

Alteration of detrital Fe-Ti oxides in Miocene fluvial deposits, central Jutland, Denmark

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Miocene fluvial sands from an outcrop at Voervadsbro in central Jutland were studied to assess the Fe-Ti oxides and their alteration products forming during a warm, humid climate and under the influence of scattered organic material. The opaque minerals and their alteration products were investigated by optical light microscope, reflection microscope, microprobe, scanning electron microscope and X-ray diffraction. The detrital Fe-Ti oxides consist of, in decreasing order, ilmenite, titanomagnetite, magnetite, rutile, hematite and silicified leucoxene. Degradation of organic matter created mildly reducing and neutral-acid conditions under which the Fe-Ti oxides (ilmenite, titanomagnetite, magnetite and hematite) were unstable. Ilmenite has a three-step alteration process: ilmenite → pseudorutile → fine leucoxene → coarse leucoxene (single crystals of rutile or anatase). Alteration of titanomagnetite commonly resulted in coarse leucoxene in a trellis texture. Alteration of ilmenite lamellae in titanomagnetite is typically complete, probably because of their small size compared to ilmenite grains. Colloidal leucoxene is an alteration product of ilmenite and titanomagnetite. The formation of colloidal leucoxene seems to be related to organic matter or elements associated with it. Magnetite has been partly dissolved, preferentially around the rim and along fissures. Hematite is rarely a detrital grain due to intensive dissolution, and the exsolution lamellae of hematite are invariably more altered than the ilmenite host. Oxidising conditions prevailed locally e.g. in coarse-grained foresets without organic material and at the atmospheric interface of bogs. In this environment dissolved iron (originating from the alteration of Fe-Ti oxides) precipitated mainly as goethite.

Keywords: Alteration, Fe-Ti oxides, ilmenite, pseudorutile, leucoxene, colloidal leucoxene, titanomagnetite, hematite, Miocene, Odderup Formation, fluvial sands, organic material, warm temperate - subtropical climate.

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Titanium-bearing minerals are of major interest as potential exploitable ores. The degree of alteration of Fe-Ti oxides is important since it increases the titanium content in the minerals, thereby decreasing the extraction costs. Furthermore, the alteration products of Fe-Ti oxides are important environmental indicators, and as such they have been used for uranium and petroleum exploration (Yurkova 1970; Prozorovich 1970; Adams *et al.* 1974; Reynolds & Goldhaber 1978).

The purpose of this paper is to describe the different Fe-Ti oxides present in Miocene fluvial deposits in central Jutland, Denmark (Fig. 1), the alteration processes, that were active after deposition, and the alteration products of different detrital Fe-Ti oxides formed in a warm, humid climate under the influence of scattered organic material.

Geological setting

During the Cenozoic there was a large basin in the north-western part of Europe: the North-west European Basin. This basin was flanked to the north-east by the Fennoscandian Shield and the Baltic Platform, to the south by the Variscan Massif and to the west by the Pennine Highs and the Scottish Highlands (Fig. 1; Bijlsma 1981; Ziegler 1987, 1990). The North-west European Basin consisted of the North Sea Basin and the North German-Polish platforms (Bijlsma 1981; Ziegler 1990). The Baltic River System supplied material from the Fennoscandian Shield and the Baltic Platform to the basin (Bijlsma 1981). In the Miocene, central Jutland was consequently the site of braided fluvial and lacustrine deposition (Rasmussen 1961; Hansen 1985; Weibel 1993). These deposits are referred

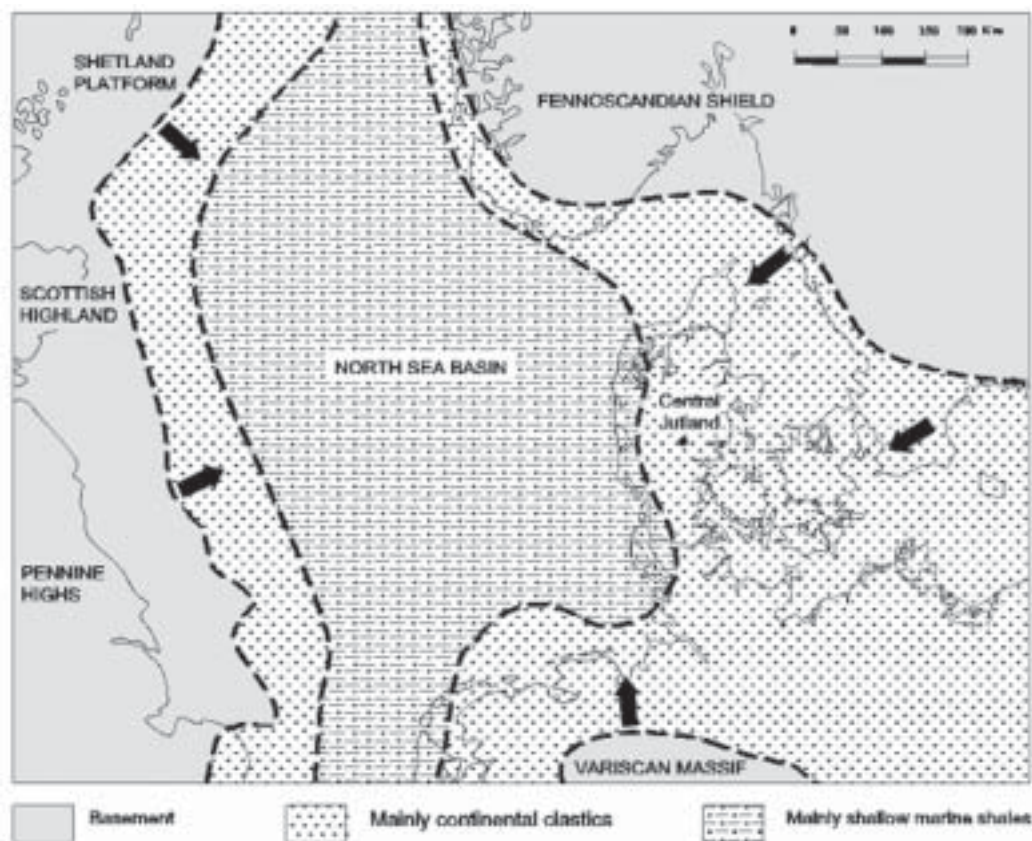


Fig. 1. Simplified palaeogeographic map of the North Sea region in Middle Miocene (modified after Bijlsma 1981; Ziegler 1987, 1990). Location at Voervadsbro indicated by a dot.

to the Middle Miocene Odderup Formation (H. Friis 1976; Hansen 1985; B. Eske Koch, personal communication 1993). The main source area was probably the south-eastern part of the Fennoscandian Shield (H. Friis 1973, 1974) which agrees with the overall dispersal pattern towards the south-west (Spjeldnæs 1975; H. Friis 1978).

Climatic and floristic investigations of deltaic-coastal sediments in the western part of Jutland (Søby-Fasterholt area) indicate a warm temperate to subtropical climate during the Miocene (Koch *et al.* 1973; E.M. Friis 1975, 1979). Molluscan investigations of the marine sediments in the southern part of Jutland showed surface water temperatures comparable with the north-western part of the Iberian peninsula – approximately 5°C higher than today (Sorgenfrei 1958). This is in agreement with other paleo-temperature investigations (Buchardt 1978; Nilsson 1983).

Sampling and methods

Two fining-upward successions are represented in the 40 m deep sand pit at Voervadsbro, central Jutland, Denmark. The sediments consist mainly of large-scale

tabular cross-bedded medium to coarse-grained sands. Some of the most coarse-grained foresets have a notable reddish colour. The lowest succession is terminated upwards by silt, with root traces, and capped by a lignite layer. Small remnants of organic material are ubiquitous in the deposits, and at one level makes up a lignite layer of approximately 0.9 m. *In situ* placed petrifying stems are found in the layer immediately above the lignite layer. A total of 22 samples were collected, generally at intervals of 3.5 m, but with more intense sampling in the proximity of the lignite layer.

Heavy-minerals were separated from other components in the sediments by sieving and fractionating in sodium polywolframate ($\text{Na}_6(\text{H}_2\text{W}_{12}\text{O}_{40})$) with a specific gravity of 2.90 g/cm³. Polished thin sections of these heavy-mineral concentrations were examined by polarised transmitted light microscopy, whereas reflected light microscopy was used for polished blocks. The present investigation is mainly based on optical microscopy but was supplemented by microprobe, scanning electron microscopy and X-ray diffraction determinations.

Six polished thin sections were selected for microprobe investigation of ilmenite, pseudorutile and leucoxene. Electron microprobe analyses were carried out on a JEOL® JXA-8600 at 15–20kV, 1nA and with a fo-

cused beam. Selected heavy-mineral concentrates of 10 samples were mounted on blocks, platinum coated and investigated by microprobe and a JEOL® JSM-840 scanning electron microscope (SEM). In order to obtain information on the mineralogy of leucoxene, selected heavy-mineral concentrates of 4 samples were crushed, mounted in holders and scanned on a Philips® PW 3710 automated X-ray diffractometer (XRD) with an automatic divergence slit using graphite monochromated CuK α radiation.

Results

Degree of alteration of Fe-Ti oxides

Fe-Ti oxides might be subject to alteration or weathering in the source area and during transport to the sites of deposition (e.g. Riezebos 1979). It is difficult to prove that all the Ti-alteration products described in this paper were formed *in situ*. Several of the altered grains, though, have a very fragile texture that would probably disintegrate mechanically during transport. The alteration zone in homogeneous detrital grains commonly has a constant thickness, suggesting that alteration occurred after abrasion of the grain ceased, i.e. after deposition. In addition, detrital grains are commonly altered along exsolution lamellae, twin planes, cracks and other zones of weaknesses. These differences in the detrital grains inherited from the source rock have resulted in different degrees of alteration of mineralogically similar grains.

Table 1. Alteration products of different Fe-Ti oxides.

Opaque mineral	Ti-alteration products	Other alteration products
Ilmenite	pseudorutile → fine leucoxene → coarse leucoxene	dissolved Fe goethite coatings
	colloidal leucoxene	dissolved Mn
Titanomagnetite	fine leucoxene → coarse leucoxene in trellis texture	dissolved Fe goethite coatings
	colloidal leucoxene	
Hematite		dissolved Fe goethite coatings
Magnetite	dissolved Fe	goethite coatings

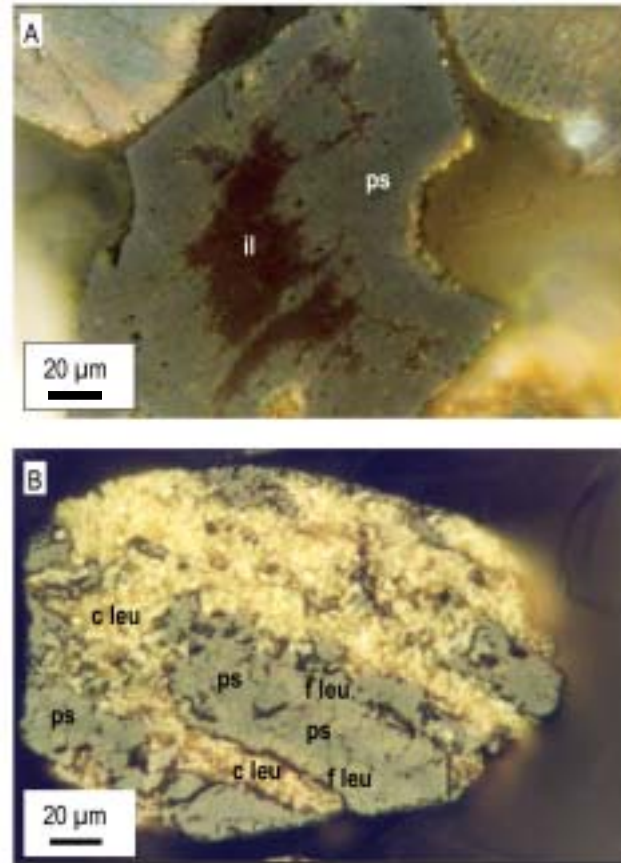


Fig. 2. A. Detrital ilmenite core (il) with a thick rim of pseudorutile (ps). The fairly constant thickness of the pseudorutile rim indicates that alteration occurred after deposition. Reflected light, oil immersion, crossed nicols. B. Completely altered detrital ilmenite showing three stages of alteration. The first alteration product is pseudorutile (ps; innermost grey cores). The second is fine leucoxene (f leu; yellow dotted rim around the grey cores), and the third is coarse leucoxene (c leu; individual yellow-white crystals). The parallel orientation of the least altered areas indicates crystallographic control from the parental ilmenite grain. Reflected light, oil immersion.

Detrital Fe-Ti oxides and their alteration products

Ilmenite

The alteration of ilmenite has resulted in three successive stages: pseudorutile, fine leucoxene and coarse leucoxene (Table 1). Leucoxene is a ubiquitous alteration product in the Voervadsbro sediments, and is actually more common than original ilmenite-grains. Pseudorutile is, on the other hand, rare, as its alteration generally continued until leucoxene was formed. In some cases the end product of ilmenite alteration is colloidal leucoxene. Colloidal leucoxene mainly occurs immediately below the top soil and the lignite layer.

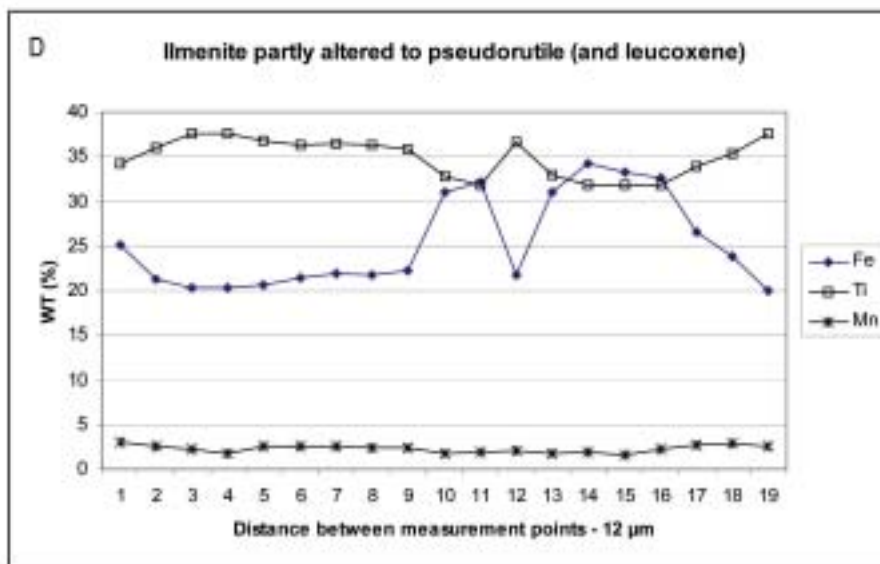
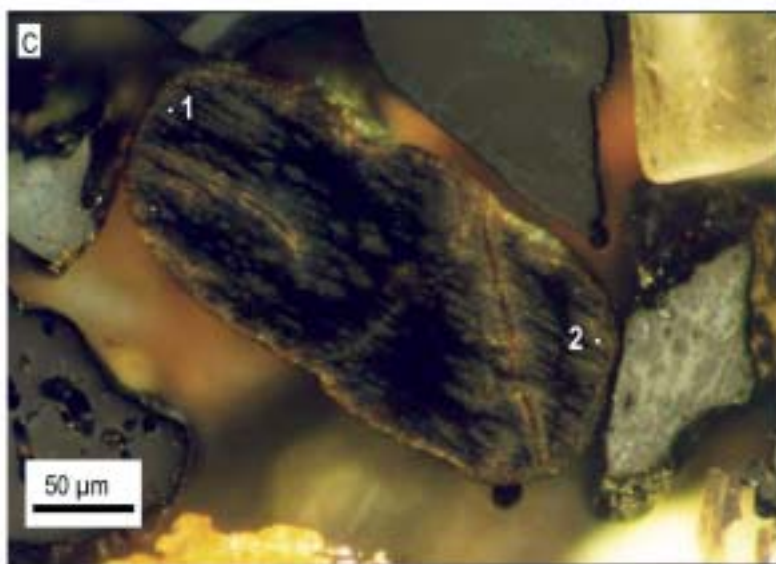
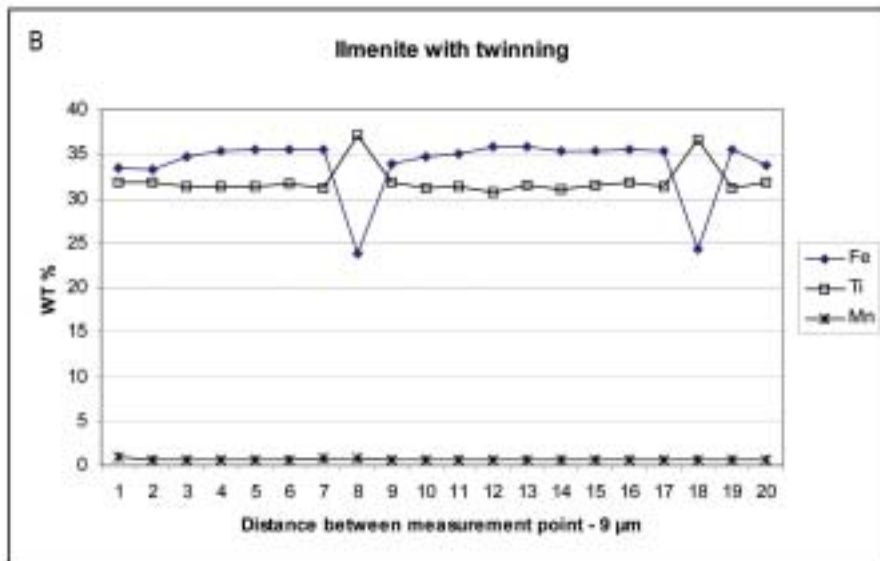
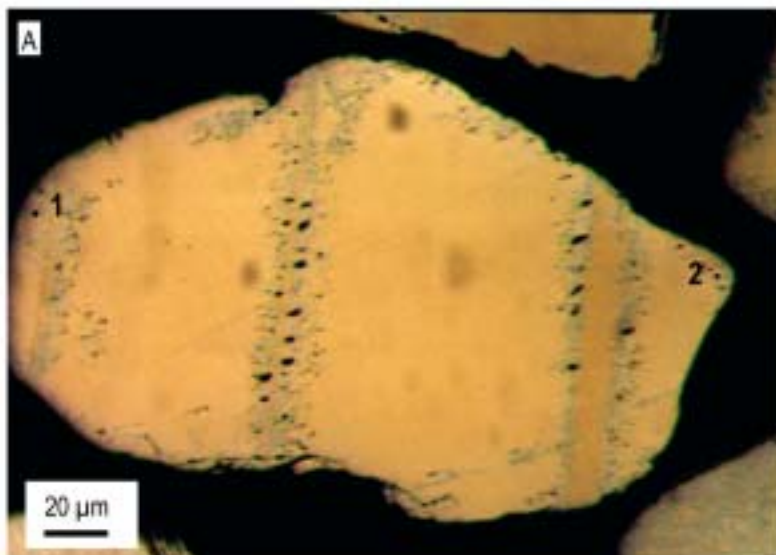


Fig. 3. A. Detrital ilmenite with beginning alteration to pseudorutile along twin planes. Points and numbers indicate the location of the line scan in Fig. 3B. Reflected light, oil immersion. B. Microprobe analysis as line scan (1–2) of the detrital ilmenite grain illustrated in Fig. 3A. C. Detrital ilmenite partly altered to first pseudorutile and second to leucoxene. The alteration begins at the rim and along fissures, and proceeds along crystallographic zones of weakness. Points and numbers indicate the location of the line scan in Fig. 3D. Reflected light, oil immersion, crossed nicds. D. Microprobe analysis as line scan (1–2) of the detrital ilmenite grain illustrated in Fig. 3C.

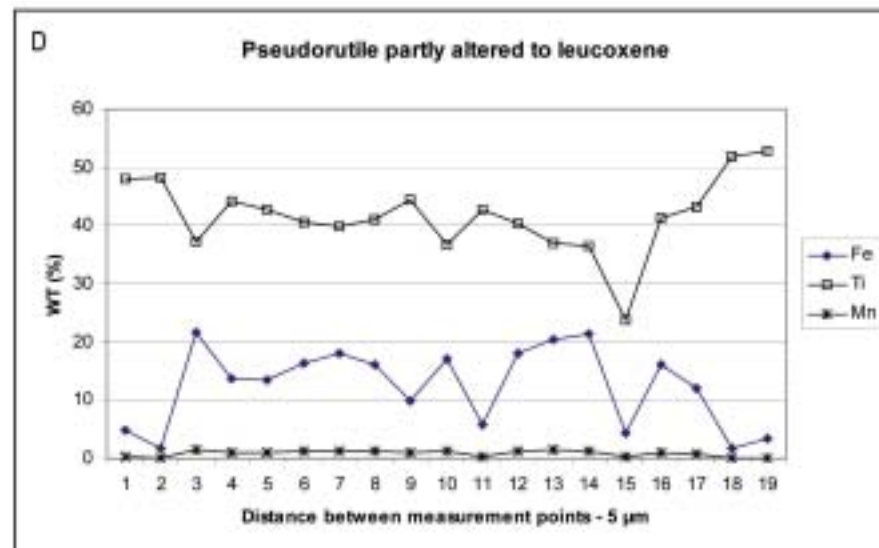
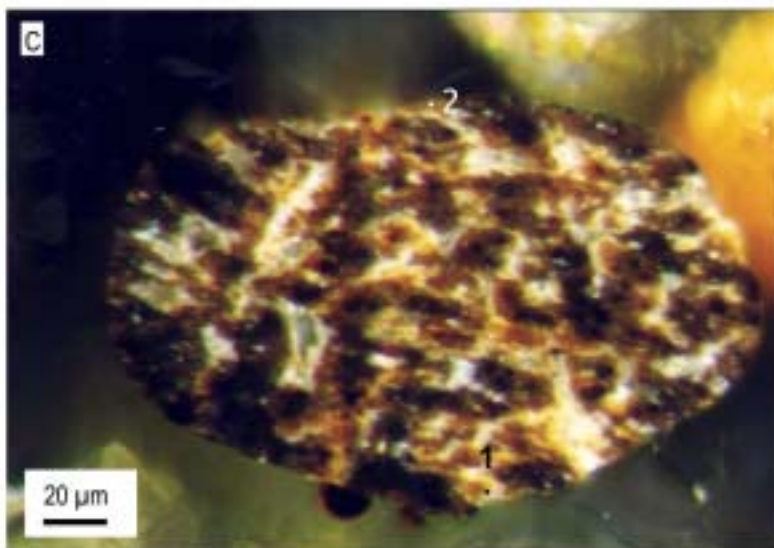
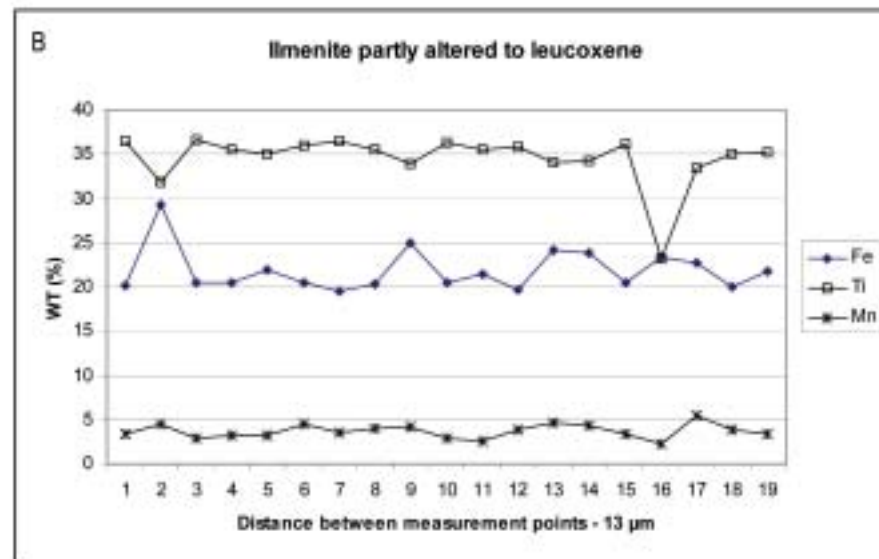
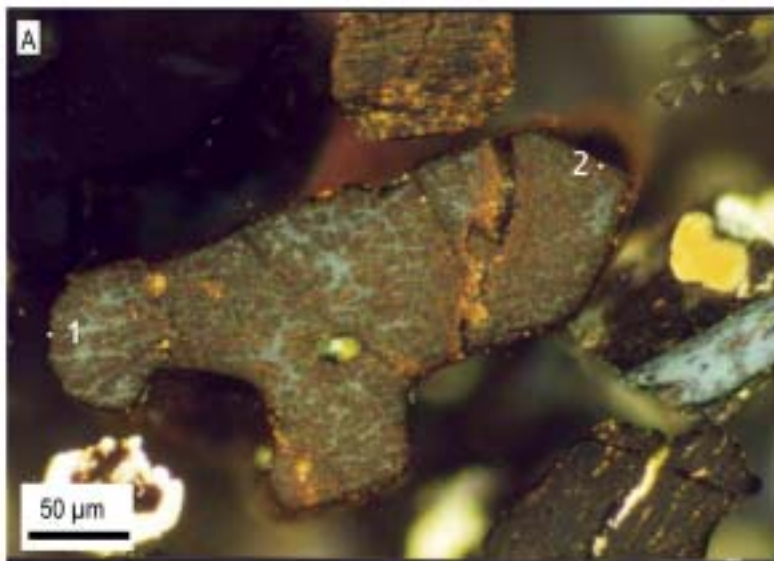


Fig. 4. A. Detrital ilmenite with scattered alteration to fine leucoxene, especially along crystallographic zones of weakness. Points and numbers indicate the location of the line scan in Fig. 4B. Reflected light, oil immersion, crossed nicols. B. Microprobe analysis as line scan (1–2) of detrital ilmenite grain illustrated in Fig. 4A. C. Pseudorutile altered to fine leucoxene. Points and numbers indicate the location of the line scan in Fig. 4D. Reflected light, oil immersion, crossed nicols. D. Microprobe analysis as line scan (1–2) of the pseudorutile grain in Fig. 4C.

Pseudorutile

Pseudorutile is an intermediary alteration product of ilmenite with the chemical composition: $\text{Fe}_2\text{O}_3 \cdot n\text{TiO}_2 \cdot m\text{H}_2\text{O}$ ($3 < n < 5$, $1 < m < 2$) (Grey & Reid 1975; Temple 1966). In the deposits at Voervadsbro, pseudorutile can be recognised optically from its grey isotropic nature with low reflectivity, no bi-reflectance and no internal reflections. Homogeneous ilmenite grains are commonly rimmed by pseudorutile that generally has a constant alteration depth (Fig. 2A). Most ilmenite grains are altered to pseudorutile along fissures, cleavage planes, twin planes or other crystallographic weaknesses (Figs 2B, 3A, 3C). The alteration of ilmenite to pseudorutile results in lower Fe-contents and constant or higher Ti-contents (Figs 3B, 3D).

Fine leucoxene and coarse leucoxene

Leucoxene is a cryptocrystalline, titanium-rich (generally $< 70\% \text{TiO}_2$) alteration product of titanium-bearing minerals (Lynd *et al.* 1954; Bailey *et al.* 1956; Golding 1961; Temple 1966; Dimanche & Bartholomé 1976; Riezebos *et al.* 1978; Morad & Aldahan 1986; Hugo & Cornell 1991; Mücke & Chaudhuri 1991). Two types of leucoxene have been observed in the Voervadsbro deposits: fine leucoxene, which is cryptocrystalline, and coarse leucoxene, which consists of individual TiO_2 crystals larger than $1 \mu\text{m}$. Traditionally, the name of the appropriate polymorph (rutile, anatase or brookite) is used for single TiO_2 crystals larger than $1 \mu\text{m}$, but in several cases it is not possible to distinguish between rutile and anatase. The term 'coarse leucoxene' has consequently been used in this paper.

Leucoxene alteration of ilmenite commences after the pseudorutile alteration around the rims and penetrates along fissures and cleavage planes (Figs 3C, 4A). In reflected light leucoxene is mainly identified by its bright white, yellow, orange or red internal reflections that can commonly be observed without crossed nicols in oil immersion. Fine leucoxene and coarse leucoxene occur as secondary and ternary alteration stages of ilmenite, respectively. When all three alteration stages are present, pseudorutile makes up the innermost part of the grain, followed by a mantle of fine leucoxene, which is rimmed by coarse leucoxene (Fig. 2B). Scattered leucoxene alteration of ilmenite results chemically in a small increase in the titanium-content and a decrease in the iron content, similar to the pseudorutile alteration (Figs 3D, 4B). Intense alteration into leucoxene, however, substantially increases the titanium-content (Figs 4C, 4D). Both rutile and anatase have been identified as 'coarse



Fig. 5. A. Fine leucoxene replaced by coarse leucoxene, here identified as anatase crystals. Reflected light, oil immersion, crossed nicols.

B. Fine leucoxene replaced by coarse leucoxene, here identified as rutile. Reflected light, oil immersion.

leucoxene' (Figs 5A, 5B), but their optical similarities commonly make distinction impossible. The crystals in coarse leucoxene may be randomly distributed, though some have similar orientations, probably controlled by the crystallography of the phase being replaced (pseudorutile or ilmenite). XRD of heavy mineral concentrations interpreted by Rietveld refinement (described by Mumme *et al.* 1996) supports the presence of anatase and rutile in the leucoxene and the absence of brookite (Svend Erik Rasmussen, personal communication 1995). The morphology of partly altered ilmenite grains is characterised by dissolution voids in which small TiO_2 crystals have precipitated, whereas leucoxene-dominated grains occur with an irregular mesh of TiO_2 crystals (Figs 6A, 6B).

Colloidal leucoxene

Colloidal leucoxene is grey with a greenish tint at low magnification and a lower reflectivity than that of the other leucoxene types. The internal reflections are bright white; yellow or orange, similar to the other leucoxene types, but some have blue internal reflections. Optically colloidal leucoxene resembles anatase more than any other TiO_2 polymorph, except for its greenish tint and reddish internal reflections. But the optical appearance of colloidal leucoxene might be influenced by the minute size of the individual crystals. Colloidal leucoxene is characterised by irregular, colloform banding and zoning surrounding remnants of ilmenite, titanomagnetite, rutile and voids (Figs 7A, 7B). Unlike fine and coarse leucoxene, colloidal leucoxene never replicates the crystallography of the parent detrital mineral. There is always a well-defined boundary between unaltered detrital relicts and colloidal leucoxene, and there is rarely trace of an earlier alteration stage.

Titanomagnetite

The alteration of titanomagnetite results in fine and coarse leucoxene with a trellis texture, and in colloidal leucoxene (Table 1).

Coarse (and fine) leucoxene in trellis texture

Titanomagnetite occurs as a magnetite host with ilmenite lamellae arranged parallel to the (111) plane of the magnetite i.e. in trellis texture. During alteration the magnetite host is dissolved and the ilmenite lamellae are altered to coarse leucoxene orientated in a trellis texture (Figs 6C, 7C). The alteration of ilmenite to leucoxene is most likely contemporaneous with the magnetite dissolution. The intermediary phase, pseudorutile has not been observed as an alteration product of the ilmenite lamellae in titanomagnetite, and fine leucoxene occurs only rarely.

Colloidal leucoxene

Alteration of titanomagnetite and ilmenite to colloidal leucoxene results in products that are very similar in appearance and have been described together above.

Magnetite

Magnetite occurs sporadically in all part of the Voervadsbro sediments. Alteration of detrital homogeneous magnetite occurs as several dissolution voids

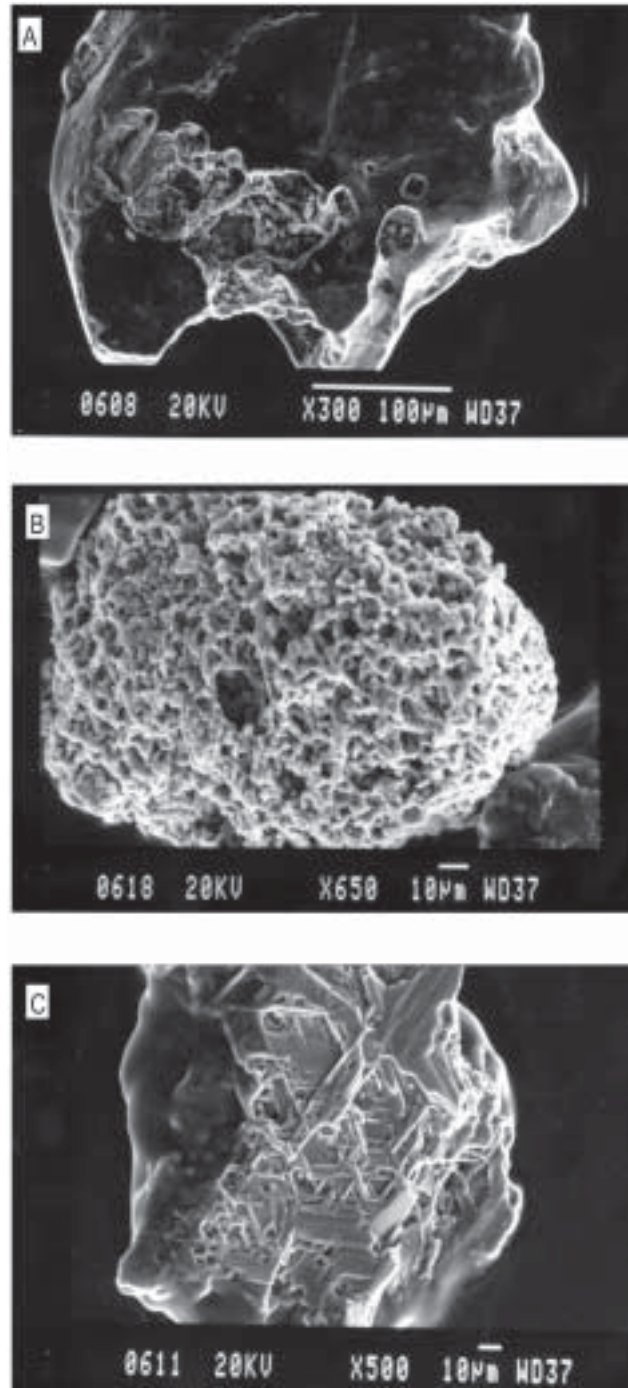


Fig. 6. A. Detrital ilmenite with dissolution voids, rimmed by coarse leucoxene. Scanning electron micrograph. Bar scale 100 μm .
B. Detrital ilmenite completely altered to fine and coarse leucoxene. Scanning electron micrograph. Bar scale 10 μm .
C. Detrital titanomagnetite altered to coarse leucoxene in trellis texture. Scanning electron micrograph. Bar scale 10 μm .

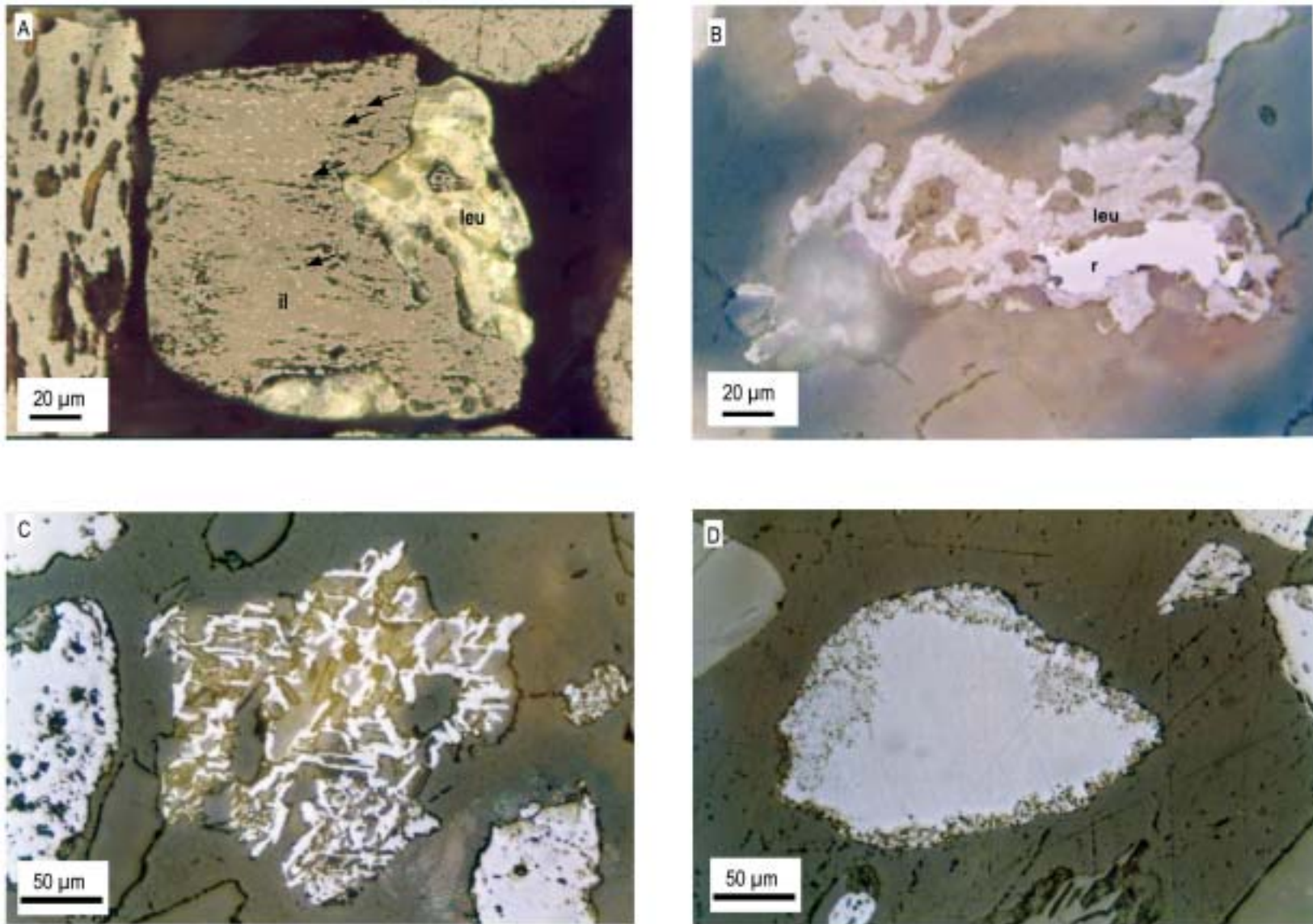


Fig. 7. A. Detrital ilmenite with exsolution lamellae of hematite. Hematite exsolution lamellae roughly in line with elongated dissolution voids (arrows) indicate an intense dissolution of hematite. The ilmenite (il) is partly replaced by colloidal leucoxene (leu). Reflected light, oil immersion. B. Detrital rutile (r) replaced by/surrounded by colloidal leucoxene (leu). Reflected light, oil immersion. C. Detrital titanomagnetite altered to coarse leucoxene in trellis texture. Reflected light, oil immersion. D. Detrital magnetite with dissolution voids around the rim. Reflected light, oil immersion.

in a rim around the grains (Fig. 7D), along parting planes and fissures or everywhere in the grains. The alteration rim has a constant thickness around the magnetite core, which indicates that dissolution took place after deposition (Fig. 7D).

Rutile

Rutile occurs as detrital grains, which are generally resistant to alteration. Some rutile grains are, however, altered to or surrounded by colloidal leucoxene (Fig. 7B).

Hematite

Hematite is common as exsolution lamellae and intergrowths in ilmenite. Hematite dissolution lamellae in ilmenite grains show evidence of more intense dissolution than the ilmenite host. Hematite as discrete grains has only been observed in the top of the lignite layer, where intensive precipitation of iron-oxides/hydroxides has also taken place.

Minor species

Silicified leucoxene

Silicified leucoxene occurs as fine or coarse leucoxene aggregates, which have been stabilised by precipitation of quartz in the pore space. Some silicified leucoxene might be detrital, as some grains have rounded rims. Other silicified leucoxene could be of authigenic origin, since delicate TiO_2 crystal facets dominate the outer rim.

Iron-oxide/hydroxide

Goethite is the dominant mineral in the clay fraction of the fine-grained part of the lowest fining-upward sequence. Several thin orange bands of goethite and limonite also occur at the top of the lignite layer. Reddish and brownish coatings of amorphous iron-oxides/hydroxides or limonite are quite common in the coarse-grained foresets.

Discussion

Sedimentological related alteration of detrital Fe-Ti oxides

The petrifying stems found just on top of the lignite layer, capping the fining upward sequence, indicate that this level reflects a former exposed surface from

which weathering of detrital minerals could take place. Earlier investigations of the Voervadsbro sediments have shown weathering of certain transparent heavy minerals related to the top of the fining upward sequence (H. Friis 1976). Unlike the transparent heavy minerals, the opaque minerals do not show a convincing weathering sequence associated with the former exposed surface. However, colloidal leucoxene seem to be most common just below the top soil and the lignite layer, i.e. close to major organic sources.

Formation of the authigenic Fe-Ti oxides

Pseudorutile

Several investigations reveal that the alteration of ilmenite takes place through a distinct grey, isotropic phase with the chemical composition: $\text{Fe}_2\text{O}_3 \cdot n\text{TiO}_2 \cdot m\text{H}_2\text{O}$ ($3 < n < 5$, $1 < m < 2$) (Lynd *et al.* 1954; Bailey *et al.* 1956; Grey & Reid 1975; Dimanche & Bartholomé 1976; Riezebos *et al.* 1978; Morad & Aldahan 1986; Hugo & Cornell 1991). Temple (1966) is the only author who describes the dark grey transitory phase as anisotropic, but nevertheless he refers it to the second phase described by Bailey *et al.* (1956), who record it as isotropic. There has been some disagreement concerning the terminology of this intermediate species, but most authors now agree that it is pseudorutile (Grey & Reid 1975; Dimanche & Bartholomé 1976; Riezebos *et al.* 1978; Morad & Aldahan 1986; Hugo & Cornell 1991). Mücke & Chaudhuri (1991), however, describes the alteration of ilmenite as a continuous process, which takes place through several intermediate stages. However, the alteration products of ilmenite in the Voervadsbro deposits can be described by 3 stages: pseudorutile, fine leucoxene and coarse leucoxene (or discrete TiO_2 -crystals).

The mechanism for alteration of ilmenite to pseudorutile presumably involves the process of oxidation and removal of iron by diffusion through the ilmenite lattice (Temple 1966; Grey & Reid 1975; Dimanche & Bartholomé 1976). Where ilmenite is altered to pseudorutile, iron has been oxidised and transported out of the grain. This process has been suggested to take place in the zone of saturation under mildly reducing conditions, enabling the oxidation process to proceed and such that iron was highly soluble (Temple 1966; Grey & Reid 1975; Dimanche & Bartholomé 1976). The presence of scattered organic material in the fluvial sediments at Voervadsbro enhanced the solubility of iron by complexing with organic acids and lowered both the pH and Eh of the ground water (cf. Adams *et al.* 1974).

Fine leucoxene and coarse leucoxene

It is generally accepted that the final alteration product of ilmenite is leucoxene, and the latter can be recognised optically by its bright red, red-brown, yellow, white or grey internal reflections (Fig. 4; Lynd *et al.* 1954; Bailey *et al.* 1956; Temple 1966; Dimanche & Bartholomé 1976; Riezebos *et al.* 1978; Morad & Aldahan 1986; Hugo & Cornell 1991; Mücke & Chaudhuri 1991). A possible explanation for the scarcity of pseudorutile in the Voervadsbro sediments compared with leucoxene, is that it is a metastable phase during ilmenite alteration (Dimanche & Bartholomé 1976). The absence of pseudorutile, as an intermediate phase during alteration of ilmenite lamellae in titanomagnetite, probably means that the alteration process has gone to completion in most titanomagnetite grains. The presence of several zones of weakness in the magnetite host of titanomagnetite resulted in its more rapid dissolution than more homogeneous magnetite. Alteration proceeded faster in small unprotected ilmenite lamellae than in large ilmenite grains, leading to the almost exclusive occurrence of the final alteration stage (coarse leucoxene).

The transformation of pseudorutile into leucoxene requires a complete rearrangement of the crystal structure since both iron and oxygen must be removed. Some authors consider that this process occurs by the complete dissolution and epitactic reprecipitation of titanium oxide on the seed material (Grey & Reid 1975; Dimanche & Bartholomé 1976; Frost *et al.* 1983). Mücke & Chaudhuri (1991), on the other hand, have observed a continuous alteration of pseudorutile into leucoxene and instead suggest a process of leaching and hydrolyzation. The morphological appearance of ilmenite with dissolution voids and in volume much smaller amounts of leucoxene indicate formation of leucoxene through a dissolution process (Figs 6A, 6B). The fact that leucoxene is commonly distributed according to the crystallography of a former phase is an indication of an incongruent dissolution process, where some of the titanium remains in place. The remaining titanium will initially duplicate the crystallography of pseudorutile, but this lattice will become unstable as iron is continuously leached. Titanium is then organised in small crystals of rutile or anatase (fine leucoxene).

The alteration of pseudorutile into leucoxene is envisaged to occur in the zone of oxidation (i.e. above the ground water table) and to be related to the decomposition of organic material which forms organic acids capable of dissolving pseudorutile (Temple 1966; Grey & Reid 1975). The sediments at Voervadsbro are now situated above the ground water table, although that may not have been the case during the main pe-

riod of weathering. The abundant plant fragments in the fluvial sands at Voervadsbro created the mildly reducing, acid conditions necessary for dissolution of pseudorutile and transport of Fe²⁺.

The single crystals of coarse leucoxene are formed from fine leucoxene by the growth of few large crystals at the expense of small ones following simple thermodynamic laws. Grey & Reid (1975) suggested that rutile was the most likely TiO₂ replacement of pseudorutile, as triply twinned rutile has a similar crystallography to pseudorutile. However, anatase is stable relative to rutile, brookite and titanium hydroxide in naturally occurring pH and Eh ranges (Adams *et al.* 1974; Pettijohn *et al.* 1987, p. 439; Banfield & Veblen 1992; Banfield *et al.* 1993). Anatase is consequently the most likely single crystal in coarse leucoxene, but both rutile and anatase occur (Figs 5A, 5B). The growth of brookite, rutile and anatase at the expense of leucoxene has been observed in other sediments (Golding 1961). The main phase of the leucoxene probably determines the mineralogy of the coarse leucoxene/the single TiO₂ crystals.

Colloidal leucoxene

Since the fragile and generally open structure of colloidal leucoxene could not have survived abrasion during transport and deposition, colloidal leucoxene must have formed *in situ*. Some of the internal voids may be the result of dissolution of detrital remnants after precipitation of the colloidal leucoxene. The space originally occupied by a detrital titanium-bearing grain is now roughly indicated by the shape of colloidal leucoxene.

Colloidal leucoxene probably consists of cryptocrystalline anatase, since it optically resembles anatase more than any other TiO₂ polymorph. Its appearance around detrital rutile suggests a TiO₂ phase other than rutile, as TiO₂ otherwise most likely would have precipitated as an overgrowth. The optical appearance as colloidal bands leads to the hypothesis that it forms by intensive dissolution of Fe-Ti oxides (titanomagnetite, ilmenite or maybe rutile) and an almost simultaneous colloidal precipitation of titanium oxide. According to Riezebos *et al.* (1978), colloidal banding and zoning of goethite indicates colloidal deposition from gels or repeated deposition of successive thin layers from solution. Titanium can be mobilised on a micro-environmental scale (Morad & Aldahan 1986); it may occur temporarily in colloidal suspension during ilmenite alteration (Golding 1961), and it may form organic complexes with organic acids (Adams *et al.* 1974). A simple reprecipitation of titanium close to the altered detrital grains, due to its low solubility, would probably result in fine leucoxene. Therefore

different conditions must have been present for the precipitation of colloidal leucoxene to occur. The association of colloidal leucoxene with concentrations of organic material indicates that the organic materials or elements associated with organic material are crucial for its formation, but at present the mechanism is not completely understood. The reducing conditions, created during degradation of organic material, may be essential for the mobilisation of iron, thus increasing the nucleation rate of anatase. Another possibility is that elements associated with organic material could promote nucleation instead of crystal growth. Experimental studies at high temperatures (450–700°C) showed that Y, as well as Cr, rare earth-oxides and possibly V, dramatically reduce the coarsening of anatase (Banfield *et al.* 1993). These elements might have a similar long-term influence at low temperatures, and where present in the sedimentary system in relatively high concentrations the precipitation of microcrystalline anatase might have been promoted. Colloidal-resembling leucoxene has not only been reported from sediments formed under extreme conditions such as: bauxite and uranium deposits, but also in marginal marine sandstones (Hartman 1959; Adams *et al.* 1974; Morad 1988). Bauxite formation is characterised by increased V and Cr, and uranium deposits are commonly associated with V (Valeton 1972, p. 93; Jensen & Bateman 1981, p. 441). Vanadium, chromium or elements with similar effects on anatase may be associated with organic matter.

Silicified leucoxene

Some grains of silicified leucoxene are probably of authigenic origin, as the grain surface is dominated by TiO₂ crystal faces, and as authigenic quartz otherwise occurs in the investigated sediments as syntaxial overgrowths or a petrifying agent in stems found *in situ* (H. Friis 1976; Weibel 1993, 1996). Pseudomorphs of titanium oxide and quartz have earlier been inferred as altered sphene (Corlett & McIlreath 1974; Morad & Aldahan 1985; Morad 1988). However, in the sediments at Voervadsbro there has been a pronounced difference in the relative timing of precipitation of TiO₂ and quartz, as well-defined TiO₂ crystals are filled in with quartz. This indicates that a titanium-bearing mineral was first altered to leucoxene, and then quartz was precipitated in the pore space, possibly initiated by the presence of quartz inclusions in the original detrital grain.

Iron-oxides/hydroxides

Dissolution of magnetite and hematite, and the alteration of ilmenite grains and ilmenite lamellae in titanomagnetite require the continuous removal of iron. In meteoric water the activity of iron is low, and the degradation of organic materials probably created mildly reducing conditions promoting the solubility of iron. There is also evidence for mobilisation and precipitation of iron. Goethite therefore occurs as a common constituent of the clay fraction and forms orange bands at the lignite layer. Grain-coatings of limonite or X-ray amorphous iron-oxides/hydroxides are also common in coarse-grained foresets, which never contain organic materials. Dissolved iron has thus precipitated mainly as goethite or amorphous iron-oxides/hydroxides where oxidising conditions prevailed, i.e. in coarse-grained foresets and in bogs at the atmosphere-water interface.

Conclusions

Alteration of Fe-Ti oxides probably began immediately after deposition under the warm temperate to subtropical Miocene climatic conditions, but it might have continued at a slow rate until today. Degradation of scattered organic matter creates a mildly reducing and neutral-to-acid environment. The detrital Fe-Ti oxides, hematite, magnetite, titanomagnetite and ilmenite, are unstable under these conditions and subject to alterations (Table 1). The different degree of alteration observed between individual grains is the result of crystallographic and structural differences inherited from the source rock (i.e. cracks, twin planes, exsolution lamellae, inclusions etc.) and mechanical influence during transport. Almost all discrete hematite grains are dissolved, and exsolution lamellae of hematite in ilmenite are more intensely dissolved than their host. Magnetite is more or less dissolved, and resistant grains are commonly rimmed by several dissolution voids. The magnetite host in titanomagnetite is typically missing, and the ilmenite lamellae have been altered to coarse leucoxene orientated in a trellis texture. Numerous crystallographic weaknesses in titanomagnetite promoted dissolution of magnetite and the alteration of ilmenite lamellae to its final alteration stage: coarse leucoxene. Ilmenite grains are altered first to pseudorutile, then to fine leucoxene, and finally to coarse leucoxene (single crystals of rutile or anatase). The alteration begins at the rim and proceeds into the grains along fissures, cleavage planes, twin planes and other crystallographic weakness zones. The transformation of ilmenite into

pseudorutile involves the oxidation and diffusion of iron through the ilmenite lattice. Alteration of pseudorutile to leucoxene may take place as an incongruent dissolution and reprecipitation of titanium onto titanium remaining in the pseudorutile lattice. Coarse leucoxene forms by the growth of fewer large crystals at the expense of several small ones. The Ti-bearing detrital grains (ilmenite, titanomagnetite and possibly rutile) are also altered to colloidal leucoxene. Formation of two different leucoxene types under apparently similar conditions is somewhat puzzling. Colloidal leucoxene is complementary to fine leucoxene formed by the complete dissolution of part of the Ti-bearing grain and colloidal precipitation of presumably cryptocrystalline anatase in colloidal bands. The formation of colloidal leucoxene seems to be related to organic matter or elements associated with it. The advanced alteration in the sediments at Voervadsbro has thus resulted in a major increase in titanium content of the remaining detrital Fe-Ti oxides.

Locally oxidising conditions prevail e.g. in coarse-grained foresets without organic material and at the atmospheric interface of bogs. In this environment dissolved iron, liberated during alteration of Fe-Ti oxides, precipitates mainly as goethite or limonite.

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