this study, both measured (143Nd/144Nd) and literature data are reported using the εNd notation, which corresponds to the deviation of any measured Nd isotopic ratio relative to the present-day value of the Chondritic Uniform Reservoir (CHUR): \[ \epsilon_{\text{Nd}} = \frac{(143\text{Nd}/144\text{Nd})_{\text{sample}} - (143\text{Nd}/144\text{Nd})_{\text{CHUR}}}{(143\text{Nd}/144\text{Nd})_{\text{CHUR}} - 1} \times 10^4 \]. Using (143Nd/144Nd)CHUR = 0.512638 (Jacobsen and Wasserburg, 1980). Note that the estimated uncertainty on measured εNd values, inferred from repeated analyses of JNd-1 standard solution is typically of about ±0.3 ε-units.

4. Results

4.1. Lithology and chronology

4.1.1. Caspian Sea

4.1.1.1. Lithology. Core GS20: The sediment from the middle basin of the Caspian Sea (core GS20) presents fine silty deposits described in details in Tudryn et al. (2014) and in Leroy et al. (2014). They are characterized as a whole by an alternation of black and grey/brownish laminae that rapidly disappear under oxidizing conditions (Photo 1a). These laminae are alternated with grey/brownish laminae, and are of early diagenetic origin, as it is the case for sediments from the South basin of the Caspian Sea (Jelinowska et al., 1998, 1999; Leroy et al., 2013a,b). In the lower part of core GS20, from the bottom at 955 cm—870 cm, the sediment became brownish or slightly pink/reddish in oxidizing conditions, while above it became rather grey-greenish.

River terraces: Early Khvalynian sediments from river terraces in the lower Volga studied here, are formed by chocolate-colour clays (or silts), well known from literature as Chocolate Clays (e.g. Leonov et al., 2002; Badyukova, 2007; Chepalyga, 2007; Svitoch, 2009; Shkhatova, 2010; Makshayev and Svitoch, 2015, and papers cited therein). The Chocolate Clays from Srednaya Akhtuba, Kolobovka and Tsagan-Aman are more or less regularly interbedded by thin, horizontal sandy or silty yellow laminae (Photo 1b,c). Scarcely macro-biological remains were observed. These sediments suggest a rather calm depositional environment, and visually may resemble varved sediments in periglacial lakes (Tudryn et al., 2013a). This sequence, of different thickness in each outcrop (2.0 m in Srednaya Akhtuba, 3.4 m in Kolobovka and 1.4 m near Tsagan-Aman), begins at the bottom with a grey/green sandy and silty sediment with oxidation traces.

4.1.1.2. Chronology. Core GS20: Six radiocarbon dates for core GS20 were already obtained from ostracod shells and have been used to build an age-depth model after calibration by the IntCal13.14C curve (Reimer et al., 2013) and application of a 370 years reservoir effect (Boomer et al., 2005; Tudryn et al., 2014; Leroy et al., 2014)(Fig. 2). Sediments in core GS20 accumulated between ~14.6 and ~2 cal kyr BP. More specifically between ~14.6 and 12 cal kyr BP or from the bottom to 600 cm depth, the sedimentary rate is of ~0.15 cm yr⁻¹.

River terraces: The studied here Early Khvalynian sediment in river terraces in the lower Volga was poor in biological remains. Nevertheless, one ¹⁴C AMS date was obtained on total organic carbon preserved fraction from Chocolate Clays on a sample from Srednaya Akhtuba (Tudryn et al., 2013a), and ten ¹⁴C AMS dates were made on marine shells from Chocolate Clays and interbedded silts from Srednaya Akhtuba, Kolobovka and Tsagan Aman, as well as from two other sites – Chernyi Yar and the Priolzh'e settlement (Fig. 1)(Leonov et al., 2002). The age obtained on total organic carbon corresponds to ~20 cal kyr BP (Tudryn et al., 2013a). This was obtained from sample representing the upper part of the sequence, and is consistent with an Early Khvalynian event around the LGM. Although the analyzed organic carbon is of non-identified origin, it could come from the basin and thus reflect the LGM time, or at least partly from the catchment area and thus be older than the time of the clay deposition.

Dates obtained on mollusc shells were previously published without application of a calibration model (Leonov et al., 2002). After application of the calibration IntCal13.14C curve (Reimer et al., 2013), the new chronology has become established between ~19.1 and 13.9 cal kyr BP (Table 1). Since these molluscs were living in shallow, well-mixed and oxygenated environments (Tudryn et al., 2013a), we assume no hard-water effect in the basin and consider the LGM time as the time of the clay deposition.

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4.1.2. Black Sea

4.1.2.1. Lithology. In both cores from the Black Sea, three distinct lithostratigraphic units, previously reported by Ross and Degens (1974) and Hay et al. (1991) for deep-sea sediments, were identified (Fig. 2). The lowest unit, Unit III, consists of alternating light and dark silts deposited under lacustrine conditions. They include brownish/reddish silts (Photo 1e), named Red Layers (Major et al., 2002; Strecie-Sliwinska, 2007; Soulet et al., 2013). These silts present a sequence of varying thickness in both cores and are interbedded by thin grey silty bands. The Red Layers are followed by dark, greigite-rich, and light-coloured, carbonate-rich bands. Unit II is a carbonate-poor, fine-grained sapropel that shows variation in organic matter content, with high values in the lower half and marked decrease in the upper half. The lower limit of the sapropel indicates the beginning of the Black Sea – Mediterranean Sea connection. The uppermost unit, Unit I, is characterized by alternating light and dark microlaminations deposited since the first occurrence of Emiliana huxleyi, a coccolithophore that largely...
comprises the light bands. Different lithological characteristics, such as sapropel in Unit II, two carbonate rich bands in Unit III, magnetic minerals changes, which are visible through magnetic susceptibility variation, and Red Layers are identified here by laboratory analyses and visually. These characteristics, that reflect environmental changes in the Black Sea and its catchment area, are ubiquitous in the Black Sea, as shown in numerous investigations. For instance, carbonate and XRF-Ca analyses for cores collected on the slope (Fig. 2f,i,j) and in the deep Black Sea, as in core BLKS 98–22 (Fig. 1), highlight similar variation in the Ca content in Unit III, with its two peaks labeled as C1 and C2 (Major et al., 2002; Strechie et al., 2002; Bahr et al., 2005, 2006, 2008; Strechie-Sliwinski, 2007; Kwiecien et al., 2008; Soulet et al., 2011b).

4.1.2.2. Chronology. Recent investigations allowed chronology establishment (Soulet et al., 2011a, 2011b, 2013). According to these authors, the deposition of the Red Layers, identified in the lacustrine Unit III, occurred during Heinrich stadial 1 (HS1) from ~17.2 to ~15.7 cal kyr BP. The two following peaks in Ca intensity observed between these episodes is correlated to the ocean-climate state of Heinrich Stadial 1 (HS1) from ~17.2 to ~15.7 cal kyr BP. The highest values of Pinus recorded in reworked pollen grains are related to the presence of Pinus pollen in the sediments of the lower Volga and the absence of Pinus pollen in the sediments of the Black Sea (Fig. 3a). Then a single peak is found at 676 cm (12.56 cal kyr BP) and afterwards very moderate values are found upward until 383 cm or 8.19 cal kyr BP. The absence of palynomorphs in samples from the river terraces in the lower Volga is largely related to the oxidising environment unfavourable to palynomorph preservation.

Clay minerals and granulometry: The Early Khvalynian Chocolate Clays on river terraces in the lower Volga are clearly dominated by illite that reaches 80%. It is followed by kaolinite, chlorite and smectite but these minerals present low abundances. The interbedded silts show broadly similar contents of illite and smectite. As contents of these minerals were measured for sediments from Srednaya Akhtuba and Kolobovka, they are reported on Fig. 3c (indicated as dots) taking into account ages obtained from mollusc shells from these sites (Leonov et al., 2002) and their subsequent calibration. In the middle basin of the Caspian Sea, the sediment, from the bottom of core GS20 until ~14–13.8 cal kyr BP, displays similar patterns as for the Early Khvalynian sediments, with illite as dominant mineral (reaching 60%), and low values for kaolinite, chlorite and smectite (Fig. 3c indicated as lines). After that, and up to 12.0 cal kyr BP, illite decreases while smectite increases and become the most abundant mineral. Granulometric analysis of core GS20 sediment shows fine particles sizes (Fig. 3b).

Neodymium: Nd isotopic compositions of the sediment were obtained for three key locations with regard to changes of clay minerals (Table 2, Fig. 3d red stars). The measurement made on the Early Khvalynian Chocolate Clays sample from Srednaya Akhtuba displays an εnt value of ~17.7. Two other measurements were made on the sediment from the middle basin (core GS20) where illite was dominant, at 970 cm depth (~14.4 cal kyr BP), and where illite decreased and smectite become dominant, at ~13.8 cal kyr BP. The absence of Pinus in the vegetation around the middle basin of the Caspian Sea and its presence at great distance in the south (Tagieva and Veliev, 2014) and in the north of the area (Bolikhovskaya and Kasimov, 2010; Tudryn et al., 2013a; Richards et al., 2014) suggest a stronger contribution from river sources to the sediment than later on, after 12.44 cal kyr BP. The highest values of Pinus and reworked elements are reached at the bottom of the core below 877 cm depth (~13.83 cal kyr BP) (Fig. 3a). Then a single peak is found at 676 cm (12.56 cal kyr BP) and afterwards very moderate values are found upward until 383 cm or 8.19 cal kyr BP. The absence of palynomorphs in samples from the river terraces in the lower Volga is largely related to the oxidising environment unfavourable to palynomorph preservation.

4.2. Clay mineralogy, grain-size, pollen and neodymium analyses

The results are presented on a calendar age scale from 19 to 12 cal kyr BP (Fig. 3). Two cores from the Black Sea indicate a continuous record that is shown from 18 cal kyr BP onwards. Results from the Caspian Sea are composed of sediments from the middle basin, which begin at ~14.6 cal kyr BP, and of sediments from the river terraces in the lower Volga, which finish at ~13.9 cal kyr BP.

4.2.1. Caspian Sea

Pollen: In core GS20, below 666 cm, three strands of information make us suspect a different source for the palynomorphs than for the upper part of the core. It is i) the irregular presence of high percentages of Pinus pollen (Fig. 2a and 3a) and the occasional occurrence of Sphagnum spore, ii) the very high occurrence of reworked pollen grains (loss of ornamentation, increase in opacity and often pre-Quaternary taxa) representing at times more than 100% of the terrestrial sum of well-preserved pollen grains (Figs. 2a and 3a), and iii) the very low palynological concentrations (below 2000 pollen and spores per ml). The absence of Pinus in the vegetation around the middle basin of the Caspian Sea and its presence at great distance in the south (Tagieva and Veliev, 2014) and in the north of the area (Bolikhovskaya and Kasimov, 2010; Tudryn et al., 2013a; Richards et al., 2014) suggest a stronger contribution from river sources to the sediment than later on, after 12.44 cal kyr BP.

Table 1

<table>
<thead>
<tr>
<th>Site</th>
<th>Lat.</th>
<th>Long.</th>
<th>Material</th>
<th>Measured 14C yr BP</th>
<th>Error ± yr</th>
<th>Age 14C cal yr BP ±1</th>
<th>Mean 14C cal yr BP</th>
<th>Error ± yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Srednaya Akhtuba (+22–25 m asl)</td>
<td>48°33.00′N</td>
<td>44°51.92′E</td>
<td>C org. 14930</td>
<td>120</td>
<td>19924–20181</td>
<td>20053 ±1</td>
<td>130 ±1</td>
<td></td>
</tr>
<tr>
<td>Kolobovka (+10 m asl)</td>
<td>48°39.21′N</td>
<td>45°28.34′E</td>
<td>Shell 13240</td>
<td>70</td>
<td>14763–15099</td>
<td>14932 ±1</td>
<td>169 ±1</td>
<td></td>
</tr>
<tr>
<td>Tsagan Aman (0 – +2 m asl)</td>
<td>47°33.02′N</td>
<td>46°40.99′E</td>
<td>Shell 12470</td>
<td>180</td>
<td>13734–14277</td>
<td>14006 ±2</td>
<td>272 ±2</td>
<td></td>
</tr>
<tr>
<td>Chernyi Yar (0 m asl)</td>
<td>48°03′N</td>
<td>46°07′E</td>
<td>Shell 15800</td>
<td>45</td>
<td>15821–16011</td>
<td>15916 ±1</td>
<td>95 ±1</td>
<td></td>
</tr>
<tr>
<td>settl. Privolzh'e (+30 m asl)</td>
<td>52°57.50′N</td>
<td>48°35.52′E</td>
<td>Shell 14030</td>
<td>85</td>
<td>15689–15971</td>
<td>15831 ±1</td>
<td>142 ±1</td>
<td></td>
</tr>
</tbody>
</table>

Figures 2f,i,j and in the deep Black Sea, as in core BLKS 98–22, highlight similar variation in the Ca content in Unit III, with its two peaks labeled as C1 and C2 (Major et al., 2002; Strechie et al., 2002; Bahr et al., 2005, 2006, 2008; Strechie-Sliwinski, 2007; Kwiecien et al., 2008; Soulet et al., 2011b).
Fig. 3. Data for Caspian (a, b, c, d) and Black (e, f, g) Seas sediments on an age scale from 19 to 12 cal kyr BP. a) Pinus and reworked pollen percentages, core GS20, b) mean grain size (black line) and mode (grey line), core GS20, c) clay minerals contents, lines for core GS20 and dots for river terraces in the lower Volga, dashed line separating core GS20 and river terraces records, d) red stars: $^{14}$Nd values, black crosses: $^{14}$C cal kyr BP ages obtained on shells from Chocolate Clays (CC) in river terraces in the lower Volga (Leonov et al., 2002; this study), e) clay minerals contents for core MD04-2754, f) clay minerals contents for core BLKS 98-11, g) $^{14}$Nd values for core MD04-2790 after Soulet et al. (2013), h) SIS margin evolution: 1) timing for Channel River floods (CRF) after Toucanne et al., 2015, 2) Gr - Gruda and Ba - Baltija Moraines advances, Lithuania (Marks, 2015), 3) Os - Ostashkov, Ve - Vepsian, Se - Sebezha, Lu - Luga and N - Neva Moraines advances, northern Russia (Marks, 2015), i) the NGRIP ice core record of $d_{18}$O (North Greenland Ice Core Project Members, 2004), YD – Younger Dryas, B – Bølling, A – Allerød, HS1 – Heinrich Stadial 1. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

core BLKS 98-11 than in core MD04-2754 (Fig. 3e,f). Nevertheless the general pattern is quite similar between 18.0 and −15.7 cal kyr BP. Smectite is a clearly dominant mineral at the beginning of two sequences until ~17.2 cal kyr BP. Between 17.2 and 15.7 cal kyr BP, when Red Layers are present in the sediment, smectite decreases while illite became dominant, with nevertheless some short-term and significant changes. After that, in core BLKS 98-11, smectite dominates reaching 60%, while in core MD04-2754, smectite and illite broadly are in equal contents. Chlorite and kaolinite present low values. Nevertheless in core MD04-2754, chlorite is clearly higher, and increases towards 15.7 cal kyr BP. Nd isotopic compositions of the recent sediments from Rivers Don, Kuban and Ropotamo present values of −14.3, −9 and −7.3 respectively (Table 2).

5. Discussion

5.1. Caspian Sea

During the Early Khvalynian transgression, the Caspian Sea water level varied from maximal values of +50 m asl to 0 m asl and several transgression phases are reported (e.g. Leontiev et al., 1977). In the northernmost part of the Caspian Sea of that time, the very characteristic Chocolate Clays were deposited. Today they are found in this now-emerged area, including river terraces in the lower Volga. Despite numerous studies on this subject, some questions still remain open and particularly the exact timing of this transgression, its correlation with climatic events in the northern Hemisphere and the time and origin of the Chocolate Clays deposit.

5.1.1. Sources of detrital material for the Caspian Sea

The main change in taphonomy in core GS20 after −13.80 cal kyr BP suggests a shift from a period with strong river transport to a period when pollen transport by air was dominant. Although it is impossible to find out which was the most important river reaching the middle basin, it is likely that the Volga played an important role in the supply of the detrital material there. This issue of detrital material origin is discussed below.

5.1.1.1. Clay minerals

On the whole, the grain-size of all the sequences in the middle basin and in Chocolate Clays from the river terraces in the lower Volga indicates a dominance of fine-grained particles. Clay fraction mineralogy in the middle basin shows a major change exactly at the same time as a change in pollen transport (Fig. 3a, c line). Before −13.8 cal kyr BP, clays are essentially composed of illite, with kaolinite as the second mineral, followed by chloride, while smectite is almost absent. A similar pattern, with a large quantity of illite is recorded for Early Khvalynian Chocolate Clays in the river terraces in the lower Volga from this study (Fig. 3c dots), and from other sites, such as Svetly Var, Torgun, Novopriolovnoye and until the moraine clay loam in the Upper Volga (Makshaev and Svitoch, 2015). The source of the Chocolate Clays, deposited in the northernmost part of the Caspian Sea during the Early Khvalynian transgression, is obviously in the catchment area of the Volga River in the East European Plain. This suggests that the lower part of the sequence from the middle basin recorded arrivals of Chocolate Clays which were transported by the River Volga to this site and that this supply stopped at −13.8 cal kyr BP. Above, illite, kaolinite and chloride decrease and smectite becomes the major clay mineral.

Clay minerals in river, lacustrine and marine sediments reflect the intensity of chemical and physical weathering of their source area (Chamley, 1989). This weathering depends on the lithology, climate and morphology of the considered environment and results in surface soils or sediment. On the East European Plain, climatic oscillations between warm and cold conditions during the Pleistocene resulted in an alternation of subaerial and subaqueous sediments; but alternation of soils and loess reflecting these oscillations predominates. Almost the entire East European Plain area is covered with these Pleistocene deposits. Under cold climates, the production of clays essentially depends on physical weathering and illite is the dominant mineral. Under temperate climate, chemical weathering prevail and smectite appears. Smectite in the dominant clay mineral in paleosols from the East European Plain and is associated with chemical weathering during warm Pleistocene stages (Perederij, 2001). High contents of smectite were reported in the Permian-Triassic red clays of the middle Volga region (Makshaev and Svitoch, 2015), in the northern Caspian Sea sediments of the river terraces in the lower Volga deposited during the Late Khazarian transgression (Tudryn et al., 2013a), and in the northern Black Sea, Kerch Peninsula sediments from the Karangatian transgression (Dodonov et al., 2000), the latter two identified as occurring during the Eemian (Mikulin) interglacial.

The supply of the smectite must have been a result of soil erosion during this time. Broadly the same content of smectite and illite were reported from Ukrainian loess horizons (Perederij, 2001) that were deposited as a result of physical weathering during cold and dry climate. After this author, in sediments from the central part of the East European Plain, kaolinite is present but chloride is quite scarce, but it is known from the lower Don and lower Dniepr (Chamley, 1989).

Considering the above, the dominance of smectite in sediments
from the middle basin of the Caspian Sea after −13.8 cal kyr BP (Fig. 3c line) suggests the erosion of the smectite-bearing rocks from the catchment area of the River Volga. In the Early Khvalynian Chocolate Clays, the absence of smectite rules out this source of detrital material. The large contents of illite indicate the mobilization of the illite-rich area and/or physical weathering in the East European Plain, or the supply from the Baltic Shield area during melting of the SIS. Indeed, Chamley (1989) pointed out an abundant occurrence of illite in Pleistocene clays in Scandinavia, which illustrates a long physical weathering through glacier action. Both East European and Scandinavian sources for Chocolate Clays were already considered (e.g. Leonov et al., 2002; Tudryn et al., 2013a). Nevertheless, as these deposits are very similar to varved clays, Leonov et al. (2002) and Chepalova (2007) suggested that Chocolate Clays resulted from the formation of mudflows rather than from the melting waters of an ice sheet. According to these authors, meltwater should transport sediments with more scattered grain sizes than those which were deposited. Mudflows could be related to the degradation of permafrost in the periglacial zone, which was widespread in the Volga catchment. Another interpretation for Chocolate Clays deposition suggested by Badyukova (2010) is that the deposition took place in a basin-like periglacial lake or lagoon with varved sediments: fine deposits during winter below ice cover and particles with various grain sizes during summer.

5.1.1.2. Neodymium isotopic compositions. To clearly identify the source area of clays delivered into the northern and middle basins of the Caspian Sea, and thus to ascertain their origin either from East European Plain or Baltic Shield area meltwater-induced deposition, we measured the neodymium isotopic composition (εNd) on fine-grained sediments from three key locations with regard to clay mineral changes. Old cratonic source regions typically exhibit lower εNd values than younger rock formations. According to geophysical and structural reconstructions, the East European Craton that consists of three segments (Fennoscandia, Sarmatia and Volgo-Uralia) is buried under the Upper Proterozoic and Phanerozoic rocks. Precambrian rocks outcrop in the Baltic and Ukrainian Shields (Bibikova et al., 2009). Recently, Toucanne et al. (2015) showed that very low εNd values (between −23.3 and −17.6) characterize sediments transported by rivers (Kīminkijoki, Neva) draining the eastern part of the Precambrian Baltic Shield; i.e. one of the oldest geological formations in Europe (Bogdanova et al., 2008). Slightly higher Nd isotopic signatures, between −16.4 and −14.1, characterize the sediment carried by rivers draining the south-east of the Baltic catchment area (Rivers Narva, Gauja, Daugava, Neman and Vistula, North European Plain, southern side of the SIS during the LGM). These values vary from −16.5 to −13.7 for LGM glaciogenic sediment collected alongside the SIS south margin in Germany and Poland. This highlights both the input of Baltic Shield material in the North European Plain by the southern SIS margins (Kjær et al., 2003), and the westward transport of sediment from Poland and the Baltic States in continuous, extensive ice-marginal valleys (Krzysztofek et al., 1999). Additional information on εNd for the East European Plain are available for some rivers supplying the Caspian and Black Seas today, with a value of εNd −12 for sediments from the lower Volga, −14 for the Upper/middle Dniepr, −9 for the lower Danube (Soulet et al., 2013) and −12.6 for Desna (Freslon et al., 2014) (Fig. 1). Complementary data from this study provide values of −14 for the lower Don, −9 for the Kuban (Rivers Don and Kuban flowing into the Azov Sea), −7.3 for River Ropotamo (southwestern Black Sea, Bulgarian coast) and −6.5 and −5.9 for Asian rivers Selid Rud and Amu Darya respectively (Table 2, Fig. 1). These data clearly indicate different neodymium isotopic compositions and thus different sediment sources.

Early Khvalynian Chocolate Clays, from river terraces in the lower Volga at Srednaya Akhtuba, consist essentially of illite (Fig. 3c dots), and the sample measured for εNd shows a very low value of −17.7 (Fig. 3d red star). This clearly identifies its old source being in the Baltic Shield area, implying the melting of the SIS and transport of detrital material into the Caspian Sea by fluvioglacial waters via the River Volga. The lower part of sediment core GS20 from the middle basin of the Caspian Sea is rich in illite in the same way as the Chocolate Clays from the river terraces of the lower Volga (Fig. 3c red line between −14.6 and 13.8 cal kyr BP). The sample from this part of the sequence displays higher εNd value (−14.0); nevertheless it always remains as low as for sediments related to the Baltic Shield area (Soulet et al., 2013; Toucanne et al., 2015). This allows the clear identification of this sediment as being deposited during the Early Khvalynian transgression, as is the case for Chocolate Clays on river terraces in the lower Volga. The measurement obtained from the sediment, from the middle basin where smectite was dominant (Fig. 3c line above −13.8 cal kyr BP), presents εNd value of −10.4.

Change in clay mineralogy and in measured values of εNd, as well as change in the pollen signature, highlights the change of the detrital material source area here. The supply from the SIS was either too weak to transport the detrital material until the middle basin of the Caspian Sea or was stopped. This suggests the modification of the northern River Volga catchment area at −13.8 cal kyr BP and a sufficient retreat of the south margin of the SIS to the North; so that the meltwater was no longer transported into the Caspian Sea. After that, the East European Plain area, rich in smectite, became the dominant provider of detrital material.

5.1.2. Chronology. The identification of the Early Khvalynian sediments in the middle basin of the Caspian Sea shows the extent of the SIS impact to the south and the Volga River capacity to transport glaciogenic material. Core GS20 has a continuous record from −14.6 cal kyr BP, and the upper limit of this impact is clearly identified at −13.8 cal kyr BP, when illite decreases and smectite becomes dominant. δ13C dates, obtained on shells collected in the Chocolate Clays from river terraces in the lower Volga studied here, show ages from −19 to −13.9 cal kyr BP (Fig. 3d black crosses, Table 1). A −20 cal kyr BP δ13C cage estimate for a sample of non-identified organic matter shows that meltwater was supplied into the Caspian Sea, including its middle basin, during the deglaciation until −13.8 cal kyr BP, and possibly at least from the LGM. These data, and these of Russian scientists (Makshaev et al., 2015; Makshaev and Svitoch, 2015), provide a clear frame for the timing of the Chocolate Clays deposition during the Early Khvalynian transgression, when the water level reached at least +20–0 m asl (sites studied here), and its ending phase at −13.8 cal kyr BP. This timing is in very good agreement with that recently published by Arslanov et al. (2015). Indeed, these authors obtained ages between 16 and 14 cal kyr BP for transgressive stages of the Early Khvalynian basin with sea levels of +35 and +22 m asl. These authors point out also that the maximum stage of +50 m asl has remained undated until now.

5.2. Sources of detrital material for the Black Sea

On the whole, smectite and illite alternately dominate the clay fraction of the sediment. Their content in core BLKS 98-11, that was collected in the axis of the Danube River on a slope of the platform constructed by sediment supplied by the Danube and Dniepr Rivers, is much higher than in core MD04-2754, which was collected close to the western Turkish shoreline of the Black Sea. This indicates that the main sources of smectite and illite must have
been in the catchment area of the Danube or Dniepr, and that these minerals must have been transported by these northern rivers.

5.2.1. Red Layers 17.2–15.7 cal kyr BP

In the Black Sea sediments, the two cores BLKS 98–11 and MD04-2754 show the dominance of illite in the Red Layers (Fig. 3e,f), as it is the case for the Chocolate Clays in the Caspian Sea. On Fig. 3g, results of the εNd analyses for core MD04-2790 obtained by Soulet et al. (2013) are also presented. This core was collected from 352 m depth, in the same area as core BLKS 98–11 (500 m depth). The very low values of εNd, between ~18.7 and ~12.2, have been recorded for the Red Layers, which were deposited in four steps. This is expressed by changes of neodymium isotopic signatures and by changes in clay mineralogy (Fig. 3e, f and g). Soulet et al. (2013) interpreted low εNd values as being a result of the release of meltwater originating from a proglacial Lake Dnásko linked to the SIS, and transported into the Black Sea by the River Dniepr via the River Berezná (Fig. 1). This interpretation does not take into account the geological context of the River Dniepr catchment area. Indeed, its catchment area includes partly the Ukrainian Shield, and that could explain low εNd values obtained by Soulet and collaborators (2013) for the Red Layers in core MD04-2790 and for samples of modern sediment from the Upper/middle Dniepr (εNd Value of ~14).

Our study shows that the Red Layers deposited in the Black Sea and the Chocolate Clays deposited in the Caspian Sea between actual river terraces in the lower Volga and its middle basin, are the same kind of material. That confirms the interpretation concerning the origin of the Red Layers in the Black Sea (linked to the SIS meltwater) proposed by Soulet et al. (2013). Indeed, no connection between the catchment area of the River Volga and Ukrainian Shield exists, and the low values of εNd in the Caspian Sea Early Khvalynian sediments can only be explained by their origin close to the Baltic Shield and in relation with the SIS activity.

5.2.2. Sediments between 18.0 and 17.2 and between 15.7 and 12.0 cal kyr BP

Before the appearance of the Red Layers at 17.2 cal kyr BP, the neodymium isotopic compositions recorded in core MD04-2790 of the Black Sea, display values between ~12 and ~11 (Fig. 3g, data after Soulet et al., 2013). The same values are recovered after the Red Layers deposition at 15.7 cal kyr BP. Moreover from ~14.0 cal kyr BP onwards, they increase above ~11. The clay mineralogy for these two intervals recorded on core BLKS 98–11 is largely dominated by smectite that decreases after ~14.0 cal kyr BP but is still dominant until 12.0 cal kyr BP (Fig. 3f). In core MD04-2754, the smectite and illite show the same pattern before the Red Layers deposition. After their deposition, broadly equal proportions of smectite and illite are recorded (Fig. 3e). It should be noted that higher contents of chloride are present in this core on the whole.

As observed above, the content of smectite is much higher in core BLKS 98–11 (collected on a slope of the platform, in the near vicinity of the Danube and Dniepr mouths), than in core MD04-2754 (collected farther away from river mouths). This suggests that the principal source of smectite must be related to the activity of the Danube or Dniepr. Such European origin of the smectite in the Black Sea sediments is generally not considered. Indeed, Stoffers and Müller (1972) attributed smectite to an Anatolian origin where it is common (e.g. Tudryn et al., 2013b), and illite to an European origin, and this interpretation of clay minerals origin in the Black Sea sediments has been accepted so far (e.g. Major et al., 2002). In core MD04-2754, clay minerals changes until 15.7 cal kyr BP are similar to these described for core BLKS 98–11 (Fig. 3e,f), indicating the same main source area. After the Red Layers deposition, smectite increases while illite decreases. They present broadly similar contents between ~15.0 and 12.0 cal kyr BP. Contents of chloride are higher than before and than in core BLKS 98–11. This difference indicates the relative decrease of the previous source impact on this site, and the increased influence of another one: a southwestern or southern source area, probably Bulgarian or Anatolian, where Stoffers and Müller (1972) reported higher contents of chloride.

5.3. A Ponto-Caspian trap and the SIS deglaciation

Our work shows that during the last deglaciation, the Ponto-Caspian basin collected meltwater and fine-grained sediment transported from the southern margin of the SIS via the Dniepr and Volga Rivers. It resulted in the deposition of characteristic red-brownish/chocolate coloured illite-rich sediments that originated from Baltic Shield area. After that, smectite-rich sediments were deposited in the Caspian and Black Seas. This common general evolution for the two seas was nevertheless differentiated over time due to the specificities of their catchment areas and to the movement of the southern limit of the SIS.

The catchment area of the Black Sea reaches Northern Belarus, Southern Lithuania and Latvia through the Dniepr and Berezná basins. The deglaciation started there before 18.3 cal kyr BP with the recession of the Gruda phase ice sheet (Rinteknecht et al., 2008; Hughes et al., 2015) (Fig. 3h-2). According to some authors, Baltia, the youngest phase of the ice margin recession, finished at ~14 cal kyr BP and the recession steps were definitely terminated at ~13.3 cal kyr BP (Rinteknecht et al., 2008; Marks, 2015). Meltwater and the detrital material from this area was only partly supplied into the Black Sea between 17.2 and 15.7 cal kyr BP (Soulet et al., 2013; this study) (Fig. 3e,f,g). Another route for meltwater was towards the North Atlantic via ice-marginal valleys from the Baltic lowlands and the Channel River (Fig. 3h-1) dated between 18.2 and 16.7 cal kyr BP (Toucanne et al., 2015). Further ice-sheet readvance during the Baltia phase did not reach the northern limit of the Dniepr catchment area to produce the meltwater evacuation into the Black Sea during its recession.

The southern limit of the SIS margin in Russia cuts the actual catchment of the River Volga in the Lake Belaye, and probably even today’s reservoir Rybinsk area (Svendsen et al., 2004; Hughes et al., 2015; Stroeven et al., 2015), both are to the south of Lake Onega (Fig. 1). The maximal extend of the SIS there was attained around 20–18 kyr (Svendsen et al., 2004; Hughes et al., 2015), and after that at least four advances were identified (Fig. 3h-3). According to Svendsen et al. (2004), only the last one (the Neva, ~13 cal kyr BP) did not reach the River Volga catchment area: the Luga phase, i.e. the previous phase, began its recession after ~14.2 cal yr BP. Our study shows that this deglaciation timing from the LGM until ~14 cal kyr BP corresponds exactly with the supply of the Chocolate Clays (via River Volga) into the Caspian Sea as far as at least its middle basin during the Early Khvalynian transgression, and with its end recorded at ~13.8 cal kyr BP. Recent publications proposed that the SIS southeastern margin retreated to the north of Lake Onega before 14 cal kyr BP (Stroeven et al., 2015; Hughes et al., 2015). However our data indicate that it must have occurred slightly later, since the Caspian Sea was fed by meltwater until ~13.8 cal kyr BP.

As pointed out by Arslanov et al. (2015), the beginning of the Early Khvalynian transgression remains to be assessed. Indeed, according to radiocarbon dating on sediments collected from northern, shallow water basin of the Caspian Sea, it started at ~34 cal kyr BP (Rezrodyukh et al., 2015), or even possibly at ~56 kyr BP (Sorokin et al., 2014). These sediments present the Early Khvalynian sequence of several meters thick and offer the possibility for
future precise identification of Chocolate Clays (as those deposited in actual river terraces in the lower Volga and in the middle Caspian basin) there. According to Bezrodkynh et al. (2004, 2015), their upper part (8–10 m thick), is composed of clays with variable-thickness sand intercalations and was deposited at depths of approximately 100 m. $^{14}$C ages on mollusk shells display values such as –23.8 and –21.6 cal kyr BP. These ages are older than those obtained on mollusk shells and on organic matter from the Choc-
olate Clays in river terraces in the lower Volga (Leonov et al., 2002; Tudryn et al., 2013a; Makshaev and Svitoch, 2015; this study) but still correspond to LGM. In the Southern basin of the Caspian Sea, Late Pleistocene reddish sediments were reported and suggested to correspond to Chocolate Clays (Kroonenberg et al., 2010; Kakroodi et al., 2015). Further clay minerals and especially neodymium iso-
topes studies should allow the clear identification of this material as transported locally or supplied from the north until the southern basin of the Caspian Sea. Clay minerals and neodymium isotopes studies should also allow the identification of the nature and origin of Chocolate Clays deposited in the actual river valley in the lower Ural, described by Makshaev and Svitoch (2015).

Our data show different timings in the meltwater supply into two major areas of the Ponto-Caspian basin. They inform indirectly on the southern SIS margin extent in the East European Plain and on meltwater evacuation routes. In the western part the East Eu-
ropean Plain, both a westward release into the North Atlantic (be-
tween 18.2 and 16.7 cal kyr BP; Toucanne et al., 2015) and a southward one into the Black Sea (between 17.2 and 15.7 cal kyr BP) occurred (Soulet et al., 2013; this study). For the eastern part of the plain, apart from a northern direction into the Barents Sea ( Svendsen et al., 2004), only a southern direction into the Caspian Sea was possible, that led to the Early Khvalyan transgressive stage(s) from LGM until ~13.8 cal kyr BP (this study). According to Arslanov et al. (2015), the Early Khvalyan transgressive stages between 16 and 14 cal kyr BP reached the water level of ~22–35 m asl, and that resulted in the Caspian Sea water overflowing into the Black Sea through the Kuma-Manych Strait (22 m asl) during this time and even until ~12.8 cal kyr BP, when water level dropped so that it could not reach Kuma-Manych Strait. Our data from the Caspian Sea confirm the possibility of such timing. Nevertheless the cores studied here from the western Black Sea area show that clay minerals originating from the SIS basin were deposited between 17.2 and 15.7 cal kyr BP and also that they were transported by the River Dniepr. Cores were thus probably collected too far from Kuma-Manych Strait to record the overflow from the Caspian Sea through clay mineralogy after 16 cal kyr BP, or the over-
flow could happen concurrently with meltwater arriving into the Black Sea by the Dniepr River.

6. Conclusions

This work allowed establishment of the following conclusions: The Early Khvalyan transgressive stage of Chocolate Clays from the lower Volga and middle basin of the Caspian Sea consist essentially of illite. Very low $^{{36}}$Nd values for this sediment clearly identify its source in the Baltic Shield area, implying the melting of the SIS and transport of this detrital material into the Caspian Sea by fluvioglacial waters via the Volga River. The Early Khvalyan transgressive stage(s) leading to the Chocolate Clays deposition in the lower Volga and middle basin of the Caspian Sea took place during the deglaciation and possibly from the LGM. As recorded by sediments from the Caspian Sea (values of $^{{36}}$Nd, clay mineralogy and pollen signature), the Chocolate Clays deposition finished at ~13.8 cal kyr BP. At that time, the southeastern margin of the SIS has retreated back so far northward that the meltwater was no longer transported into the Caspian Sea. The cessation of fluvioglacial supply into the Caspian Sea resulted in the modification of the northern part of the River Volga catchment area and a proportionally increased influence from the drainage of East European Plains area, its part that is rich in smectite. Thus the latter became the dominant clay mineral in sediments after ~13.8 cal kyr BP.

Our results show that illite is the dominant clay mineral in the Red Layers deposited in the Black Sea between ca. 17.2 and 15.7 cal kyr BP, that these Red Layers and the Chocolate Clays from the Caspian Sea present the same kind of sediment, and confirm that Red Layers originated from the Baltic Shield area and were transported into the Black Sea from the southern SIS margin during the deglaciation by Dniepr River, as proposed Soulet et al. (2013).

Before the deposition of the Red Layers in the Black Sea (bet-
tween ca. 18 and 17.2 cal kyr BP) and after the deposition of the Red Layers/Chocolate Clays in both seas (from ~15.7 in the Black Sea and from ~13.8 cal kyr BP in the Caspian Sea), smectite became the dominant clay mineral until 12 cal kyr BP. The East European Plain is identified as the source for smectite deposited in the Caspian Sea sediments. In the Black Sea, smectite originated either from the East European Plain or from the Danube River catchment area. This is an important result since previous studies considered smectite as only being of Asian origin.

Our investigation shows that during the last deglaciation the Ponto-Caspian basin collected meltwater and acted as a trap for fine-grained sediment transported from the southeastern margin of the SIS via the Dniepr and Volga rivers. In the eastern part of the East European Plain, the supply of meltwater from the SIS margin into the Caspian Sea took place through the LGM and the subsequent deglaciation. That led to the Early Khvalyan transgressive stage(s) and so-called Chocolate Clays deposition on river terraces in the lower Volga and until at least the middle basin of the Caspian Sea. The meltwater supply stopped at ~13.8 cal kyr BP; this indicates that the southeastern SIS margin retreated so far north that the meltwater was no longer transported into the Caspian Sea. In the western part the East European Plain, both a westward release of meltwater into the North Atlantic (from ca. 20 to 16.7 cal kyr BP; Toucanne et al., 2015) and a southward one into the Black Sea (between 17.2 and 15.7 cal kyr BP) occurred (Soulet et al., 2013; this study).

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