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Palaeoclimate indicators (clay minerals, calcareous nannofossils, stable isotopes) compared from two successions in the late Jurassic of the Volga Basin (SE Russia)

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A study of clay mineral and calcareous nannofossil abundances in late Jurassic–early Cretaceous sediments from the Volga Basin, SE Russia, is presented. From these results, we are able to compare some general patterns of mineralogical and palaeontological change for the Volga Basin to the palaeoclimate models developed for northern Europe and beyond. The two successions examined comprise calcareous mudstones with black organic-rich shale horizons, overlain by a series of phosphatic silty sands. Clay mineralogical results show a progressive decrease in kaolinite and the concomitant increase of smectite and illite through the middle Volgian, followed by an abrupt increase in kaolinite in the late Volgian. The clay mineral evidence suggests increasing aridity at the end of the Jurassic, similar, in part, to many western European successions. Because of differential settling of clay minerals, superimposed upon this possible climatic signature is likely to be the effect of relative sea-level change. Calcareous nannofossil analysis from a single section reveals a shift through the middle Volgian from low nutrient, warm water assemblages dominated by *Watznaueria* to cooler surface water and high nutrient assemblages dominated by *Biscutum constans*. These observations suggest that increased aridity is also associated with climatic cooling. Black shales are associated with increased productivity, higher sea levels and increases in smectite content. Hence, periods of low (chemical) hinterland weathering during semi-arid conditions are paradoxically associated with relatively nutrient-rich waters, and organic-rich shales. Comparison of published carbon and oxygen stable isotope results from this and other sections to the clay mineral and nannofossil data confirms the palaeoclimatic interpretation. This study significantly improves the published biostratigraphically constrained clay mineral database for this time period, because other European and North American successions are either non-marine (and thus poorly dated), absent (through penecontemporaneous erosion) or condensed.

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KEY WORDS late Jurassic; palaeoclimate; clay minerals; calcareous nannofossils; stable isotopes

1. INTRODUCTION

Published sedimentological, clay mineral, microfossil, and stable isotope evidence from northern Europe suggests that relatively humid climates were prevalent during the Oxfordian–Kimmeridgian, late Valanginian and mid-Aptian (e.g. Deconinck *et al.* 1985; Hallam 1986; Ruffell and Batten 1990; Weissert and Mohr 1996; Wignall

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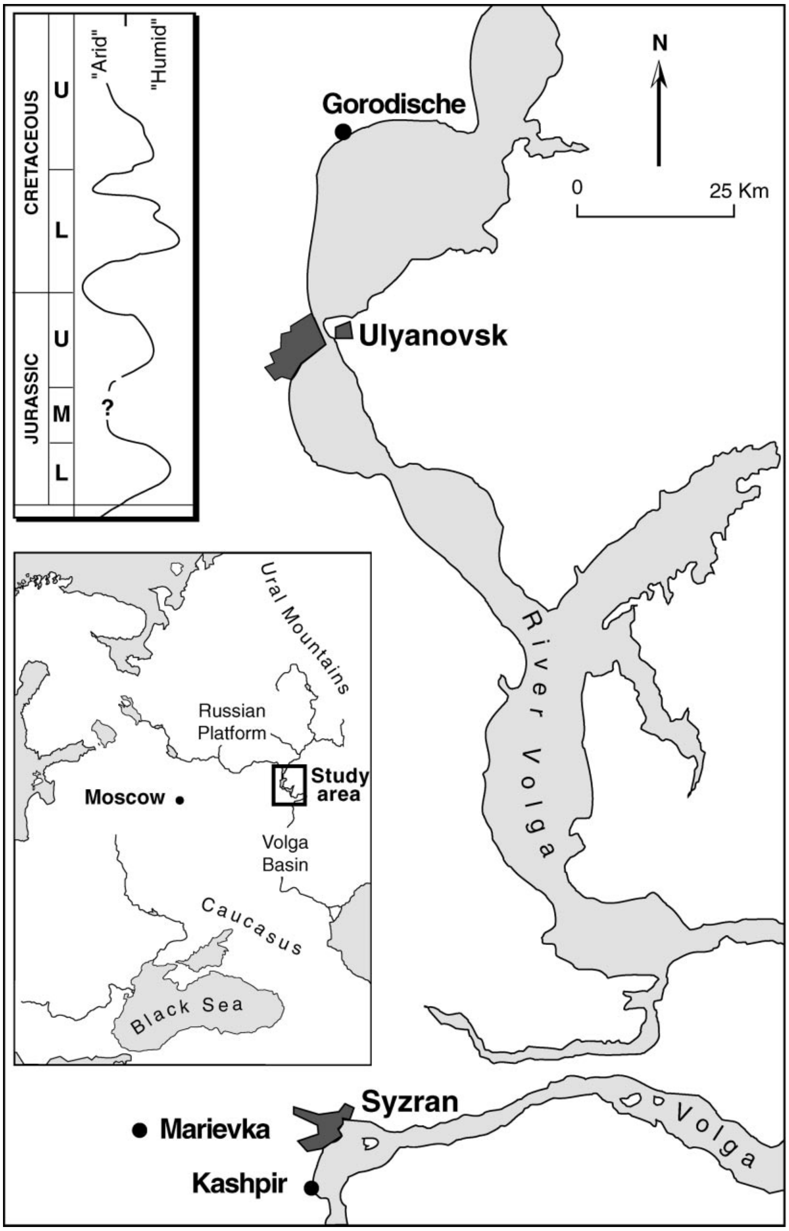

Figure 1. Location map of the Volga Basin showing the locations of Gorodische and Kashpir. Lower inset shows the location of the study area. Upper inset shows general palaeoclimatic trends for northwestern Europe through the Jurassic and Cretaceous.

and Ruffell 1990). Apparent increases in smectite clays and decreases in kaolinite, in conjunction with the occurrence of evaporite minerals, suggest that semi-humid phases were separated by more semi-arid periods, most typically in the late Kimmeridgian–late Ryazanian and Barremian–early Aptian in many areas of northern and western Europe (Hallam *et al.* 1991; Daoudi and Deconinck 1994; Frakes *et al*. 1992; Ruffell and Rawson 1994: Figure 1 (lower inset) shows location). The more humid periods have been tentatively correlated with climatic warmth, whilst semi-arid phases in the early Cretaceous have been correlated with cooling (e.g. Weissert and Lini 1991; Frakes *et al.* 1992; Price *et al.* 2000). These general observations depend on samples being derived from biostratigraphically well-defined horizons, represented by a few sections throughout the world. General circulation model (GCM) simulations of the Cretaceous (e.g. Price *et al.* 1998) suggest, however, that cool climate episodes do not necessarily result in a global increase in continental aridity. The overall trend of semi-arid conditions at the Jurassic–Cretaceous boundary and in the Barremian may be applied to many of the successions of the North Atlantic Rift and Tethys (Ruffell and Rawson 1994). However, minor variations are documented (Gröcke *et al.* in press), some of which are elucidated upon here.

The extent and therefore significance of Jurassic–Cretaceous arid conditions beyond the northwest European region and Tethys has, however, not been fully examined. Hallam (1986) suggests that Jurassic–Cretaceous aridity was the product of an orographic effect, induced by concomitant orogenesis at this time. He cites the documented tectonism of the Cimmerides as a possible candidate. Whilst tectonic activity is common at this time in many parts of the world, the Hallam (1986) model should only work in certain (orographic) areas. By contrast, Weissert and Mohr (1996) link Jurassic–Cretaceous aridity to the growth of carbonate platforms, records of negative $\delta^{13}C$ excursions and a general deceleration of the global carbon cycle. Weissert and Mohr's (1996) model should thus be global in its applicability. We use data similar to those utilized by Hallam (1986) and Weissert and Mohr (1996), as well as other authors, to test whether a palaeoclimate signal is observable through the late Jurassic of a section never before studied with these aims in mind.

It is the purpose of this paper to explore in detail clay mineral abundances through a late Jurassic–early Cretaceous succession from eastern Europe (Volga Basin, SE Russia). A concurrent analysis of calcareous nannofossils has also been undertaken. Calcareous nannofossils have been used to decipher the palaeoecological conditions of surface waters, in particular the availability of nutrients and palaeotemperature (Mutterlose 1996), both of which can be related to clay mineralogy. It has been identified that distinctive late Jurassic–early Cretaceous nannofossil assemblages were latitudinally bound, and in turn were partly controlled by temperature (Mutterlose and Ruffell 1999; Mutterlose and Kessels 2000). Thus there is independent evidence to analyse the palaeoclimatic sensitivity of the clay mineralogical patterns and this can be used to develop a more fully integrated model of regional palaeoclimate.

Gröcke *et al.* (in press) compared carbon, oxygen and strontium stable isotope analyses from pristine belemnites collected at the same horizons in this study to similar analyses made from late Jurassic sediments sampled in New Zealand. Their work demonstrated similar isotopic signatures in the two locations. We use the same data here, and compare these to the published isotope curves of Jones *et al.* (1994) and Price *et al*. (2000).

2. GEOLOGICAL SETTING

The Volga Basin is an area of intra-cratonic subsidence bounded to the south and west by the foreland of the Caucasus, to the east by the Urals and to the north by a gentle tectonic slope on to the Russian Platform (Figures 1, 2). The width of the basin varied through time (Baraboshkin 1997) and in the earliest Cretaceous was about 500 km east to west and over 2000 km north to south and located at a palaeolatitude of *c*. 40–45°N. Land areas may have existed to the southwest and northeast of the study area, with marine connections to the Boreal and Tethyan seas. The general succession is variable, with late Palaeozoic, Mesozoic and Cenozoic successions frequently preserved throughout the area. Intra-basinal 'highs' are common and these are thought to have provided some of the clastic sediment observed in the basin fill. Post-depositional burial of the Mesozoic rocks rarely exceeds a few hundred metres. The late Jurassic sediments examined are typical epeiric sea type deposits, with broadly similar stratigraphy and lithology extending for hundreds if not thousands of kilometres (Baraboshkin 1997). Thus rapid lateral changes in stratigraphy (and thus depositional environment) are not recorded.

Three late Jurassic–early Cretaceous outcrops were examined in the Volga Basin adjacent to the River Volga (Figure 1). The successions at Gorodische and Kashpir were found to be argillaceous, rich in belemnites and thus suitable for study. The section at Marievka is rich in quartz sandstones and carbonate and thus clay mineralogical analyses were not utilized from this section as diagenesis could be more prevalent. Belemnites from Marievka were incorporated into the parallel study to this work (Gröcke *et al.* in press) and the resultant data are used in our

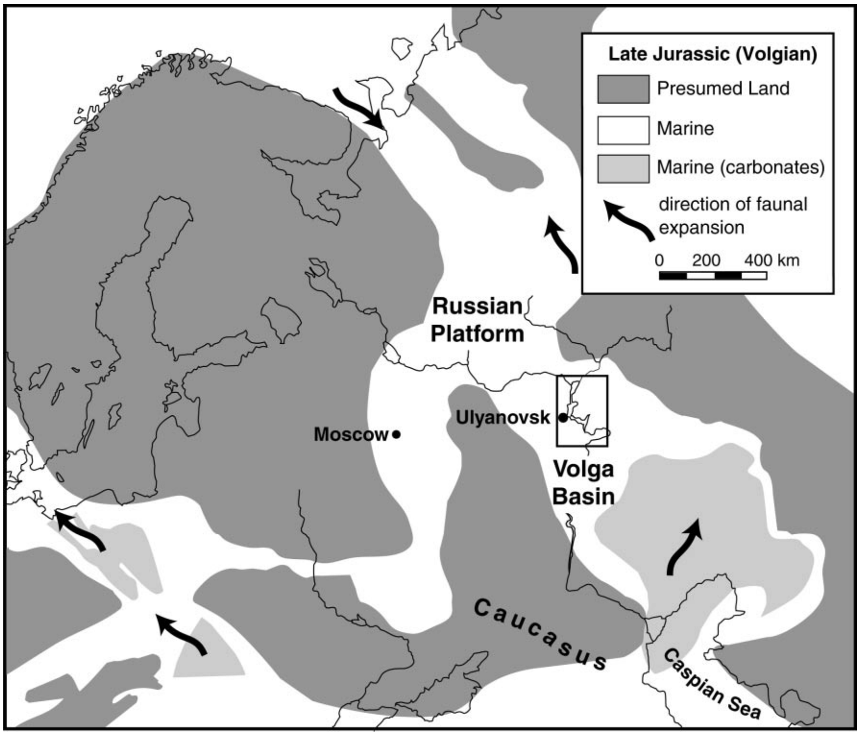

Figure 2. Palaeogeographic setting of the Russian Platform and Volga Basin during the middle Volgian (*Virgatites virgatus* ammonite Zone) (Sazanova and Sazanov 1967).

discussion. The early and mid-Volgian of the Volga Basin (Figure 3) corresponds to the Tithonian of parts of northern Europe, whilst the late Volgian is equivalent to the lower parts of the Berriasian (Casey *et al.* 1977; Hantzpergue *et al.* 1998). The succession studied at Gorodische village (25 km north of Ulyanovsk) represents the stratotype of the Volgian (Gerassimov and Mikhailov 1966). This succession comprises middle Volgian Dorsoplanites (*D. panderi*–Epivirgatites *E. nikitini* ammonite Zones), calcareous mudstones with four 0.5 to 1 m-thick black organic-rich shale horizons overlain by a thin (*c*.2 m) late Volgian Kashpurites (*K. fulgens*–Craspedil *C. nodiger* ammonite Zones) silty sand horizon with abundant phosphatic nodules. This highly fossiliferous succession includes belemnites, ammonites and bivalves (Kuleva *et al.* 1996; Hantzpergue *et al.* 1998). A number of palaeoenvironmental and climatic studies have been derived from this succession (e.g. Kuleva *et al.* 1996; Baraboshkin 1998; Riboulleau *et al.* 1998).

The Kashpir section is situated some 150 km south of the Gorodische type section (Figures 1, 5). The lowest exposed parts of the sedimentary succession comprise rhythmically bedded (pale) calcareous mudstones with intercalations of dark grey organic-rich shales. In contrast to the Gorodische succession, the shales are thinner (a few centimetres as opposed to decimetres). This lower part of the succession is dated on the basis of the ammonite fauna as middle Volgian (*D. panderi* Zone) and thus is the same age as the lower part of the Gorodische section. Our examination of the calcareous nannofossil assemblage also suggests a middle Volgian age (Figure 3). These mudstones and shales are overlain by a cross-stratified silty sand succession containing concentrations of reworked phosphatized fossil debris and abundant phosphatic nodule horizons (Figure 4). The age ranges seen in Figure 3 indicate that this part of the succession is latest Volgian to early Valanginian (Baraboshkin, personal observation, 1999). This scheme is broadly comparable with those of Casey *et al*. (1977), Shulgina (1985) and Hantzpergue *et al*. (1998), although Gerassimov (1969) suggests that much of this silty sand succession is late Volgian in age.

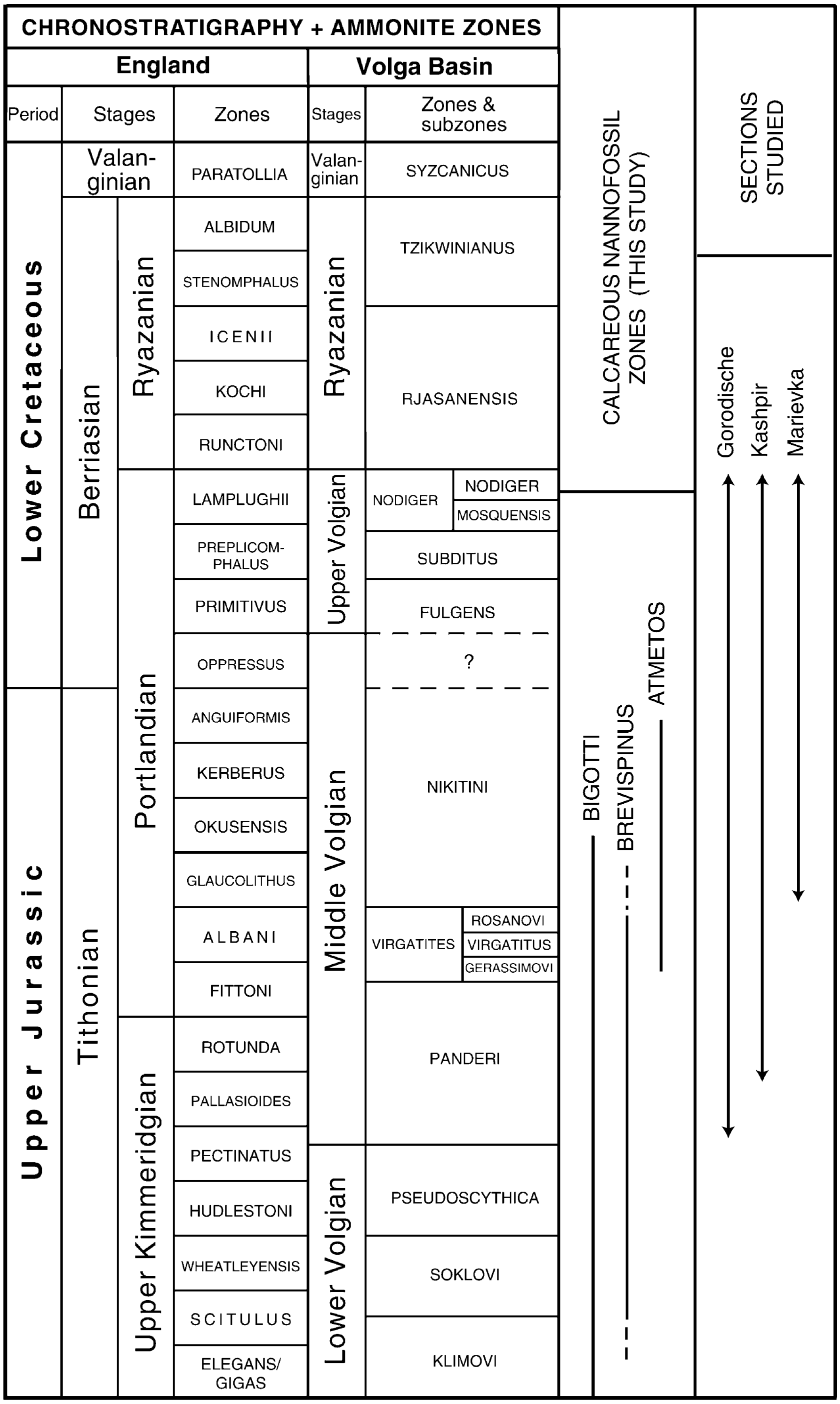

Figure 3. Comparison of ammonite biostratigraphy between England and the Volga Basins (Casey 1973; Casey *et al.* 1977; Hantzpergue *et al.* 1998). Nannofossil zones identified in this study and age ranges of the sections.

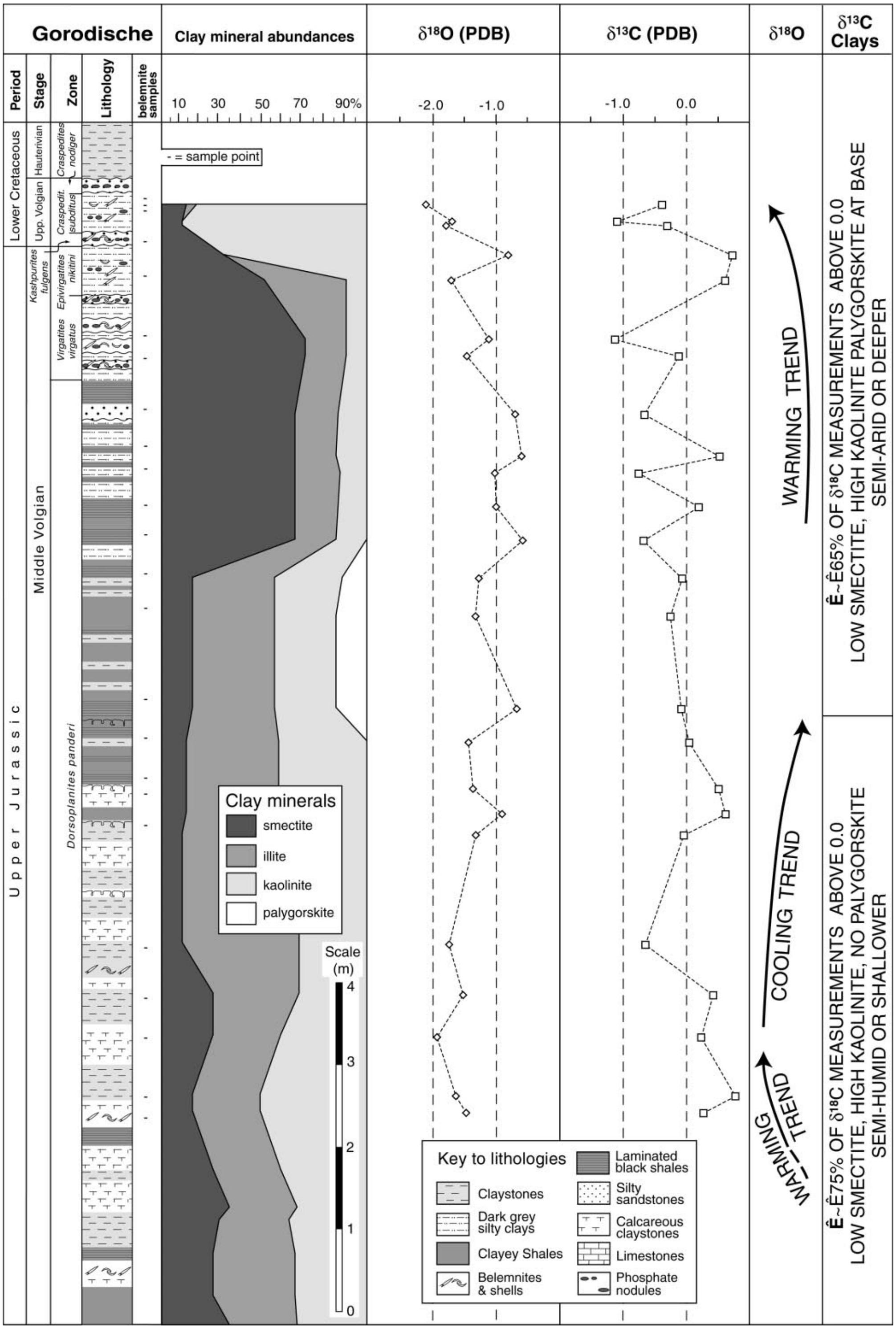

Figure 4. Clay mineral variation and interpretation during the late Jurassic–early Cretaceous interval at Gorodische. Generalized sedimentary log and biostratigraphy from field observations and data in Hantzpergue *et al.* (1998). δ^{13}C from Gröcke *et al.* (in press).

3. ANALYTICAL PROCEDURES

3.1. Clay mineralogy

Forty-two samples from Kashpir and 31 samples from Gorodische were analysed for their clay mineralogy. The preparation of clay samples for X-ray diffraction (XRD) analysis followed one of two procedures, for bulk rock (hand ground) and clay fraction analysis (after Tucker 1988). The results presented here are largely from the clay fraction analysis. Clay fractions were centrifuged (750 rpm, 3.5 min), air dried, glycolated and heated to 600°C. XRD was performed using a Siemens AS2000 machine using Cu radiation. Quantification of the results was made from bulk rock using the SIROQUANT package or Rietveld analysis (Bish and Post 1993). Clay fractions were measured using the formula of: kaolinite/2.5 + chlorite/2 + smectite + mixed-layer + illite = 100% (after Bish and Post 1993). Determination of the whole peak area between the smectite peak (*c.* 6°2theta) and the illite peak (*c.* 10°2theta) was made using the XRD trace of the air-dried slide. Thereafter, we separated the same area of the glycolized XRD trace into illite, smectite and mixed-layer peak areas, calculating the percentage proportions of these areas. Finally, calculation of the total peak-area proportions of the three minerals from the trace of the air-dried slide was made. These methods provide good statistical accuracy although the amounts of chlorite and mixed-layer minerals remain uncertain.

3.2. Calcareous nannofossils

A total of 110 samples from the Volga Basin sections were examined for calcareous nannofossils. A total of 58 samples at 2–6 cm intervals were evaluated from the pale–dark rhythms of the Kashpir section. This resulted in five to 19 samples for each lithological unit, depending on the thickness of individual beds. This sample density was significantly higher than the clay mineral samples. Simple smear-slide preparations were examined under the light microscope using a magnification of 1500×. The abundance of calcareous nannofossils in the late Jurassic material was variable. Calcareous nannofossils may constitute between 0% and 20% of the total rock. Abundances for each sample were gained by counting at least 300 specimens or all specimens in at least 200 fields of view. These analyses produced a very large dataset, unsuitable for full discussion in the context of this paper, although the main and relevant results are discussed below.

3.3. Stable isotopes

Isotopic analyses of belemnite specimens were carried out on a VG PRISM Series II mass spectrometer with an on-line common acid bath system at the University of Oxford. The $\delta^{18}O$ and $\delta^{13}C$ compositions are reported in per mil (‰) notation with respect to the Peedee Belemnite (PDB) international standard. Calibration of the isotopic results to PDB was achieved via a laboratory standard (Carrara Marble) calibrated against NBS19. Reproducibility for both $\delta^{18}O$ and $\delta^{13}C$ was generally better than $\pm$ 0.1‰, based upon multiple sample analysis. Elemental concentrations (Mn, Sr, Mg and Fe) were determined by inductively coupled plasma mass spectrometry (ICPMS) on *c.* 20 mg subsamples. Reproducibility, based upon replicate analysis, was estimated generally to be less than $\pm$10% of the measured concentration for Sr and Mg, and $\pm$ 25% for Mn and Fe.

4. RESULTS

4.1. Clay mineral variation

The clay mineralogical content of the two sections studied is similar, with smectite, illite and kaolinite dominating to varying degrees. The smectite peaks on XRD traces are sharp, suggesting a regular crystalline structure. Smectite increases in abundance through the middle Volgian in both sections (Figures 4, 5). This is most apparent in the Gorodische section where smectite increases quite abruptly in the middle of the black shale-dominated part

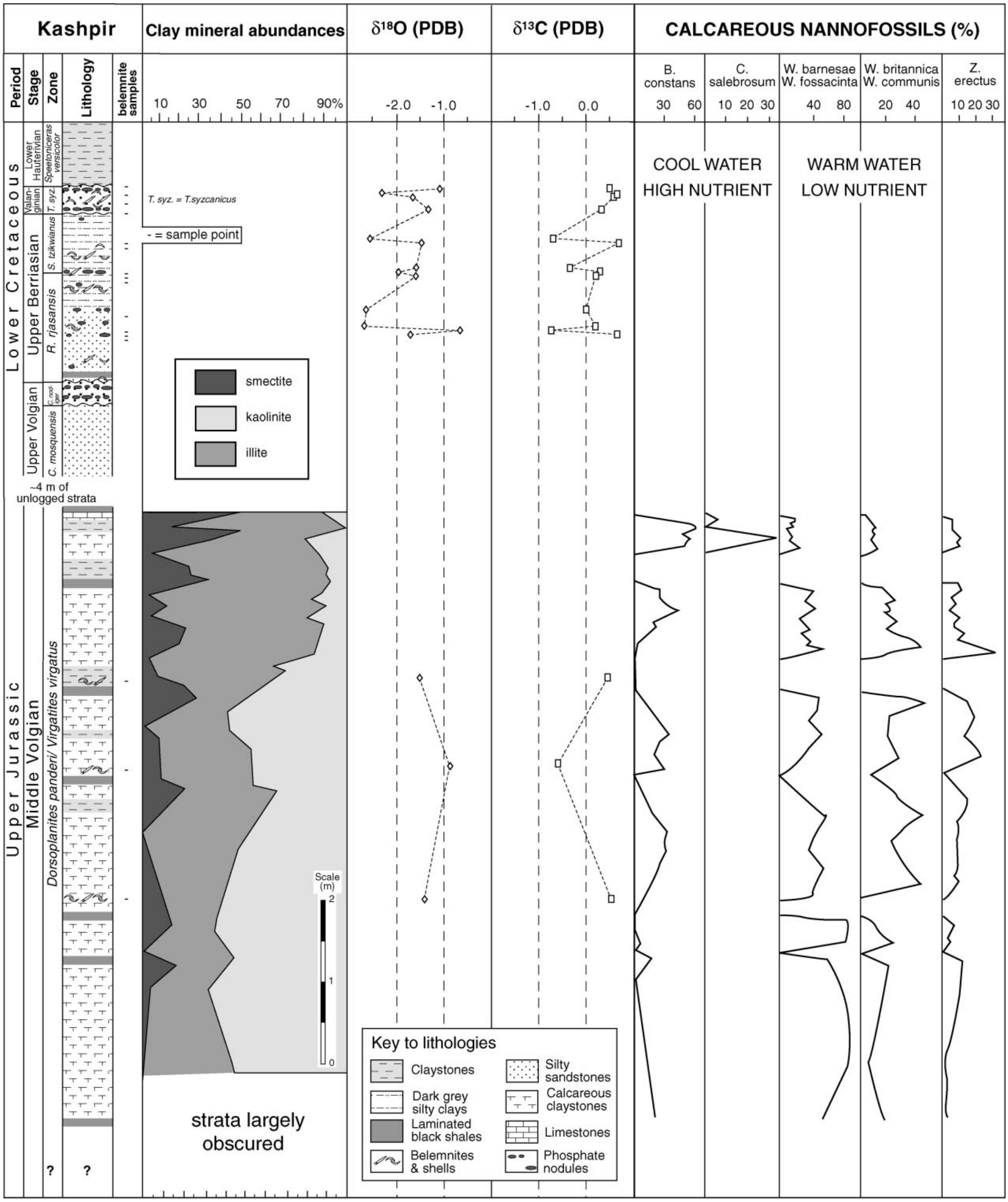

Figure 5. Clay mineral and calcareous nannofossil variation during the late Jurassic–early Cretaceous interval at Kashpir. Generalized sedimentary log and biostratigraphy from field observations and data in Hantzpergue *et al.* (1998). $\delta^{13}C$ from Gröcke *et al.* (in press).

of the succession (mid-*D. panderi* Zone). A sharp increase in kaolinite occurs in the late Volgian at Gorodische. In the Kashpir section, pale–dark rhythms are very apparent, where black shales and dark clays contain more smectite than the pale clays. Illite shows more variation between the two sections studied, decreasing (at the expense of smectite) in the Gorodische section and increasing (at the expense of kaolinite) in the Kashpir section. Kaolinite behaves in a similar manner in both sections, decreasing into the middle Volgian. Also notable is the presence of the clay mineral palygorskite in the Gorodische section. This mineral appears in the middle of the black shale succession and its disappearance is concomitant with the sudden increase in smectite and decrease in kaolinite.

4.2. *Calcareous nannofossil variation*

The presence of *Ethmorhabdus gallicus* throughout both successions allows an assignment to the *E. gallicus* nannofossil Zone (NJ 17b; Bown and Cooper 1998), which corresponds to the *D. panderi* ammonite Zone. The calcareous nannofossils have Boreal affinities, confirming observations made by Bown and Cooper (1998). The calcareous mudrock beds at Kashpir (Figure 5) yield a well-preserved rich and diverse nannoflora, dominated by Watznaueriaceae. The most common species include *Watznaueria barnesae*, *W. britannica*, *W. communis*, *W. fossacincta*, *Zygodiscus erectus* and *Biscutum constans*. All six black shale beds are essentially barren of calcareous nannofossils although occasional heavily etched specimens of *W. barnesae* occur. These observations clearly suggest a diagenetic overprint in the black shale horizons, causing dissolution of calcareous nannofossils and leaving only a few heavily etched and overgrown (dissolution resistant) placoliths. The composition of the assemblages from calcareous mudrocks shifts from *Watznaueria*-dominated to *B. constans*-dominated assemblages in the uppermost part of the Kashpir section. *B. constans* constitutes up to 50% of the overall abundance. These horizons also show an elevated number of *Crucibiscutum salebrosum*.

4.3. *Stable isotopes*

Petrographic and scanning electron microscope analyses reveals that the belemnites were mostly translucent and retained the primary concentric banding that characterizes belemnite rostra. A number of samples, particularly those obtained from the silty sand horizons, were partially weathered (especially around the margins) and frequently displayed partial replacement by phosphate preferentially along the concentric growth bands.

Trace-element variation has consistently been employed as a technique to identify primary biogenic calcite. The measured concentrations of Mn in our material are in the range 3–205 ppm; Mg 431–1951 ppm; Sr 634–1718 ppm; and Fe 7–1131 ppm. Based upon the study of modern organisms, relatively low concentrations of Mn (<100 ppm) and Fe (<200 ppm) generally occur in molluscan shell carbonate (e.g. Milliman 1974). Such studies indicate that Sr and Mg is more variable and occurs in much higher concentrations. Similarly, trace-element abundances have been widely used in conjunction with belemnite isotopic palaeothermometry (e.g. Jones *et al.* 1994; Ditchfield *et al.* 1994; Price *et al.* 2000) and reveal that high concentrations of Fe and Mn are commonly associated with relatively negative δ^{18}O and δ^{13}C values indicative of diagenetic alteration. Although no such trend was observed in this study, where Fe and Mn values exceeded 200 and 100 ppm respectively, these isotopic results were excluded from the generation of a palaeotemperature curve. It is of note that the highest Fe and Mn values recorded are derived from those belemnites obtained from the silty sand horizons, an observation that is consistent with poor preservation observed in hand specimen. The low Mn and Fe values consistently recorded for most of the belemnites from all localities are consistent with minimal diagenetic alteration.

The belemnites display a comparatively small range of δ^{18}O values (-2.49 to -3.01‰ at Gorodische and -2.45 to -3.34‰ at Marievka). δ^{13}C values also show a moderate degree of stability through the sections analysed and plot near to 0‰ in the middle Volgian. However, in the Early Cretaceous the δ^{13}C values show much more variation ranging from $+1$ to -1‰. This variations is most likely the result of the early Cretaceous sequences being more condensed than the late Jurassic.

5. DISCUSSION

5.1. Clay mineral evidence: this section compared to others

The analysis of clay mineral assemblages from marine successions can provide detailed information reflecting weathering processes on adjacent continental areas and, hence, provide significant palaeoclimatic information (Ruffell and Batten 1990; Sellwood and Price 1993). Complications in using clay minerals as climatic indicators include differential settling; for example, kaolinite and illite tend to be deposited in shallow water settings. Additionally, under conditions of increased burial, clay diagenesis becomes prevalent. For example, smectite converts to illite via an intermediate stage of mixed-layer minerals (Nadeau *et al.* 1985). The distribution of detrital clay minerals within clay-rich, shallow-buried marine sediments can thus be regarded as reflecting provenance, sediment sorting and weathering processes on the adjacent continental areas. Declines in the relative amounts of kaolinite and increases in smectite are considered to be the result of transgressive conditions or increases in aridity and a 'drying out' of the continental source area. Detrital illite (the white mica of Jeans (1978)) is often prevalent in mudrocks. Illite is often thought to be the product of physical erosion dominating in the hinterlands (Ruffell and Batten 1990).

The observed increase in smectite clays (and palygorskite) through the middle Volgian section at Gorodische may suggest therefore either transgressive conditions or an increase in aridity in the hinterlands. The origin of the palygorskite is worthy of some discussion. In the modern environment this mineral forms in desert soils and is commonly found in red-bed successions that are devoid of kaolinite (Jeans 1978). The presence of this mineral in the Russian successions is notable in that a proximal land source is not known from palaeogeographic reconstructions (Figure 2). The presence of palygorskite may indicate either long transport paths or the existence of hitherto unknown proximal landmasses in the late Jurassic of the Volga Basin. The economic interest in black shales in the basin has resulted in extensive exploration programmes: thus the palaeogeography is well-known and a proximal land-source unlikely (Sazanova and Sazanov 1967). If positively linked to a phase of aridity, then it is possible that the palygorskite was wind blown. A return to more humid conditions and near-shore deposition in the late Volgian is possible as kaolinite becomes the dominant component of the clay fraction.

The increase in illite and to a lesser degree smectite and concomitant decrease in kaolinite observed in the middle Volgian of Kashpir (Figure 5) also suggests an increase in relative sea level or aridity during that time. Furthermore, to the south of the Volga Basin in the Caspian region (Figure 2), extensive evaporite deposits of late Jurassic age are known (Baraboshkin 1999). An areal expansion of this evaporite-forming environment took place from the middle to late Volgian and separated the Volga Basin from Tethys (Baraboshkin 1999). The changes in clay mineral assemblages appear to correlate well with observations regarding an increase in aridity towards the end of the Jurassic. Although published clay mineral data often indicate a wide variety of clay assemblages around the Jurassic/Cretaceous boundary, depending mainly on local sedimentary environments, a decrease in kaolinite contents and increase in smectite is commonly recorded at several localities in western Europe and North Atlantic successions (Daoudi and Deconinck 1994; Deconinck *et al.* 1985; Hallam *et al.* 1991; Wignall and Ruffell 1990).

The differential settling of clay minerals, superimposed upon any climatic signature, is likely to be the effect of relative sea-level change. Major changes in relative sea-level have been interpreted by Sahagian *et al.* (1996) for the comparatively tectonically quiescent Russian Platform and Siberia. These authors describe a sea-level rise, punctuated by a series of sharp falls throughout the Callovian to mid-Volgian. The increase in both thickness and occurrence of argillaceous units through the middle Volgian at Gorodische and Kashpir may also be indicative of a relative rise of sea-level. At both sites the clay-dominated units are overlain by phosphatic silts and sands (Figures 4, 5). These exhibit various features indicating they have been generated by more than one phase of phosphogenesis and condensation including complex internal small-scale unconformities, scour marks, and beds of amalgamated reworked phosphatized fossil debris. Major occurrences of condensed phosphorites have been associated with periods of sea-level rise (Arthur *et al.* 1985), although Föllmi (1996) highlights that subsequent reworking and concentration of phosphatic particles into phosphorites could occur during subsequent sea-level falls. The broader picture from the rest of southern Europe (Baraboshkin 1999) suggests overall regressive conditions through the latest Jurassic. The local (this study) and regional evidence for a sea-level fall would be compatible with increased kaolinite deposition. Instead, we observe the gradual disappearance of this clay mineral species; the opposite trend to the observed declines in the relative amounts of kaolinite and increase in smectite during transgressive conditions. Further, we note that the increase of kaolinite at Gorodische during the late Volgian is concurrent with the change to arenaceous sedimentation, indicating greater hydrodynamic energy, and possibly shallower conditions. Kaolinite is known to be preferentially deposited in near-shore conditions as it flocculates and may be of larger crystal size than other clay minerals (Jeans 1978).

5.2. Calcareous nannofossil evidence: this section compared to others

The analysis of calcareous nannofossils from the Kashpir section yielded a number of distinct trends that aid the interpretation of possible controls upon clay mineral distributions. The occurrence of *W. barnesae* is compared to the occurrence of kaolinite within the succession. *W. barnesae* is a cosmopolitan species, which is dissolution resistant and hence high abundances of this species are indicative of a diagenetic overprint (Roth and Krumbach 1986; Mutterlose 1996). Furthermore, it is an ecologically robust species which is often the first to settle new niches (Mutterlose 1991) and has also been considered to indicate low-nutrient (Erba *et al.* 1992) and warmer surface waters (Mutterlose and Kessels 2000). A shift from assemblages dominated by *Watznaueria* to assemblages dominated by *Biscutum constans* (and elevated numbers of *C. salebrosum* and *Z. erectus*) is observed in the uppermost part of the Kashpir section. This change is mirrored in a decrease in kaolinite, noted above. Both *B. constans* and *Z. erectus* have been interpreted to be taxa indicative of upwelling, cool surface water and high nutrient supply (Roth and Krumbach 1986; Erba *et al.* 1992; Mutterlose and Ruffell 1999). Likewise, Mutterlose (1996) suggested that *C. salebrosum* was also adapted to cool waters. Such observations lend credence to the interpretation that increasing aridity was associated with concurrent climatic cooling influencing the clay mineral assemblages. Albeit limited, the isotopically derived palaeotemperature estimates of Riboulleau *et al.* (1998) derived from the Volga Basin also suggest variable but cooling trends during this interval. Similar postulated increases in aridity during the early Cretaceous have also been tentatively correlated with a cooler climate (e.g. Weissert and Lini 1991; Frakes *et al.* 1992). Results from GCM studies of the middle Cretaceous (Price *et al.* 1998) suggest that cool climate episodes do not necessarily result in a global increase in aridity whilst continental soil moisture is controlled by evaporation and precipitation, which in turn are not controlled solely by temperature. Price *et al.* (1998) demonstrated that although during globally cooler conditions continental aridity was likely to decrease in lower latitudes, in more temperate and higher latitude regions moist soil areas would contract considerably.

The apparent cyclicity seen in the nannofossil assemblages (Figure 5) is considered to be a direct result of a preservational bias. At Kashpir black shales are observed to become thicker with a notable decrease in vertical spacing through the examined part of the succession. The gradual increase in black shales occurs as high-nutrient-related and cool-water nannofossils appear (Figure 5). Such observations may suggest that the deposition of the black shales is productivity driven, although increased erosion and hence nutrient transfer from the continents to oceans would normally be expected to occur during periods of enhanced chemical weathering in a warm and humid environment (e.g. Weissert and Mohr 1996). Such a scenario would be expected to produce increased levels of kaolinite, whereas at Kashpir the opposite in fact occurs: organic-rich shales are associated with increases in smectite and therefore the proposed high productivity may not be runoff related. Furthermore, if increases in smectite are considered as a result of transgressive conditions, the black shales may have been deposited in deeper conditions permitting suppressed oxidation and destruction of organic matter. We interpret the Volgian sediments studied here as an overall shallowing-up succession with higher-order transgressive pulses depositing black shales (lower part) and reworking phosphate nodules (higher part).

5.3. Stable isotope evidence (published, from this section and others)

Samples of pristine belemnites were taken from the same stratigraphic horizons as the clay and nannofossil samples used in this study. The results (Gröcke *et al.* in press) are placed alongside our data (Figures 4, 5) as they form an integral part of our argument for palaeoclimatic change. The isotope data also add to the database for this time period in Europe as well as aiding the correlation of Tethyan and Boreal stratigraphies.

Weissert and Mohr (1996) have compiled a carbonate carbon isotope stratigraphy for the late Jurassic. Their $\delta^{13}C$ curve is marked by one major positive carbon isotope excursion during the middle to late Oxfordian and a second minor positive excursion during the Kimmeridgian. The observed decrease in kaolinite and increase in illite and smectite clays through the Volgian occurs at the same level as a fall in $\delta^{13}C$ (Gröcke *et al.* in press) and correlates in part with lower $\delta^{13}C$ values observed by Weissert and Mohr (1996). We agree with Weissert and Mohr's (1996) findings that it is positive carbon-isotope excursions that are likely to be associated with enhanced chemical weathering in a warm and humid climate. An association of organic-rich units at both Gorodische and Kashpir with relatively low $\delta^{13}C$ values is also in agreement with Weissert and Mohr (1996) who suggest that episodes of enhanced organic carbon burial during the Kimmeridgian and early Tithonian were not reflected by prominent positive excursions in the C-isotope record. High rates of preservation of organic carbon are usually linked to carbon isotope excursions since organic carbon is preferentially enriched in the lighter isotope ^{12}C, and therefore its removal from the ocean reservoir renders the ocean waters relatively enriched in ^{13}C. Weissert and Mohr (1996) suggest that carbon release from weathering more or less equalled carbon burial and carbonate production during this time and hence steady $\delta^{13}C$ values were maintained. The growth of carbonate platforms is especially pertinent to both Weissert and Mohr's (1996) model as well as this study. The late Jurassic succession in the Tethys Ocean was characterized by the dominance of coral–algal and mollusc-bearing limestones. The widespread occurrence of these limestones was linked by Hallam *et al.* (1991) and Weissert and Mohr (1996) to an increase in arid conditions at this time.

5.4. Discussion of palaeotemperatures and palaeoprecipitation

Assuming that the isotopic compositions of the belemnites do represent primary marine values, a number of assumptions regarding the palaeotemperature of the Volga Basin during the late Jurassic–early Cretaceous may be made. Calcite palaeotemperatures for this section are recorded in Gröcke *et al.* (in press). However, the results are very pertinent to this study and are discussed below.

At Gorodische the oxygen-isotope data show a gradual shift to being more positive from the base to the top of the mid-Volgian (Figure 4) and are thus consistent with a cooling trend. A rapid shift to more negative values (and hence warmer temperatures) is observed in the Upper Volgian. Additional results from the latest Volgian–earliest Ryazanian at Kashpir and Marievka also indicate warmer palaeotemperatures, but reveal a considerably wider range of values, alluding to somewhat fluctuating palaeoclimatic or palaeoenvironmental conditions during this time, accentuated by irregular sampling in each location. Such a fluctuating trend has been identified from a number of other sedimentological and faunal studies (e.g. Frakes *et al.* 1992).

The temperatures observed in this Volgian interval (16 to 18°C) are similar to those calculated from the stable-isotope analysis of late Jurassic belemnites from East Greenland (palaeolatitude, 45° to 50° north; Bowen, 1966) and are considerably warmer than those calculated by Ditchfield (1997) who suggests a possible palaeotemperature range of 5.3–10.4°C for the Tithonian–Valanginian based on endemic belemnites from Svalbard (palaeolatitude 65° north). It is likely there was approximately 25° of latitude between the Volga Basin (40° north) and Svalbard during the latest Jurassic. Using such values would provide a gradient of *c.* 0.4°C for every degree of latitude, which if extrapolated to northern polar regions may suggest sub-freezing temperatures in those regions.

The change from warming to cooling trends in the *panderi* Zone of the two main Volga Basin sections studied is coincident with a shift to negative $\delta^{13}C$ values (Figure 4). The end of the cooling trend, in the mid-*D. panderi* Zone is coincident with the final disappearance of kaolinite and the palygorskite influx (Figures 4 and 6). Based on this vertical resolution, cool climates appear to occur at the same time as arid climates and light carbon isotope values. The warming trend that is evident through the rest of the Middle Volgian (*virgatites*, *virgatites nikitini* Zones) has its peak in the early Upper Volgian, when kaolinite appears once again in the section. Thus warming and humid climates appear to be coincident, although a continued fall toward negative $\delta^{13}C$ values does not conform to the model. In the Tethys, $\delta^{13}C$ does start to become more positive in the Berriasian (Ryazanian equivalent of this section: see Figure 6), which we would anticipate in the Ryazanian of the Volga sections studied.

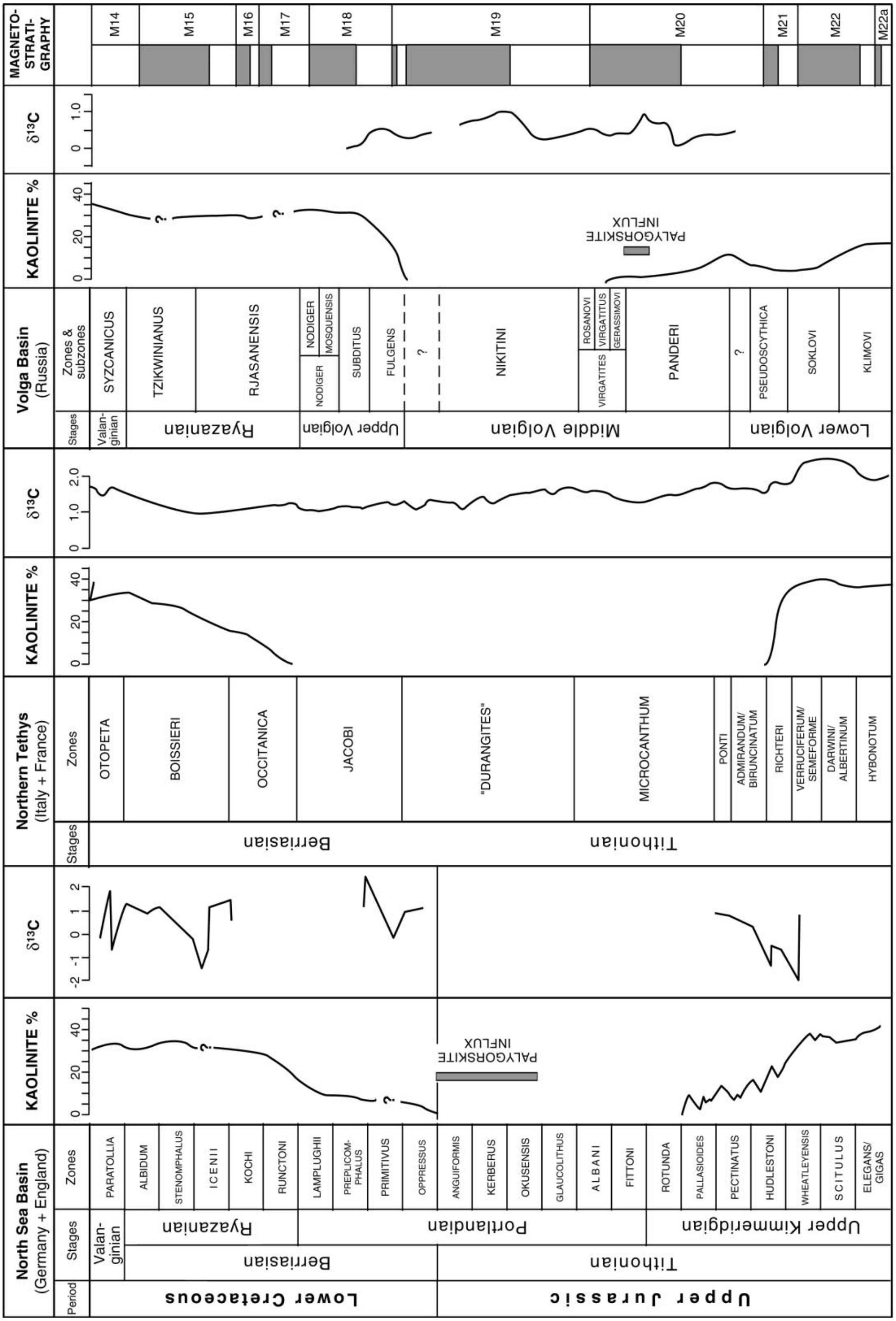

Figure 6. Comparison of kaolinite percentage (estimates) with generalized $\delta^{13}C$ values from this succession and two key areas of Europe. North Sea Basin data after Wignall and Ruffell (1990), Allen (1998), Hallam *et al.* (1991), Gröcke (2001), Jones *et al.* (1994) and Price *et al.* (2000). Northern Tethys data after Deconinck *et al.* (1985), Hallam *et al.* (1991), Weissert and Lini (1991) and Weissert and Mohr (1996). Volga Basin after Gröcke *et al.* (in press) and this study.

6. CONCLUSIONS

6.1. General

Late Jurassic palaeoclimates in NW Europe have previously been examined using sedimentary facies, palaeontology, mineralogy (especially clay mineralogy) and stable isotopes (Hallam 1986; Sellwood and Price 1993; Weissert and Mohr 1996). Since the Jurassic–Cretaceous Boreal succession of the Volga Basin is over 1000 km to the east of the European sections, our data significantly extend the comparable database. Clay mineralogical results from the two successions examined show a progressive decrease in kaolinite and the concomitant increase of smectite and illite through the middle Volgian. Only in the late Volgian does kaolinite become the dominant component of the clay fraction. The data suggest that during the late Jurassic, parts of the Volga Basin were characterized by semi-arid climates, extending the widespread view (Allen 1998) that this arid or semi-arid episode was at least regional in extent. Because of differential settling of clay minerals, superimposed upon this possible climatic signature is likely to be the effect of relative sea-level change. In addition, the data we have collected, as well as those of Gröcke *et al.* (in press), allow a significant gap in our data on Jurassic–Cretaceous climates to be filled. Currently, there is extensive clay mineralogical data from late Jurassic and early Cretaceous successions throughout Europe (Hallam *et al.* 1991) and North America (Schudack 1995). However, in nearly all cases, problems exist in the correct interpretation of the data. In southern England, France, Germany, Spain and North America, the Jurassic–Cretaceous is represented by non-marine red-beds and limestones (the 'Purbeck' facies; Allen 1998), making correlation to global ammonite or microfossil biostratigraphic schemes problematic. In the North Sea, the Jurassic–Cretaceous is represented either by an unconformity, multiple unconformities or condensed beds with no appropriate clay-bearing units.

6.2. Specific

The Kashpir section preserves an excellent nannofossil assemblage. Calcareous nannofossil analysis reveals a shift through the middle Volgian from low-nutrient, warm-water assemblages dominated by *Watznaueria* to cool surface water and high-nutrient assemblages dominated by *Biscutum constans*. These observations suggest that locally, increased aridity is also associated with climatic cooling. Through this middle Volgian succession we also observe an increase in the thickness and occurrence of black shales which correlate (approximately) with an increase in smectite and an increase in productivity-related nannofossils. The association of low (chemical) hinterland weathering during semi-arid conditions with nutrient-rich waters and organic-rich shale deposition still requires explanation. The controls upon deposition of organic-rich shales are interpreted to be a combination of high (marine) productivity and sluggish circulation that was more or less synchronous with greater aridity in the hinterlands. Whilst the entire black shale–mudstone succession represents an overall shallowing-up environment, individual black shale horizons may have been preserved through higher-order transgressive pulses or increased water depths. The final questions then are: when did these events take place, where did they take place and what was their effect?

6.3. The timing of late Jurassic palaeoclimate change

The first indications of a palaeoclimate change are in the late Jurassic throughout Europe. Figure 6 summarizes the evidence. In the North Sea Basin, through Germany and in southern England, kaolinite begins its dramatic fall in abundance through the *hudlestoni* Zone (note that Kimmeridgian Zones of the United Kingdom are considered biochronozones and thus some authors suggest they should not be italicized: see Wignall and Ruffell (1990) for explanation and also discussion of clay mineralogy). The scant carbon isotope evidence at this stratigraphic level suggests that positive values are still present (Jones *et al.* 1994). Kaolinite disappears completely in the rotunda Zone (Hallam *et al.* 1991). The reappearance of kaolinite is poorly dated, this part of the succession being either strongly condensed (North Sea, eastern England) or in non-marine facies (southern England, Germany: Ruffell and Rawson 1994). Palygorskite is present just below what is thought to be the Jurassic–Cretaceous boundary (Allen

1998). In the heart of the Tethyan successions (southern France, northern Italy), kaolinite is absent throughout the *richteri* Zone of the Tithonian, some time before this clay mineral is absent in the North Sea and UK successions (Deconinck *et al.* 1985). A dramatic fall in carbon isotope values just prior to this in the *verruciferum/semiforme* Zone (Weissert and Mohr 1996), suggests that if clays and carbon isotopes are sensitive to climate change, then the carbon isotopes reacted more quickly. The Tethyan reappearance of kaolinite is in the early Berriasian, concomitantly with a rise in δ^{13}C (Figure 6). In the successions studied here, kaolinite is still present in the middle Volgian, a long after it became absent in the North Sea, southern England and France: paradoxically, palygorskite is also present in the middle Volgian, in association with kaolinite and long before its appearance in southern England. Kuleva *et al.* (1996) also presented some clay mineralogical analyses from these sections and showed the appearance of kaolinite in the *fulgens* Zone (Figure 6). The δ^{13}C curve displays overall more negative values but maintains a similar trend to the Tethyan successions, just as Gröcke *et al.* (in press) demonstrated for their correlation of these data with New Zealand.

This study confirms and significantly extends the overall patterns of palaeoclimate change developed for more northern areas of Europe. The study also shows the diachroneity of clay mineral changes. There may be a lag time effect in the transport of clays from the hinterland, which could be different from basin to basin. The diachroneity may also be in the timing of the climate change itself as the modifiers of climate (temperature, global circulation, local circulation) may all take effect to different degrees at different times. Conversely, the widespread nature of the nannofossil, clay mineral and isotopic changes shows that a linked palaeoclimate–circulation change did take place. The nature and distribution of this climate change can be further elucidated by analysing palaeotemperature proxies from the polar Arctic and by analysing all palaeoclimate proxies from the Jurassic–Cretaceous of the southern hemisphere.

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