DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2008/6

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Rikke Weibel, Roger McLimans, Dirk Frei, Nynke T. Keulen
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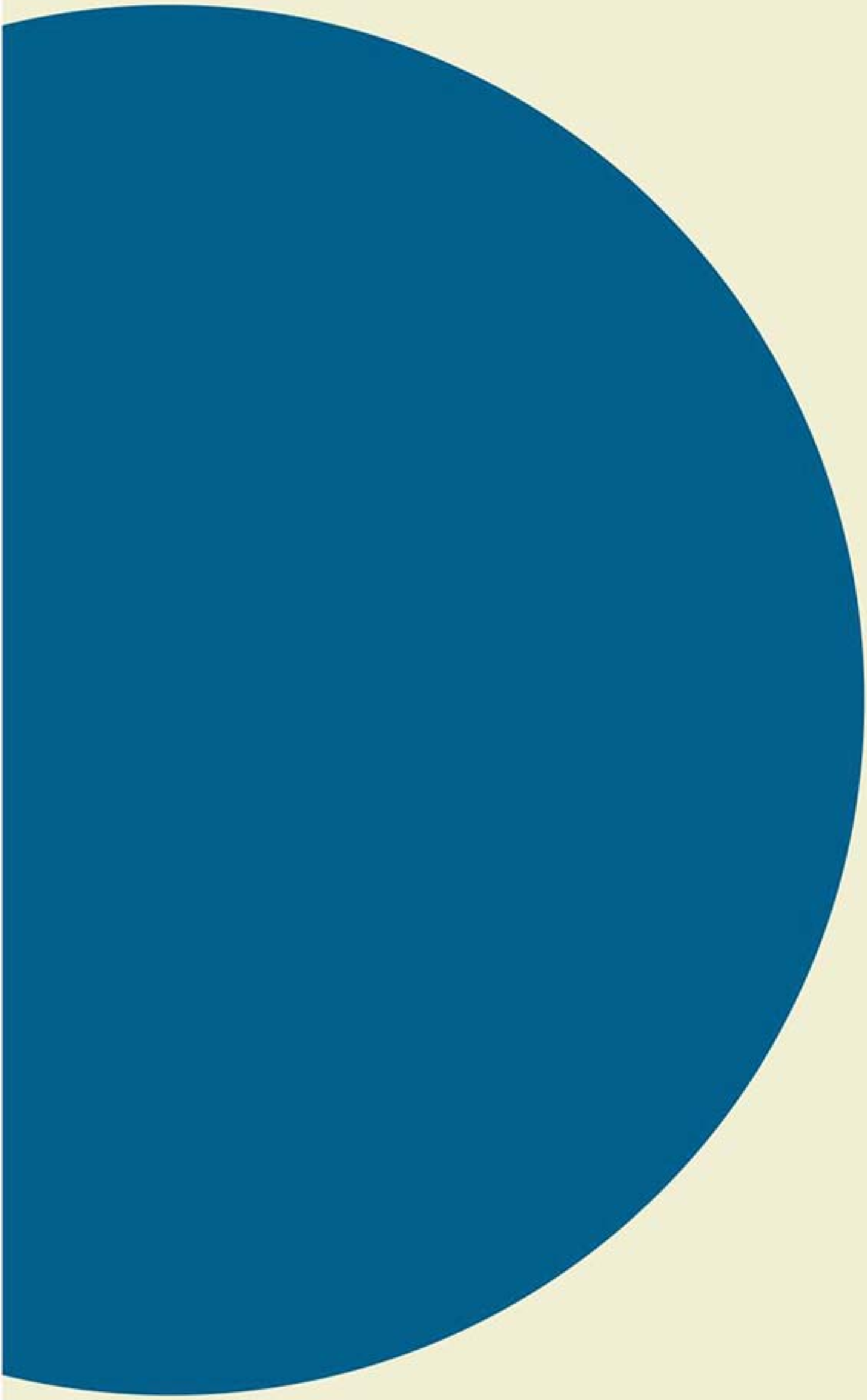

GEOLOGICAL SURVEY OF DENMARK AND GREENLAND
MINISTRY OF CLIMATE AND ENERGY

GEUS

DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2008/06

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Contents

Abstract

A wide range of ilmenite ores are investigated to increase the knowledge of the effect of the incorporation of phosphorus in ilmenite grains. The analytical methods of XRF (X-ray fluorescence), electron microprobe (qualitative analyses and element mapping), and CCSEM (computer controlled scanning electron microscopy) are utilised to obtain and compare the results. Methods of extracting the phosphorus from the ilmenite ore are also tested.

CCSEM, as developed by GEUS for DuPont, is now a routine method for the determination of the major and minor elemental composition of ore minerals and is used in the investigation of ilmenite ore in order to evaluate the ore quality. All CCSEM results are systematically stored in a geochemical database and archived for any further evaluation. Compilation of the CCSEM data on the ilmenite ores from three countries (India, Madagascar and Denmark) show increasing phosphorus content in ilmenite with increasing amounts of titanium, which in turn indicates increasing degree of alteration. Ilmenite samples from Cretaceous-Jurassic deposits from the island of Bornholm, Denmark, and from Miocene lignite deposits in Poland are exceptions to this general trend, as they contain ilmenite rich in titanium but yet are low in phosphorus content. That has lead to our hypothesis that ilmenite grains with high titanium and low phosphorus contents are a result of alteration in a fresh water environment. However, the hypothesis needs to be validated by studies of ilmenite grains whose histories are known to include marine or fresh water systems.

Electron microprobe analyses, both quantitative analyses and element mapping, show clearly that in most ilmenite samples phosphorus is incorporated in those parts of the grains that are altered to leucoxene. Ilmenite and leucoxene of increased phosphorus content commonly have higher abundance of other impurities, such as aluminium, silicon and calcium. Those observations have lead to the suggestion that phosphorus could be present in extremely small, submicroscopical, apatite or alumino-phosphate/alumino-sulphate-phosphate crystals. The ratio of phosphorus to aluminium, silicon and calcium shows a wide range in samples of ilmenite from different deposits and thus may reflect variations in surrounding environment during alteration of ilmenite.

Three Australian ores, Iluka, Doral, and Bemax, were of special interest as they behave differently during chlorination. Iluka and Doral are ilmenite ores low in phosphorus, but high in titanium. But the Bemax ilmenite grains, though high in titanium and low in aluminium, silicon, calcium is high in phosphorus. The Bemax ilmenite contains inclusions of phosphorus-bearing minerals (monazite) and phosphorus-bearing intergrowths. Thus, it is important to know the mineralogical textures as well as chemical composition to interpret the origin of the phosphorus content.

Besides looking for naturally leached ilmenite grains, artificial leaching was investigated. Phosphorus can be leached out of ilmenite with several acids (HCl, HNO_3, H_2SO_4, $C_2H_2O_4$), of which oxalic acid is the most effective. However, the dissolution of phosphorus also results in other elements, including Ti and Fe, being leached out.

Introduction

Since the presence of phosphorus is a problem in the chlorination of ilmenite ores, studies have been undertaken to characterise the residence and incorporation of phosphorus in ilmenite. The quality of ilmenite ores has been shown in earlier studies to be associated with their source rocks (Bernstein et al. 2005; Lloyd et al. 2005; McLimans et al. 2005; Bernstein et al. 2008). However, previous studies have shown that phosphorus is not necessary inherited from the source rock but rather incorporated during the alteration of the ilmenite grains (Dirk Frei, personal communication 2006; Weibel 2007). Therefore it is logical to look into the ability of different environments to influence the composition of the altered ilmenite grains. It would be interesting to find a specific natural environment, where ilmenite is altered by natural leaching without accompanying phosphorus incorporation. Ilmenite grains from different source rocks and several depositional environments have been analysed over the years (Bernstein 2003, 2004a, 2004b; Frei et al. 2005; Knudsen et al. 2005; McLimans et al. 2005; Weibel 2007; Bernstein et al. 2008). CCSEM results from these studies are stored in the geochemical database at the Geological Survey of Denmark and Greenland (hereafter called GEUS) and are available for further investigations such as the present study on phosphorus in ilmenite ores. Of particular interest are the Australian ores (Iluka, Doral and Bemax) due to their different behaviours during chlorination.

Of equal importance is to find an artificial way of leaching which specifically removes phosphorus from ilmenite. In addition, methods were therefore investigated to extract phosphorus from ilmenite ores.

Another problem was how to rate the ore quality and which methods to apply for such an evaluation. X-ray diffraction (XRF), microprobe analyses, and computer controlled scanning electron microscopy (CCSEM) are used and compared in the present study to obtain data on the phosphorus content of ilmenite. Each method has advantages and disadvantages. XRF is an inexpensive method of bulk analysis but provides neither textural nor mineralogical data on how phosphorus sits in the ilmenite lattice. CCSEM is a more expensive method but in addition to bulk chemistry, it provides the chemical analysis of individual ilmenite grains. However, it has limits in the resolution of mineralogy and localisation of phosphorus, especially in minerals of low abundance, such as monazite, which is limited by the probability of encountering a monazite grain in a typical sample mount. Microprobe is the most expensive method but offers the maximum amount of information in the control of the source of data, textural observations, and selectivity. The number of grains analysed by the microprobe, though, is typically limited, as the method is more time consuming compared to the CCSEM method. The best approach is a combination of more than one method, such as XRF and either CCSEM or microprobe. The evaluation of ilmenite ore quality in the geochemical database (illustrated by warning by ‘traffic lights’) is briefly mentioned.

Samples

Numerous samples have been applied in this report as the purpose is to compile results from various investigations regarding the phosphorus in ilmenite grains. The alteration of ilmenite from bed rocks to rivers and dunes has been investigated in samples taken by Stefan Bernstein during field work in Madagascar in 2005 (Table 1). An important reason for including the Madagascar samples in the present study is the possibility of comparing the alteration of ilmenite with a well-constrained origin and depositional environment. The results from the Madagascar samples are compared with CCSEM results from ilmenite ores from Denmark and Poland which are already in the geochemical database. All previously analysed samples from these countries are utilised therefore the individual samples are not listed here, but can be found in the geochemical database. This is a continuation of previous investigations where the phosphorus content of all samples from Denmark, India and Madagascar analysed by CCSEM at GEUS were compared with their depositional environment as extensive information for these samples, together with their origin are stored in the geochemical database (Weibel 2007).

Commercial ilmenite ore samples which are used or under consideration for titanium pigment production are also included in the present investigation (Table 2). The origin and depositional environment are less well-constrained for these ilmenite ore samples, as the ores may contain mixtures from several locations. The work has focused, in particular, on the different ilmenite ores from Australia: Iluka, Doral and Bemax, as they behave very differently during chlorination. The Ilkuka and Doral ilmenite ores are considered high quality ores, whereas the Bemax ore behaves problematically.

Table 1. Field samples from Madagascar

GEUS No.	Environment	Investigations			
		CCSEM	Rerun CCSEM	Microprobe	Leaching experiment
2000754	Active coastal dune	X		X	
2000755	Ancient dune	X		X	
2001024	Altered gneiss	X		X	
2001025	Weakly or not altered gneiss	X		X	
2001028	Tropical soil	X		X	
2001034	Kaolinised gneiss	X		X	
2001035	Sediments on kaolinised gneiss	X		X	

Table 2. Ilmenite ore samples used in this report

GEUS No.	Sample	Investigations			
		CCSEM	Rerun CCSEM	Microprobe	Leaching experiment
2002602	UKRAINIAN 92203-24	X		X	
2001142	DORAL 102208-97	X		X	
2001180	INDIAN E105202-7	X		X	
2002802	VIETNAMESE E98651-105	X		X	
2003302	East Tennessee	X		X	X
2003303	Florida	X		X	X
2003305	Malaysia	X		X	X
2003304	India	X		X	X
2003306	Ukraine	X		X	X
2003307	Vietnam	X		X	X
2001178	AUSTRA-ILUKA E1005202-19	X		X	
2002102	MALAYSIAN 10.13.03-35A	X			
2001140	ILUKA-VIRGINI 101503-91	X			
2001141	ILUKA-FLA 101503-93	X			
2001179	AUSTRA-CSL E105202-2	X			
2003530	Australian BEMAX ilmenite	X			
2003531	Australian BEMAX leucoxene	X			
2003532	Australian BEMAX rutile	X			
2003533	Brazil Imerys	X			
2003577	539 BEMAX leucoxene	X			
2003578	540 BEMAX leucoxene	X			
2003579	603 BEMAX leucoxene	X			
2003580	626 BEMAX leucoxene	X			
2003582	Beach Minerals Co. Ilmenite	X			
2003583	DPSR Syntetic rutile	X			
2003584	RBM ore	X	X	X	
2003585	CRL ore	X	X	X	
2003586	BEMAX ore	X	X	X	
2003587	SREP ore (synthetic rutile)	X	X	X	
2003588	Ti West ore	X	X		

Methodology

The CCSEM (computer controlled scanning electron microscope) results are compared with results from element mapping by electron microprobe analyses performed at GEUS and XRF (X-ray fluorescence) results performed at DuPont.

The CCSEM analyses are obtained from carbon coated, polished mounts using a Phillips XL 40 scanning electron microscope equipped with a Thermo Nanotrace 30 mm^2 detector surface window and a Pioneer Voyager 2.7 10 mm^2 window Si(Li) detector energy dispersive X-ray analysis (EDX) system. The electron beam is generated by a tungsten filament operating at 17 kV and 50–60 µA. The number of measured grains varies from 1000 to 2000. X-ray data are corrected for atomic number, absorption or fluorescence effects by the Proza correction scheme prior to semi-quantitative, standard-less calculation of elemental concentrations using the Vantage or Thermo Noran System Six software packages (Bernstein et al. 2008). Further data reduction is performed using a software package developed at GEUS (Frei et al. 2005).

The element mapping and quantitative analyses of the ilmenite grains are obtained by electron microprobe analyses on a JEOL© JXA-8200 at an acceleration voltage of 15 kV and a beam current of 15 kV. Carbon-coated polished mounts of the ilmenite ores are applied for the tests. Probescan is used for element mapping of selected areas of the leucoxene-altered ilmenite grains. Approximately 20 ilmenite grains from each sample are analysed. The quantitative analyses of leucoxene result in relatively low totals mainly due to intragranular porosity, and polishing and carbon-coating problems, and to some extent non-analysed elements, such as H_2O (in pseudorutile) and REE. Therefore the quantitative results are normalised to 100 %.

Samples for XRF analysis are machine crushed in a tungsten carbide mortar. Glass discs are prepared by fusing 0.75 g of ignited powder with 5.25 g sodium tetraborate for 1–1½ hours in Pt/Au crucibles over gas burners before it is poured into a Pt/Au mould (Kystol & Larsen 1999). The glass discs are analysed with a Phillips PW 1606 wavelength dispersive multichannel XRF spectrometer equipped with a Rh-anode X-ray tube operating at 50 kV and 50 mA. Kystol & Larsen (1999) recommend that the lower limits of detection for the main elements are, in general, twice the precision, which is one standard deviation of experimentally repeated analyses over time of a set of international standards. The recommended detection limits for the main elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and P) varied from 0.01 wt% for P_2O_5 to 0.3 wt% for SiO_2 (see Kystol & Larsen 1999 for more detailed information).

Leaching experiments are done with 1 g of crushed sample leached with 10 ml acid (HCl, H_2SO_4, HNO_3) in closed Teflon (PTFE = polytetrafluorethylene) vessels for approximately 16 hours at 130°C. In the experiments with boiling oxalic acid 10 g of crushed sample is dissolved in 100 ml solution. The element concentrations in the extracts are measured on an Elan 6100DRC ICP-MS using PerkinElmers TotalQuant methods, which is a semi-quantitative method for low-atomic-numbered elements but almost quantitative for high-atomic-numbered elements (Jørgen Kystol personal communication 2007).

Results and discussion

The discussion of the results is organised into four major sections:

1. Phosphorus in ilmenite ore inherited from the source rock?
2. Alteration of ilmenite and the incorporation of phosphorus
3. Alteration of ilmenite in different environments
4. Phosphorus content measured by different methods
5. Possible ways of removing the phosphorus – leaching experiments

Phosphorus in ilmenite ore inherited from the source rock?

The Australian Bemax samples are distinct in that the phosphorus content is related to intergrown silicates or inclusions rather than the leucoxene altered parts of the ilmenite grains (Figs 1, 2). The other Australian samples investigated, Doral and Iluka, have low phosphorus contents and typically only rare intergrown silicates and inclusions. There seems to be a major difference between the Bemax ilmenite ore and the other Australian ilmenite ores. Doral only produces ilmenite ore from Western Australia, and Iluka only supplies ilmenite ore from Western Australia to customers using chlorine extraction methods (Iluka 2007, Doral 2007, Bemax 2007). The Bemax samples probably originate from ilmenite ore from the Murray Basin or may be a mixture of ilmenite ore from the Murray Basin and Western Australia. Consequently, the Bemax ilmenite ore probably had different source rocks - Palaeozoic and Proterozoic rocks and was deposited in Pliocene beach-barrier systems and associated dunal sands. Doral and Iluka ilmenite ores, on the other hand, mainly had Archaean source rocks and were deposited as Holocene and Pleistocene beach sands. The differences in major source rocks could be an explanation to the increased amount of phosphorus-bearing silicate-intergrowths and inclusions found in the Bemax samples.

Phosphorus inherited from the source rock is an atypical occurrence. Therefore this report focuses on the way phosphorus enters the ilmenite grains during their alteration.

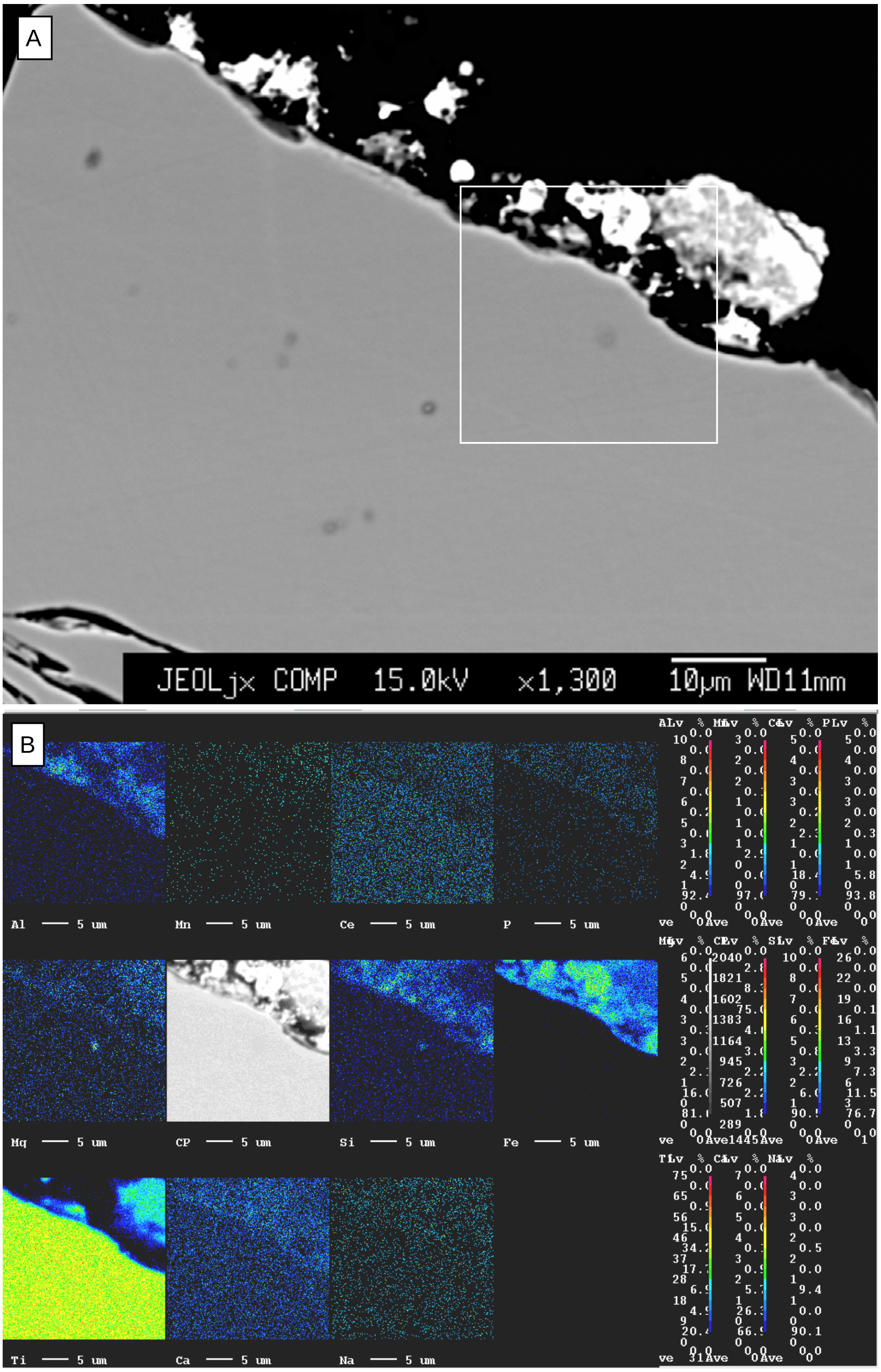

Fig. 1. *A. An ilmenite grain with leucoxene rim or overgrowths? (2003586 Bemax ore, element map 07 (07-08-2007). B. Electron microprobe element maps of Al, Mn, Ce, P, Mg, Si, Fe, Ti, Ca and Mn of selected area (white box). Phosphorus is located in the leucoxene rim.*

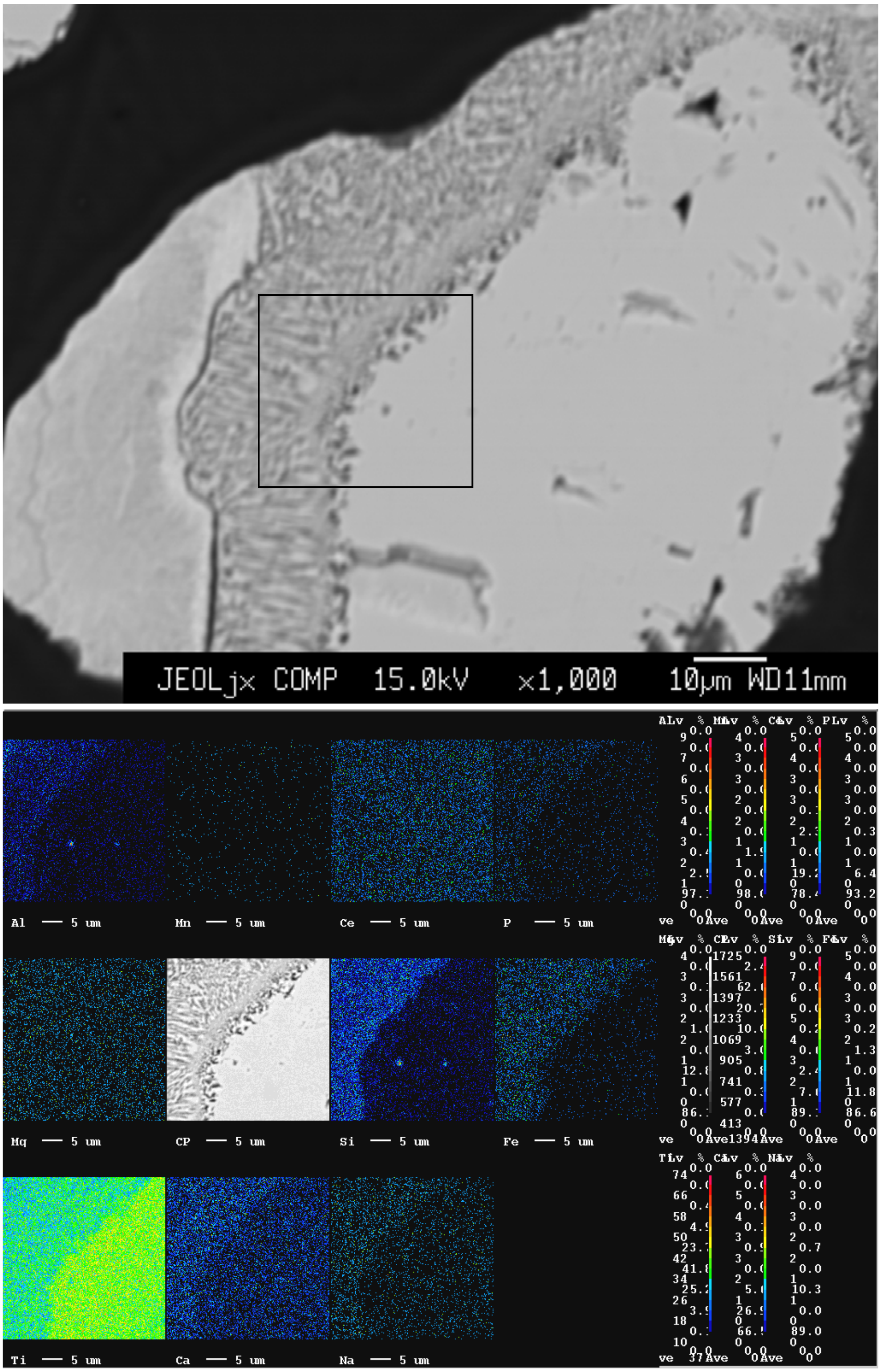

Fig. 2. *A. An ilmenite grain (grey) intergrown with silicates (darker grey), 2003586 Bemax, element map 002 (07-08-2007). B. Electron microprobe element maps of Al, Mn, Ce, P, Mg, Si, Fe, Ti, Ca and Mn of selected area (black box). Phosphorus is located in the intergrown silicates.*

Alteration of ilmenite and the incorporation of phosphorus

The alteration of ilmenite takes place in two steps: first ilmenite is altered to pseudorutile, which in turn is altered to leucoxene (Temple 1966; Grey & Reid 1975). Pseudorutile forms by iron diffusion through the ilmenite lattice and oxidation of the remaining iron (Grey & Reid 1975; Dimanche & Bartholomé 1976). Leucoxene forms by a complete rearrangement of the crystal structure and presumably takes place by an incongruent dissolution process followed by epitactic precipitation in a porous network (Dimanche & Bartholomé 1976; Weibel 2003). SEM investigations of leucoxene grains show substantial intragranular porosity (Weibel 2003), which occasionally may be filled in with other authigenic phases (cf. Weibel & Friis 2004). Element maps and element traverses are excellent methods to visualise the major chemical changes that take place during alteration of ilmenite.

Manganese and magnesium are common constituents in detrital ilmenite grains (Bernstein 2003, 2004a, 2004b; Lloyd et al. 2005; McLimans et al. 2005; Weibel 2007; Bernstein et al. 2008). Manganese seems to remain in the first alteration product of ilmenite, pseudorutile, and commonly occurs, in relatively increased amounts, at the border between pseudorutile and leucoxene (Bernstein 2004a). Frost et al. (1986) explains this as a relative increase related to different oxidation potentials of Mn^{2+}/Mn^{3+} and Fe^{2+}/Fe^{3+}, which means that while iron is oxidised manganese remains Mn^{2+}, which is too large to diffuse through the lattice. First in the second step of the ilmenite alteration (when pseudorutile is altered to leucoxene), does the manganese go into solution along with iron as this involves dissolution of pseudorutile (Fig. 3; Frost et al. 1986). Magnesium follows iron, in most investigated ilmenite grains, during its leaching out of ilmenite, which seems logical as Mg^{2+} and Fe^{3+} have similar effective ionic radii (cf. Shannon & Prewitt 1969; Shannon 1976).

Several investigations (Bernstein 2004a; Dirk Frei personal communication 2006; Weibel 2007) have shown that an increase in the titanium content in ilmenite in certain samples is followed by increased phosphorus content. The element maps constructed for ilmenite grains from Indian ore samples clearly show a relationship between the alteration of ilmenite and an increased phosphorus content (Weibel 2007). Similar observations were noted for other ilmenite ore samples with high phosphorus content (Weibel 2007).

An increase in phosphorus content is typically associated with increased amounts of aluminium, silicon and calcium, although the dominant impurity varies between the different samples (Frost et al. 1983; Frost et al. 1986; Bernstein 2003, 2004a; Weibel 2007). Consequently, it has been suggested that phosphorus is incorporated in microinclusions of apatite (Bernstein 2004a) or alumino-phosphates and/or alumino-sulphate-phosphates (Weibel 2007). During the alteration of ilmenite to leucoxene the grain becomes more porous, leaving intragranular space for precipitation of tiny alumino-phosphate minerals or other phosphate-bearing minerals.

Aluminium and silicon are enriched during the first stage of alteration of ilmenite (into pseudorutile) due to iron depletion, but the main increase in these elements arises in the second stage alteration, the dissolution of pseudorutile and precipitation of leucoxene (Frost et al. 1983). Frost et al. (1986) consider this a result of co-precipitation and adsorption of aluminium and silicon from the surrounding solutions onto the newly-formed alteration products. Anand & Gilkes (1984) observed, in transmission electron microscope studies, minute crystals of gibbsite, kaolinite and halloysite in altered ilmenite grains from laterite soils. Weibel & Friis (2004) found iron-oxide/hydroxide needles, possibly lepidocrosite, impregnating the outermost part of the porous leucoxene network and related it to flushing by saline brines. A similar precipitation of other minute minerals reflecting the surrounding pore fluid is likely to take place in other environments.

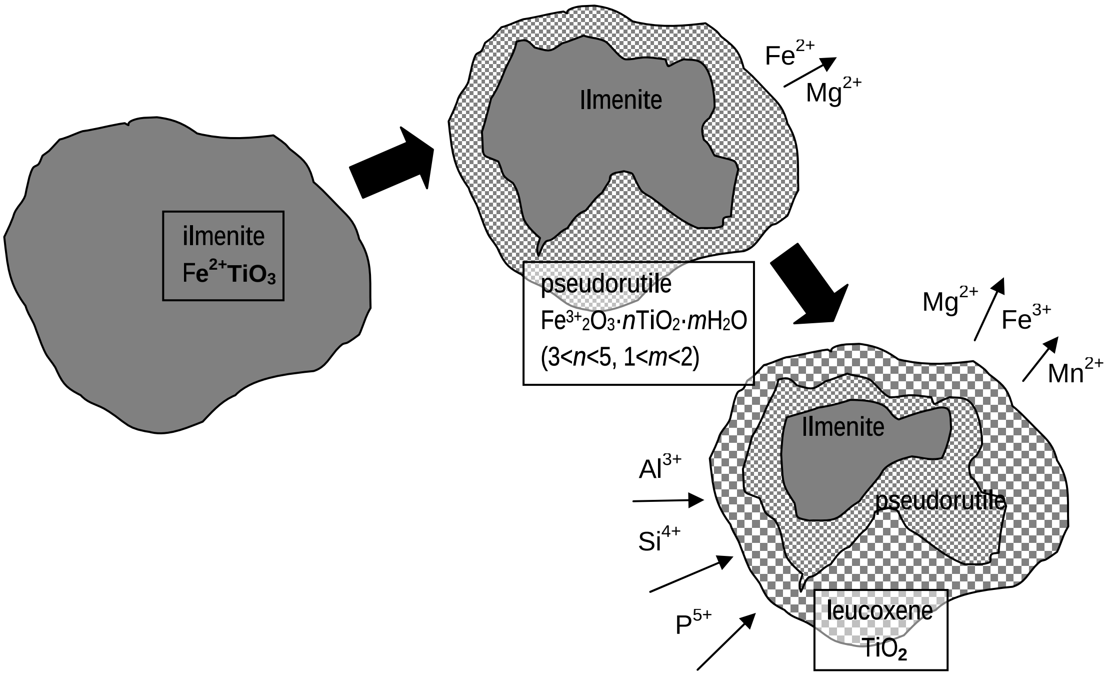

Fig. 3. *Cartoon showing the two-step alteration of ilmenite firstly to pseudorutile and secondary to leucoxene.* Fe^{2+} *and* Mg^{2+} *are released during the alteration of ilmenite to pseudorutile.* Mn^{2+} *is first released during the subsequent alteration of pseudorutile to leucoxene. At this stage other ions (such as* Si^{4+}, Al^{3+}, P^{5+}*) also enter the porous network of the altered grain, where they form authigenic phases or maybe substitute for some of the titanium.*

Alteration of ilmenite in different environments

Although numerous ilmenite ores are analysed by CCSEM, the source area and the depositional environment are only known for those samples collected during our own field work in Madagascar, India, Poland and Denmark. The sources are less well defined for Poland and Denmark compared to India and Madagascar. Field work gives the advantage that the ilmenite grains occurrence in their source rock can be associated with an ilmenite ore deposit close by and therefore assists in the evaluation of the influence of the source and the depositional environment on the alteration of ilmenite. Therefore, the ilmenite alteration can be described from bed rock from both India and Madagascar (Bernstein 2004a, 2004b), and associated soil pockets and weathering products on the bed rocks from Madagascar. The bed rock occurrence of ilmenite can be compared with the ilmenite alteration found in river deposits, dunes and beaches.

Alteration of ilmenite in their bed rocks and associated sediments

Field work in Madagascar and India has made it possible to (1) investigate the alteration of ilmenite in the source rocks and (2) compare that with the ilmenite alteration in the nearby depositional environments. In several of the investigated Indian rock samples, ilmenite shows signs of alteration that begins along grain boundaries and penetrates along fractures (Bernstein 2004b). Some ilmenite grains in the rocks from the khondalite belt (group of metamorphosed aluminous sediments) show intense or even complete alteration, but as these ilmenite grains cannot be found in rivers draining the khondalite belt the survival potential for such intensely altered grains is probably low (Bernstein 2004b). Unaltered ilmenite grains have phosphorus concentrations below the detection limit of the electron microprobe (0.01 wt%), whereas the altered parts can have elevated phosphorus concentrations (Bernstein 2004b). High phosphorus contents are typically associated with increased calcium values (Bernstein 2004b).

Alteration of ilmenite in sediments sourced directly from bed rocks

The ilmenite grains in relatively fresh bed rock samples (gneiss) from Madagascar have increased phosphorus contents at the transition between the altered and unaltered parts of the grains (Fig. 4). Where deep kaolinisation of the basement gneisses has occurred in Madagascar, only quartz and opaque minerals are left behind. Ilmenite grains from these heavy mineral concentrates have alterations varying from weak, to moderate and up to high. The phosphorus content and the titanium content increase with the degree of alteration (Fig. 5).

Soil formation in cracks in the Madagascar gneiss leads to a rare and distinct ilmenite alteration with an abrupt change from unaltered ilmenite to a rutile alteration rim (Fig. 6). This ilmenite alteration in tropical soils is very distinct and can easily be recognised. The formation of this rutile alteration rim only takes place during soil formation, as it has not been described from any other depositional environment.

Active coastal dunes along the coast in southern Madagascar are dominated by leached ilmenite grains, but also contain some unleached ilmenite grains. The alteration of ilmenite typically starts along the rims (Fig. 7) and continues inwards along cracks and crystallographic weakness zones, e.g. cleavage planes or twin planes (Figs 7 and 8). When colloidal leucoxene replaces ilmenite grains (Fig. 9) no relics of the original ilmenite crystallography can be seen. Instead, leucoxene appears in bands of different thickness and different chemical composition. Stabilised dunes (contrary to active, still moving, dunes) occurring inland in southern Madagascar contain only leached ilmenite grains, without the presence of primary unleached ilmenite grains. As the active dunes near by contain both altered and relatively fresh ilmenite grains indicating that the alteration begins during weathering in the bed rock and continues in the dunes.

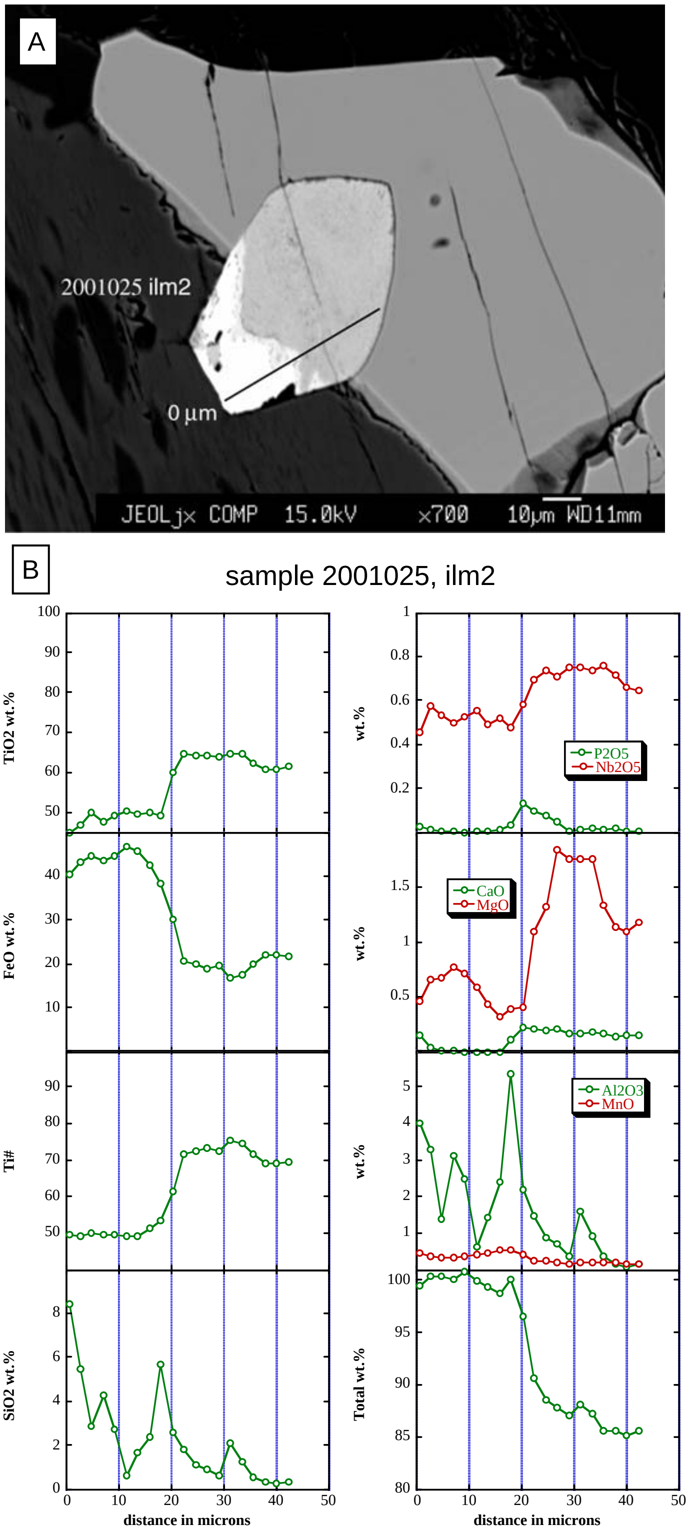

Fig. 4. *A. An ilmenite grain from weakly altered gneiss in Madagascar (2001025). A sharp transition can be observed between altered and unaltered parts of the grains (backscatter microphotograph sample 2001025, ilm2). The black line indicates the line scan performed by electron microprobe. B. Electron microprobe line scan shows an increased titanium content in the altered parts together with increased MgO, Nb_2O_5, and CaO. Increased P_2O_5 (and Al_2O_3) values occur only at the transition from altered to unaltered ilmenite.*

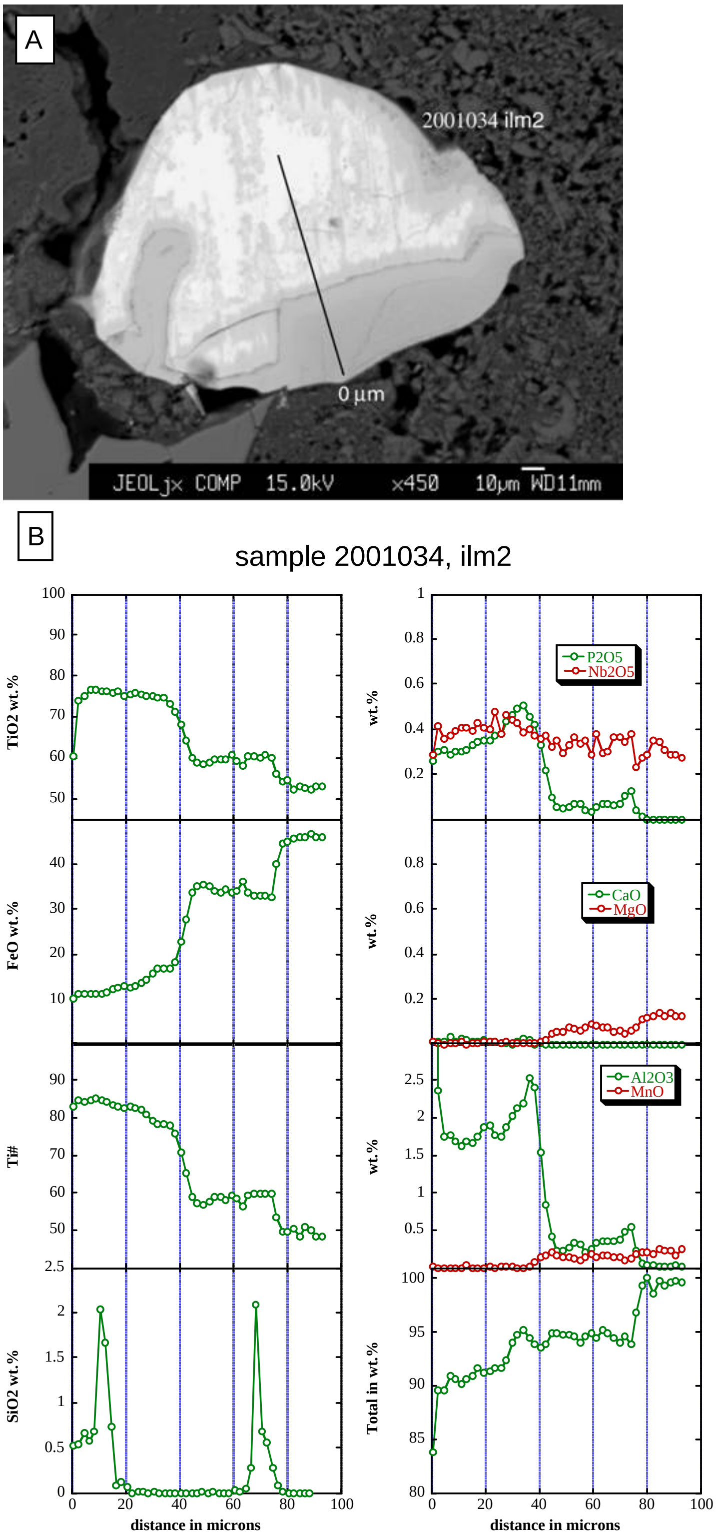

Fig. 5. *A. An ilmenite grain from deeply kaolinised gneiss in Madagascar (2001034). Three domains can be observed, unleached, moderately leached and highly leached (backscatter microphotograph sample 2001034, ilm2). The black line indicates the line scan performed by electron microprobe. B. Electron microprobe line scan shows an increased titanium content in the most altered parts together with increased amounts of P_2O_5 and Al_2O_3.*

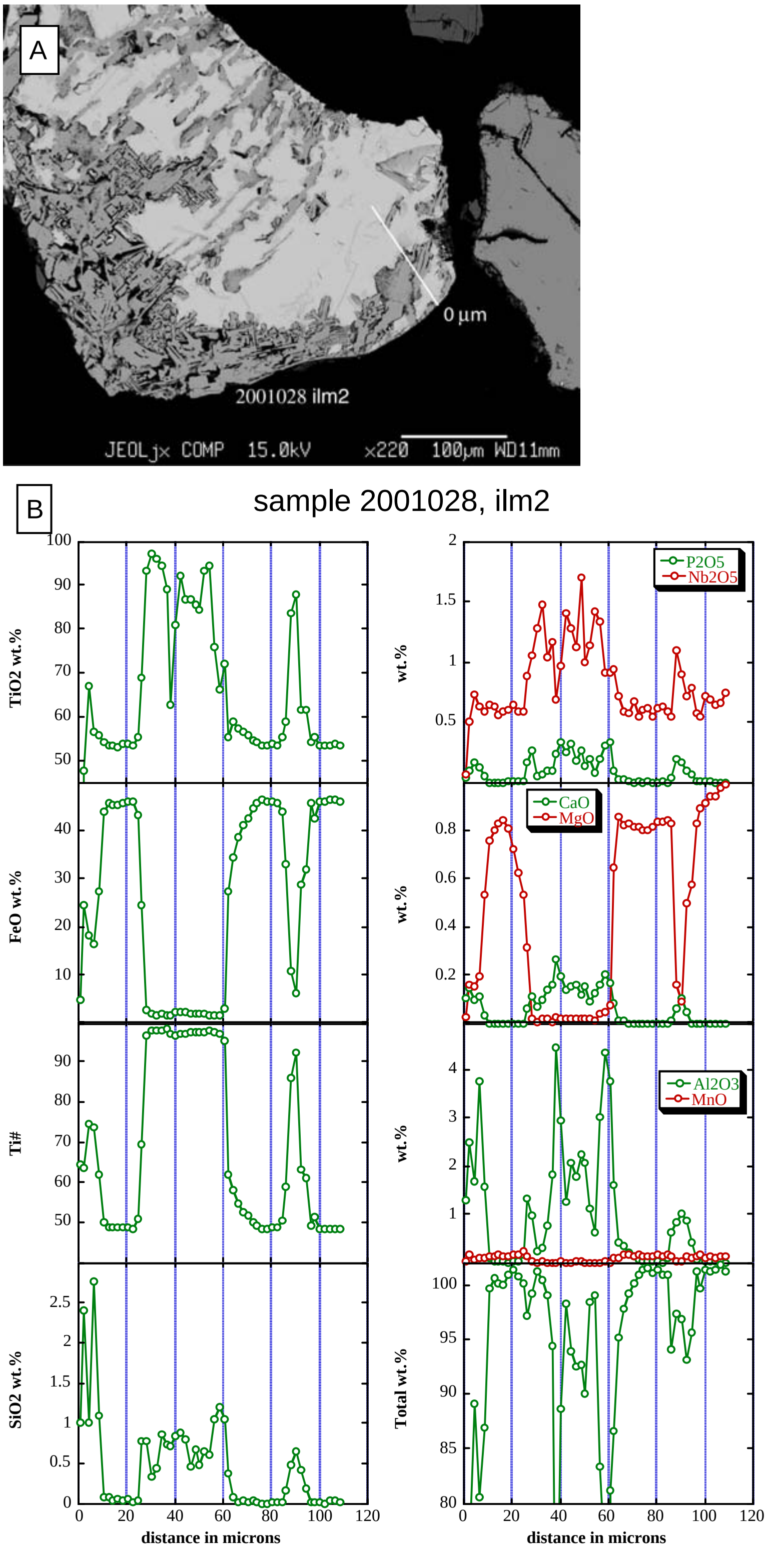

Fig. 6. *A. The ilmenite grain shows an abrupt change between the altered and the unaltered part of the grain from tropical soil formed in a wide crack between gneiss blocks (backscatter microphotograph sample 2001028, ilm2). The white line on the grain indicates the line scan performed by electron microprobe. B. Electron microprobe line scan of ilm2 shows abrupt change in the titanium content in the altered part, which has rutile composition. The altered part has also increased amounts of P_2O_5, Al_2O_3, CaO and Nb_2O_5.*

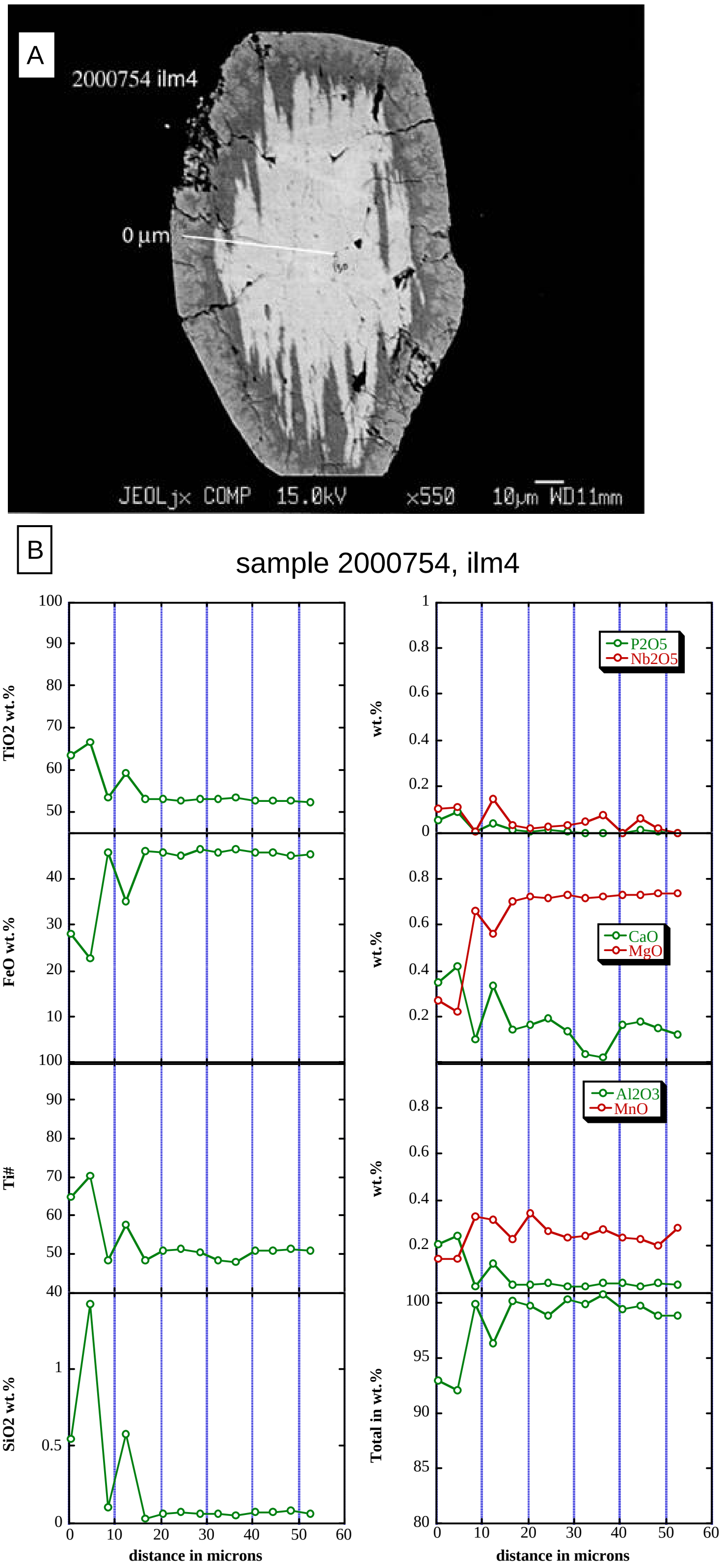

Fig. 7. *A. Epitaxial leaching of ilmenite grain with relict ilmenite core from active coastal dunes Madagascar (backscatter microphotograph samples 2000754, ilm4). The white line indicates the line scan performed by electron microprobe. B. Electron microprobe line scan shows increased titanium along the rim associated with weakly increased P_2O_5, Nb_2O_5, Al_2O_3 and CaO.*

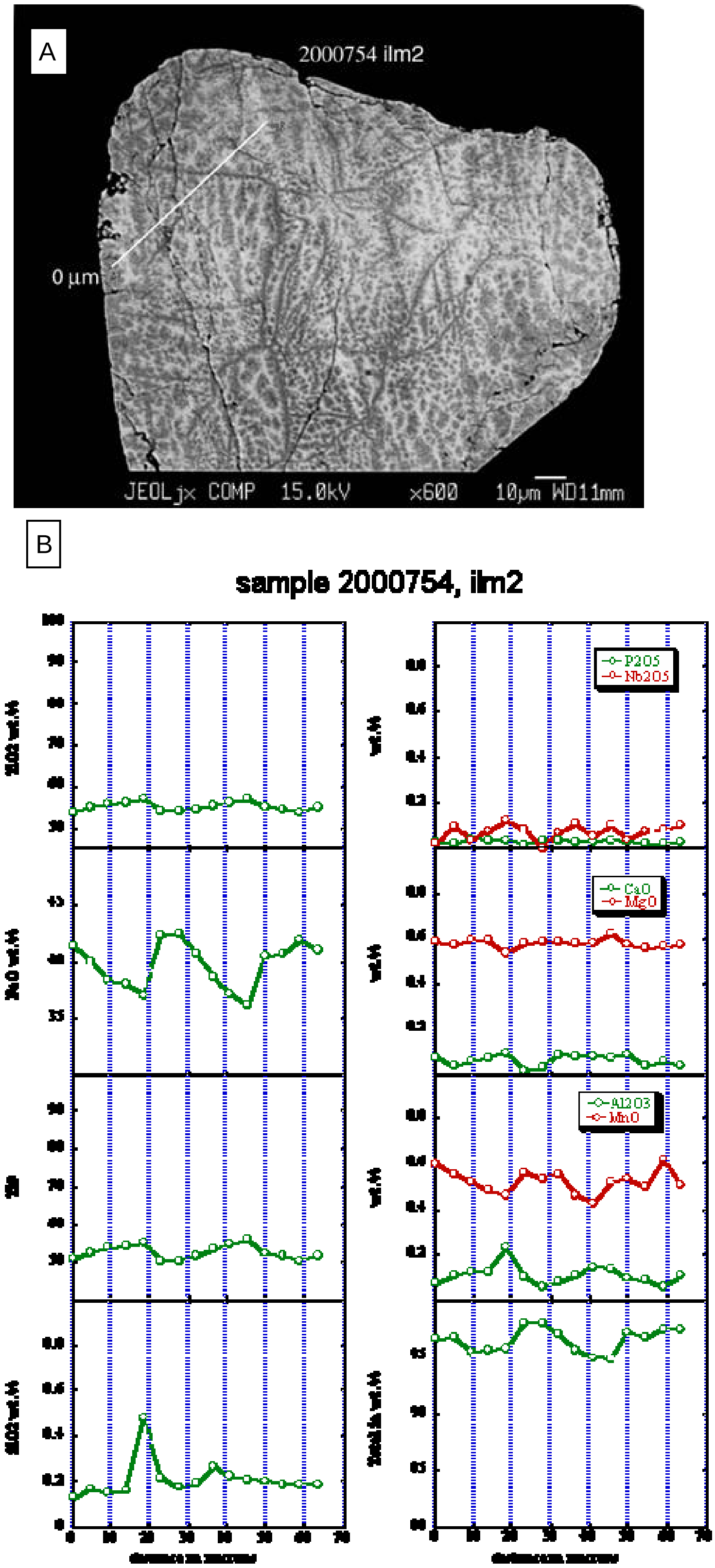

Fig. 8. *A. Patchy altered ilmenite grain with relict internal crystal morphology from active dunes in southern Madagascar (backscatter microphotograph sample 2000754, ilm2). White line indicates the line scan performed by electron microprobe. B. Electron microprobe line scan shows varying degrees of leaching. The low total may indicate oxidation of* Fe^{2+} *to* Fe^{3+}*.*

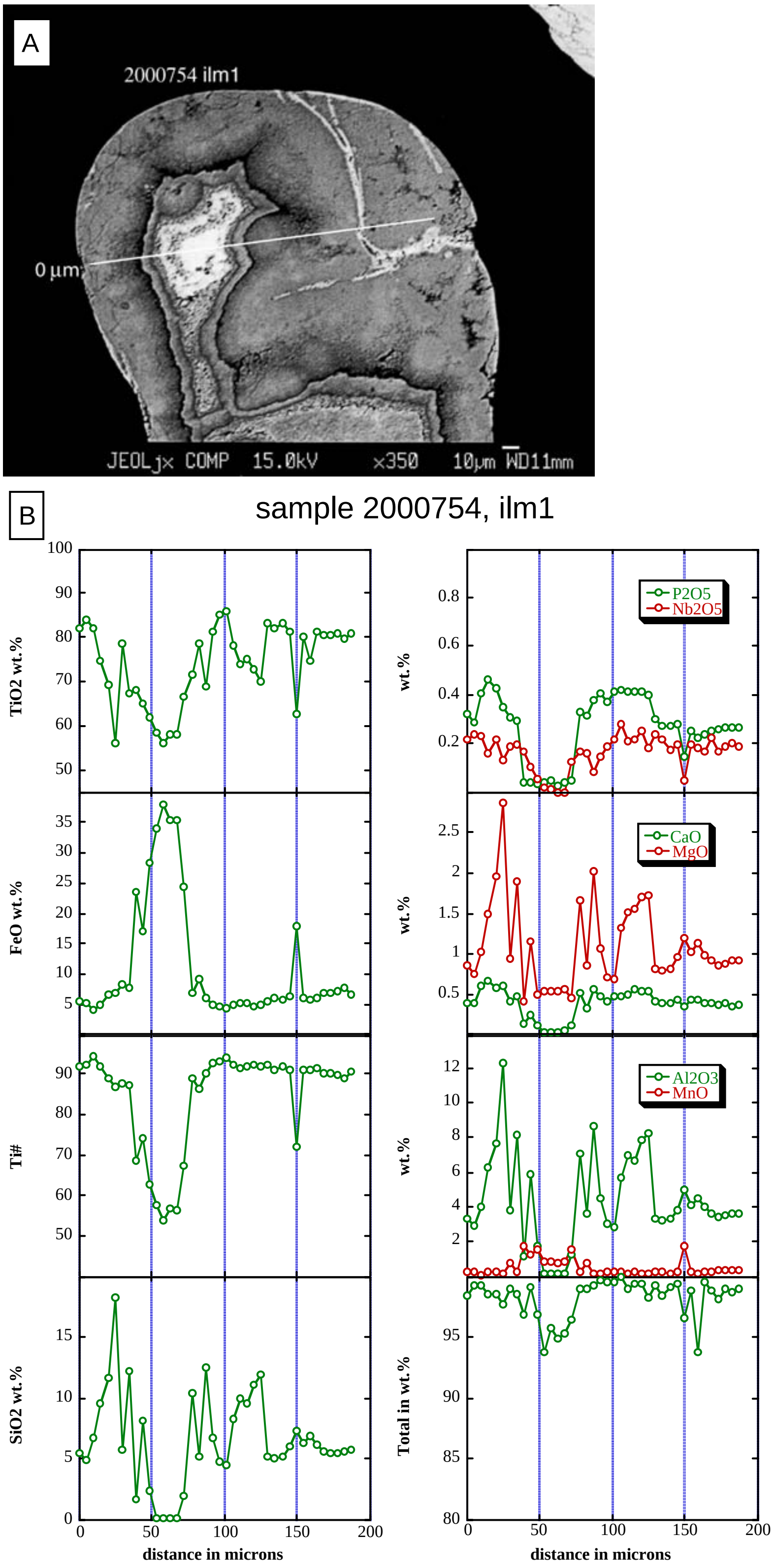

Fig. 9. *A. Colloidal leucoxene precipitated around small ilmenite remnants from active dunes southern Madagascar (backscatter microphotograph samples 2000754, ilm1). White line indicates the line scan performed by electron microprobe. B. Electron microprobe line scan shows increased titanium along the rim associated with bands of weakly increased* P_2O_5*,* Nb_2O_5*,* Al_2O_3*, CaO and MgO.*

Alteration of ilmenite in the outer or upper shoreface

Investigations on ilmenite ores from India show that there is a very general increase in the aluminium, silicon and titanium contents in ilmenite ores in traverses from shoreface to lagoonal environment (Fig. 10; Bernstein 2003). The phosphorus content seems to follow the other anions (Fig. 10). The local variations in impurities possibly reflect local differences in phosphorus, silicon and aluminium abundances in the depositional environment.

The ilmenite in Indian and Madagacar beach sands and dunes are more altered (has a higher titanium content) and contains more phosphorus than ilmenite in rivers in the same areas (Weibel 2007). Shoreface sands in a barrier island environment (Voerslunde) from Denmark contain ilmenite enriched in titanium and phosphorus compared with the contemporaneous outer shoreface – shallow marine Miocene deposits (Skjern-Stauning) (Fig. 11; Weibel 2007). The highest degree of ilmenite alteration and incorporation of phosphorus seems to take place in the shoreface zone and in the back-barrier environment.

Alteration of ilmenite in fresh water environment

Compilation of all the CCSEM data for India, Madagascar, Denmark and Poland shows the general relation that phosphorus increases with increasing titanium content (Figs 11 & 12; Weibel 2007). These results are consistent with elemental mapping by electron microscopy, i.e. the phosphorus content increases as the ilmenite grains are altered to leucoxene. However, interesting exceptions are represented by ilmenite samples from Cretaceous–Jurassic deposits from Bornholm, Denmark (Fig. 11), and from Miocene lignite deposits in Poland, which contain ilmenite enriched in titanium but are low in phosphorus contents (Fig. 12). This suggests that ilmenite grains with high titanium and low phosphorus contents might be found in fresh water deposits. However, this needs to be verified, as the previous results from fluviatile deposits in Denmark (Addit in Fig. 11) show extremely high phosphorus contents, which is either typical for the Danish fluviatile deposits or reflects a local high-phosphorus sediment.

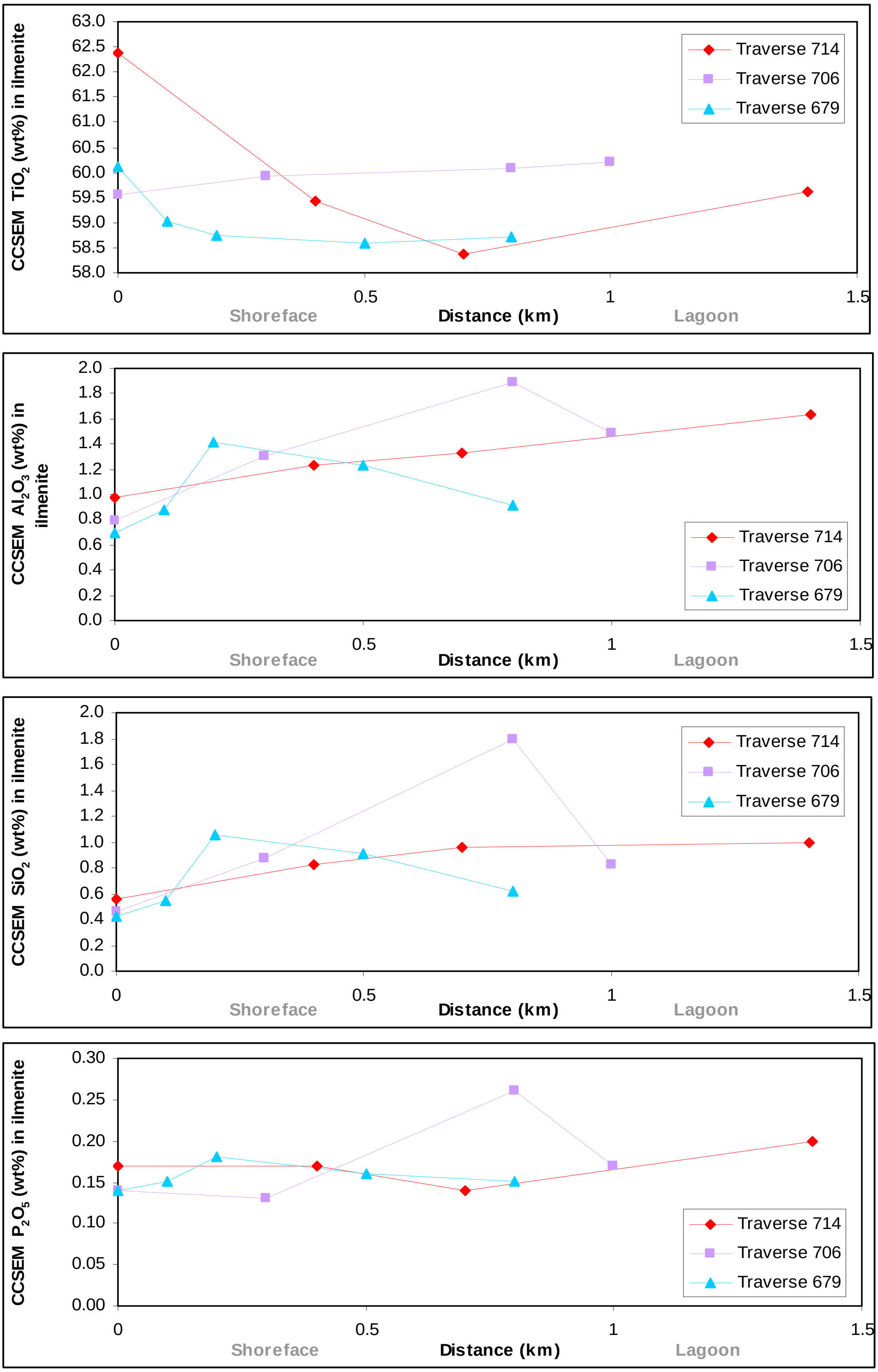

Fig. 10. *Average ilmenite composition by CCSEM in traverses from shoreface to lagoon, Ashtamudi Loaggon, India (modified after Bernstein 2003).*

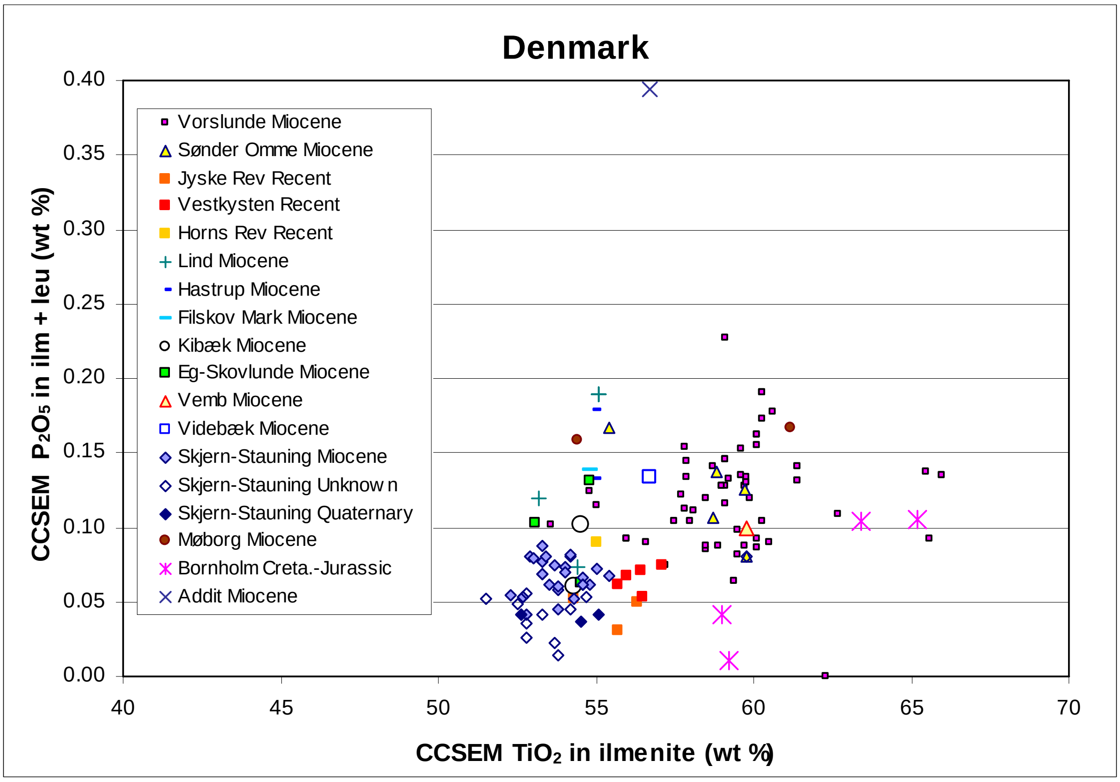

Fig. 11. *Graph showing general increasing TiO_2 content in ilmenite grains from Denmark with increasing P_2O_5 content in ilmenite and its alteration products obtained by CCSEM.*

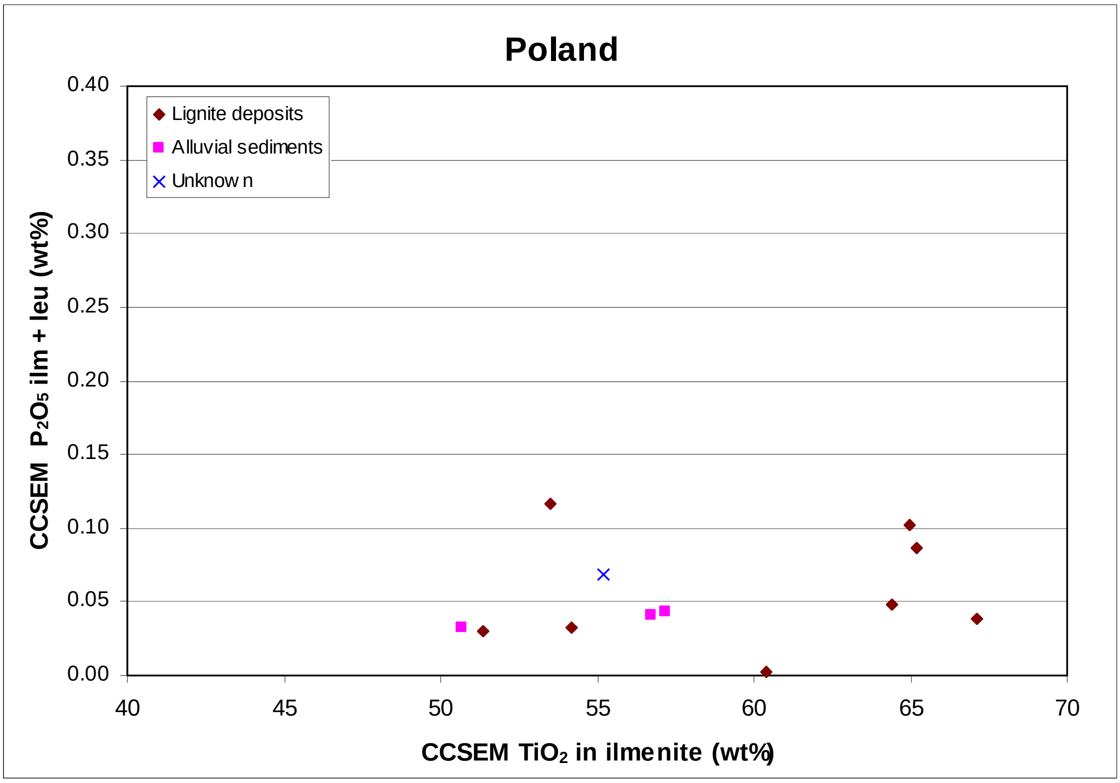

Fig. 12. *Graph showing general increasing TiO_2 content in ilmenite grains from Poland with increasing P_2O_5 content in ilmenite and its alteration products obtained by CCSEM.*

Phosphorus content measured by different methods

The comparison of different phosphorus-measuring methods shows that there is a correlation between the total phosphorus content from XRF and the phosphorus content in Ti-bearing minerals from CCSEM (Fig. 13, Table 3). The discrepancy between total phosphorus content from XRF and the total phosphorus content from CCSEM is mainly due to an over- or under-estimation of the total phosphorus content by the CCSEM method in samples containing grains of monazite and xenotime (Fig. 13). Monazite and xenotime typically occur as 1 or 3 grains out of 1500–2000 grains, therefore the accuracy of the total phosphorus content obtained by CCSEM is very low. In order to avoid the effect of rare large phosphate grains, it is preferably to use the phosphorus content in Ti-minerals. These two distributions show a fairly good match, with a slight over-estimation of the total phosphorus content measured by the CCSEM (Fig. 14). The phosphorus content in Ti-minerals, measured by CCSEM, is the value that is used for the phosphorus 'traffic light' (red, yellow and green colours indicating the expected behaviour of the ilmenite ores) in the geochemical database (also shown in Table 3). Ilmenite ores with a CCSEM phosphorus content in the Ti-minerals below 0.1 wt % should cause no problems during production (indicated by a green 'traffic light' in the geochemical database), whereas a problematic response could be expected for ilmenite ores with a CCSEM phosphorus content in the Ti-minerals above 0.1 wt % (indicated by a red 'traffic light' in the geochemical database). Caution must be taken during production at borderline situations with CCSEM phosphorus contents in the Ti-minerals at 0.1 wt % (indicated by a yellow 'traffic light' in the database). This new evaluation of the ore quality was based on several ilmenite ore samples (except the Bemax samples).

Possible sources for the systematic off-set between the CCSEM and XRF results could be:

a. Trace amounts of phosphorus in the epoxy mount. The electron beam activates up to a few micrometre below the surface of the grain. Small volumes of epoxy resin can thus be included in the measurements of small, thin or porous grains. Two hundred point measurements on the epoxy resin were analysed for phosphorus and all showed negative results. Thus it is assumed that no phosphorus is present in the epoxy mount, or in the carbon coating.
b. Classification of small amounts of zirconium as phosphorus. The zirconium and phosphorus peak in the EDX spectrum overlap, which might be a source of 'extra' phosphorus. The XRF data shows that trace amounts of zirconium are present in the samples; part of the excess phosphorus might in fact be zirconium.

The amount of phosphorus stated for the 'traffic light' is, for the reasons mentioned above, in most cases an upper limit to the amount of phosphorus present in the Ti-minerals. The limit set by the 'traffic lights' is conservative in an attempt to be aware of all ilmenite ore that may cause problems during chlorination. However, this also means that some good ilmenite ores may show up with red or yellow 'traffic light' (Table 3). But at least precautions could be taken during their trial production.

The Bemax samples have fluctuating phosphorus contents when measured by CCSEM, and typically low phosphorus contents when measured by XRF (Table 3). So the Bemax samples are not clearly distinguishable by having much higher phosphorus contents as could have been expected from the problems the ores have been causing during chlorination. The fluctuating phosphorus content obtained by CCSEM analysis could indicate sampling problems and that the Bemax samples may not have been representative of the complete ore shipments. Consequently, new ore samples were taken and carefully split down to aliquots, which were analysed by XRF and CCSEM at the CCAS Laboratory at DuPont and GEUS, respectively. The XRF and CCSEM analyses on the same aliquots showed good correlation, though generally higher phosphorus content is obtained by the CCSEM method (Fig. 14). Repeated CCSEM analyses have been performed on selected samples in order to evaluate whether the difference was random or systematic (Fig. 15). In those cases where the difference was systematic, it could be related to the recent change of CCSEM software. There appears to be a systematic error between measurements with the old and new software: the CCSEM results obtained with the new software are systematically lower in phosphorus contents than those obtained with the older software (Table 4, Fig. 15). However, the XRF results do not show substantially higher phosphorus contents and the electron microprobe element maps only show increased phosphorus contents in rare leucoxene overgrowths in inclusions and silicate-intergrowths. Therefore, the comparatively small systematic error in the phosphorus measurements using the new CCSEM software cannot account for the observed problematic behaviour of the Bemax samples during production/chlorination.

The average phosphorus content in ilmenite and its alteration product obtained by electron microprobe correlates well with the average phosphorus in ilmenite and leucoxene obtained by CCSEM (Table 3, Fig. 16). This is notable, as the electron microprobe results comprise measurements at 4 to 12 points of approximately 40 single grains per sample, whereas the CCSEM results are based on scanned areas of 1000–2000 grains per sample. The accuracy and precision of phosphorus measurements is substantially higher for the electron microprobe than the CCSEM. However, the statistical validity is much higher for CCSEM results than for the electron microprobe due to the larger number of grains analysed by CCSEM. The bulk CCSEM analysis has a reproducibility error of < 0.2 wt% for major elements, < 3 wt% for minor elements and < 15 wt% for trace elements. This error is dependent on the measuring time and the measuring conditions.

The microprobe and CCSEM data are in better agreement than the XRF and CCSEM data possibly because the operator selects ilmenite on the probe and the CCSEM selects ilmenite on the basis of chemistry so that it is very likely that a grain defined as ilmenite (42–67 atomic percent titanium) is going to have trace elements, including phosphorus, similar to grains picked as ilmenite with alteration on the microprobe. Thus the items that cause the biggest difference in data, especially phosphorus data, namely monazite, are not included in the CCSEM result for ilmenite.

Table 3. Comparison of P_2O_5 content measured by different methods

GEUS No.	Sample	Scott rank	Bulk P_2O_5 (wt%)	Total P_2O_5 (wt%)	Ilmenite + leucoxene P_2O_5 (wt%)	Traffic light alert	Ilmenite alteration product P_2O_5 (wt%)
			XRF	CCSEM	CCSEM		Micro-probe
2002602	UKRAINIAN 92203-24	1	0.12	0.135	0.119	🔴	0.12
2001142	DORAL 102208-97	10	0.03*	0.335	0.038	🟢	0.04
2001180	INDIAN E105202-7	1	0.15	0.266	0.126	🔴	0.16
2002802	VIETNAMESE E98651-105	7	0.11	0.155	0.073	🟢	0.17
2003302	East Tennessee		0.32	0.206	0.206	🔴	0.26
2003303	Florida		0.16	0.172	0.172	🔴	0.21
2003305	Malaysia		0.18	0.168	0.123	🔴	0.10
2003304	India		0.13	0.222	0.123	🔴	0.12
2003306	Ukraine	3	0.12	0.144	0.109	🔴	0.15
2003307	Vietnam		0.14	0.313	0.099	🟡	0.11
2001178	AUSTRA-ILUKA E1005202-19	8	0.08	0.069	0.069	🟢	0.04
2002102	MALAYSIAN 10.13.03-35A	8	0.15	0.173	0.118	🔴	
2001140	ILUKA-VIRGINI 101503-91	10	0.07	0.083	0.083	🟢	
2001141	ILUKA-FLA 101503-93	5	0.15	0.168	0.168	🔴	
2001179	AUSTRA-CSL E105202-2	8	0.08	0.112	0.112	🔴	
2003530	Australian BEMAX ilmenite		0.14	0.095	0.042	🟢	
2003531	Australian BEMAX leucoxene			0.259	0.134	🔴	
2003532	Australian BEMAX rutile		0.02	0.113	0.113	🔴	
2003533	Brazil Imerys			0.032	0.032	🟢	
2003577	539 BEMAX leucoxene			0.352	0.109	🔴	
2003578	540 BEMAX leucoxene			0.050	0.050	🟢	
2003579	603 BEMAX leucoxene			0.262	0.096	🟡	
2003580	626 BEMAX leucoxene			0.205	0.066	🟢	
2003582	Beach Minerals Co. Ilmenite			0.067	0.11	🔴	
2003583	DPSR Syntetic rutile			0.026	0.026	🟢	
2003584	RBM ore		0.028	$0.036^{\#}$	0.036	🟢	
2003585	CRL ore		0.031	$0.031^{\#}$	0.031	🟢	
2003586	BEMAX ore		0.026	$0.053^{\#}$	0.053	🟢	
2003587	SREP ore (synthetic rutile)		0.026	$0.026^{\#}$	0.026	🟢	
2003588	Ti West ore		0.056	$0.040^{\#}$	0.040	🟢	

** indicates an average value for all Doral samples. # indicates that these samples have been rerun (see Table 2 and Fig. 20). The ‘traffic light alert’ is explained in more details in the text.*

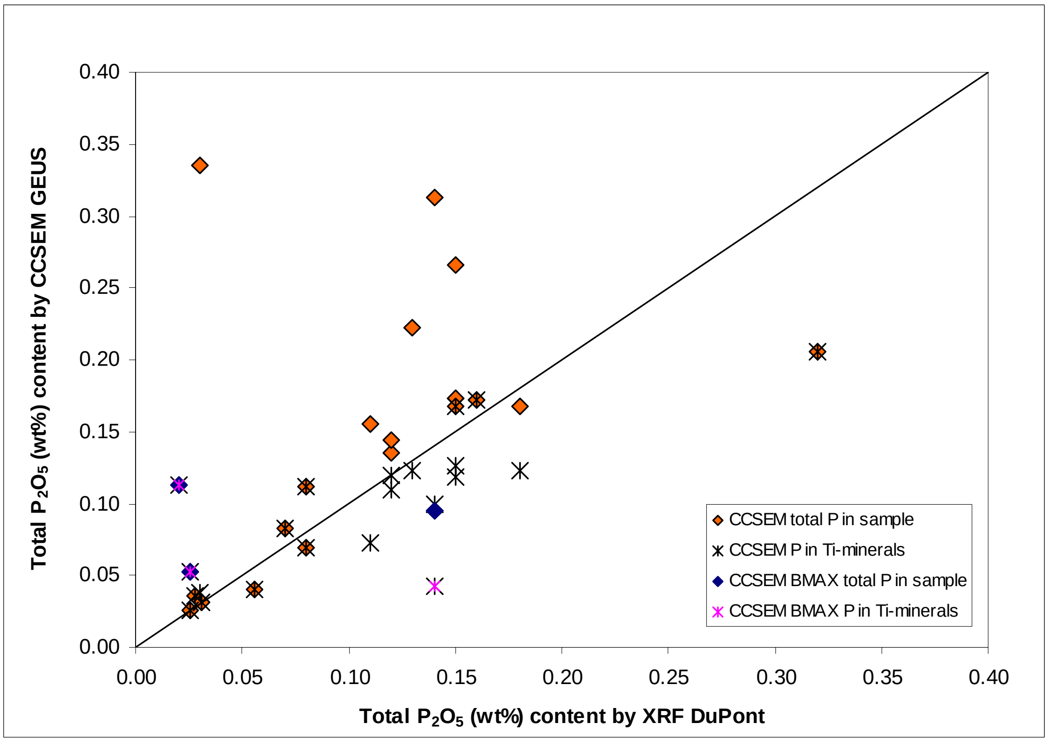

Fig. 13. *Comparison of P_2O_5 (wt%) measurements by XRF and CCSEM methods performed on the same samples. The line indicates a theoretical 1:1 correlation between XRF and CCSEM. The discrepancy between total P_2O_5 (wt%) measured by CCSEM measurements and measured by XRF is mainly due to the presence of rare monazite and/or xenotime grains, which can be over-represented by the CCSEM method.*

Table 4. *Repeated CCSEM analyses of selected samples*

GEUS No.	Sample	Original P_2O_5 (wt%)	Mean all P_2O_5 (wt%)	St Dev	CCSEM error (%)	Rerun							
						1	2	3	4	5	6	7	8
2003584	RBM	0.036	0.038	0.002	4.4	0.040	0.039						
2003585	CRL	0.031	0.035	0.004	10.1	0.038							
2003586	Bemax	0.053	0.052	0.004	7.4	0.055	0.049	0.056	0.056	0.045	0.057	0.058	0.052
2003587	SREP	0.026	0.028	0.003	9.3	0.027	0.032						
2003588	TiWest	0.040	0.062	0.010	17.6	0.063	0.076	0.065	0.067	0.067			

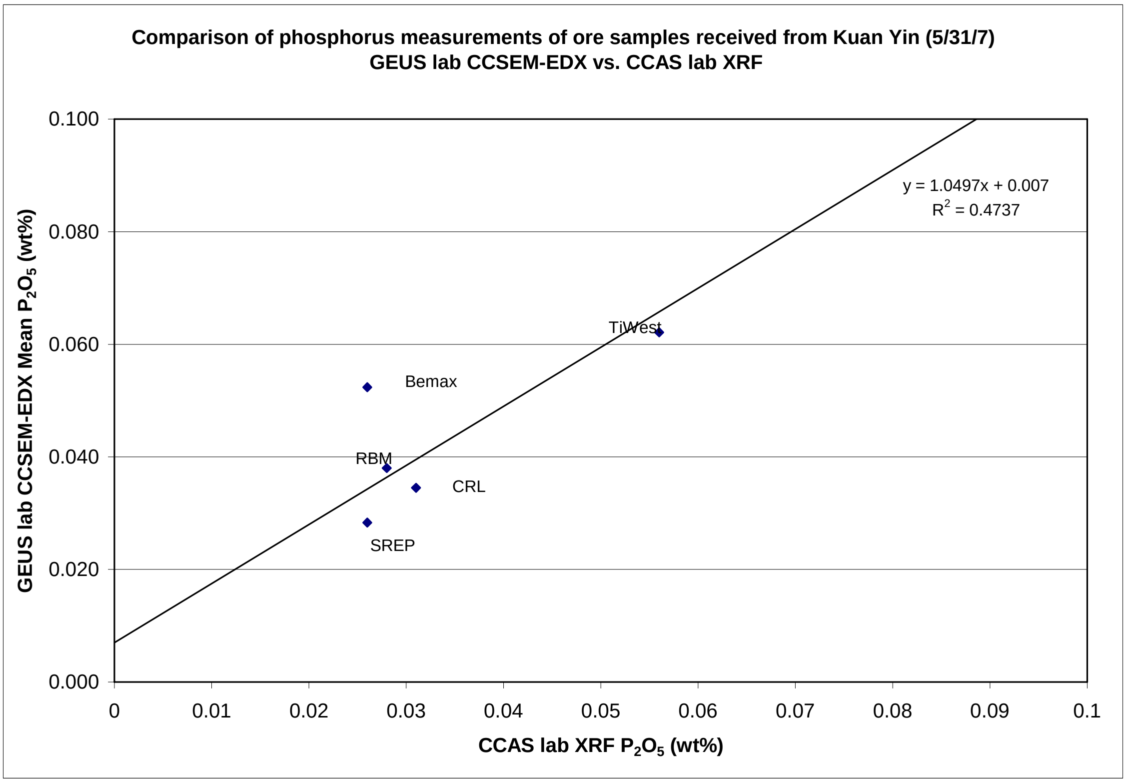

Fig. 14. *Comparison between P_2O_5 content in Ti-minerals in ilmenite ore samples from the Kuan Yin plant, Taiwan (5/31/7) using ilmenite ores from at least five different sources measured at GEUS laboratory by CCSEM and at CCAS laboratory, DuPont by XRF.*

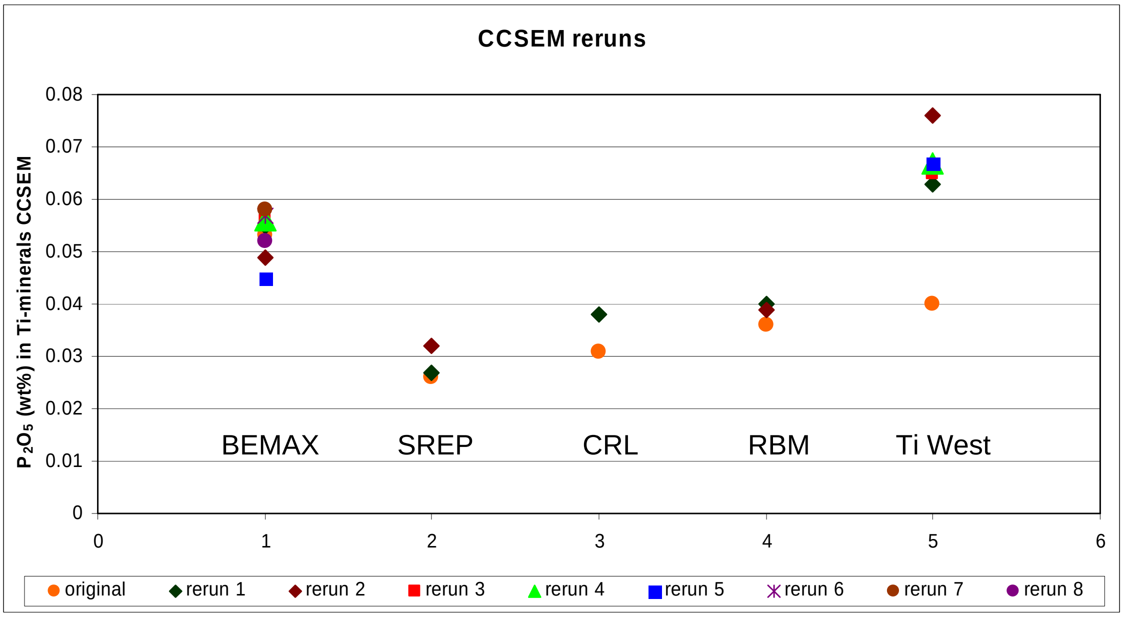

Fig. 15. *CCSEM analyses repeated up to eight times show a general systematic small increase in the P_2O_5 content when the ilmenite ore is measured by the new software compared (rerun 1-8) to the original results. Note that Bemax shows the largest change after repeated analyses.*

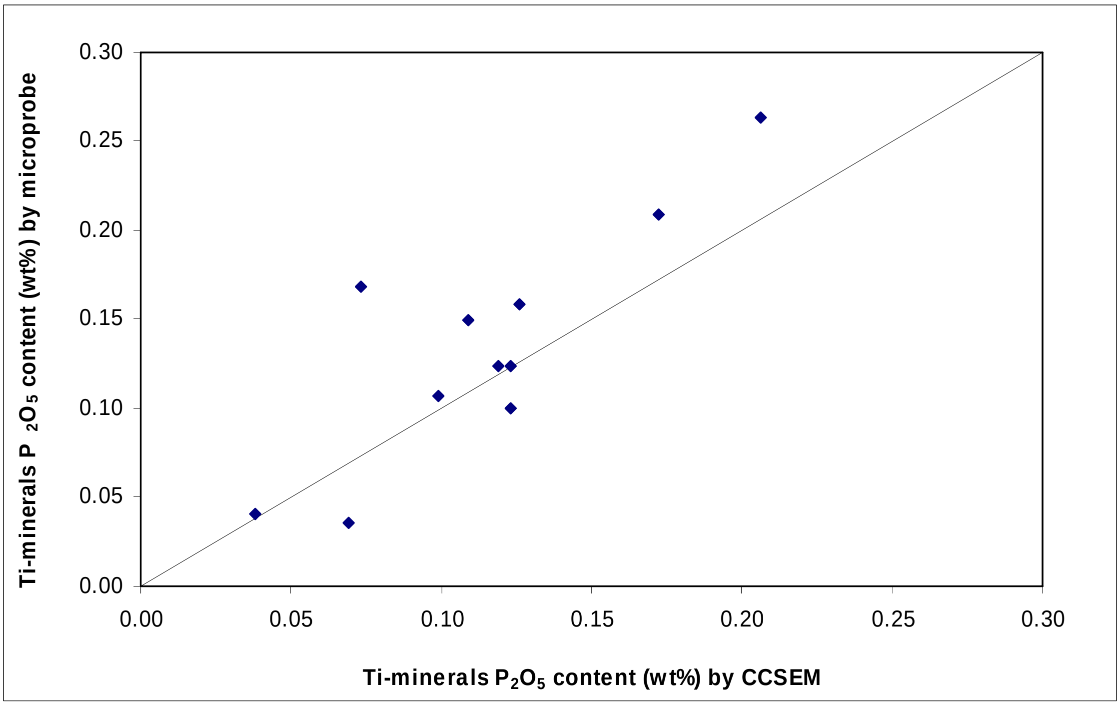

Fig. 16. *Relatively good correlation between the P_2O_5 content in ilmenite and its alteration product obtained by electron microprobe and the P_2O_5 content in Ti-bearing minerals obtained by CCSEM. The line indicates a theoretical 1:1 correlation between CCSEM and electron microprobe results.*

Possible ways of removing the phosphorus – leaching experiments

Leaching experiments were performed in order to identify possible treatment of ilmenite ore to remove phosphorus prior to chlorination. Laboratory experiments were performed with several different solutions (10% HCl, 20% HNO_3, 20% H_2SO_4 and 10% oxalic acid ($C_2H_2O_4$) at ambient and boiling temperatures.

The highest amounts of phosphorus are extracted from samples with the highest original phosphorus content (sample 2003302; Tables 5, 6). Likewise, the highest amounts of other trace elements extracted are from ilmenite ore samples with the highest primary content of these elements (Table 5, 6). The most efficient leaching solutions are oxalic acid and sulphuric acid. Sulphuric acid at 130°C dissolves the highest amounts of phosphorus (Table 6). But even at ambient temperatures oxalic acid typically dissolves more than or similar amounts as the other solutions. The exceptions are silicon and aluminium, which seem to be independent of the original content in the ilmenite ore. Unfortunately, titanium and iron in the ilmenite ore are also brought into solution during the leaching experiment. The pre-treatment of ilmenite ore by leaching is therefore not the best solution to the phosphorus problem.

Synthetic rutile production involves a two stage process (Kumari et al. 2001; Iluka 2007). In the first stage Fe^{3+} in ilmenite is reduced to Fe^{2+} typically by heating the ilmenite ore in rotary kilns in the presence of a reductant (e.g. carbon). In the second stage the iron is removed by oxidation and leaching with acids (Kumari et al. 2001; Iluka 2007). If the leaching experiments were repeated with reduced ilmenite ore this probably would enhance the degree of leaching and lead to higher and more conclusive amounts of elements in the effluents. Also leaching with ammonium chloride (NH_4Cl) with addition of small quantities of carbonyl compounds such as glyoxal, glucose and sucrose could be tested, as this has proven to accelerate the rusting (oxidiation) and leaching of the reduced ilmenite (Kumari et al. 2001). However, if it is correct to assume that SREP is the synthetic rutile product from Iluka (SREP in Table 3) which is produced from the standard Iluka ilmenite ore by artificial leaching (Austra-Iluka and Iluka-FLA in Table 3) then this more costly, higher grade product is not improved by a reduced phosphorus content.

Table 5. Chemical composition of ilmenite ores applied for leaching experiments (selected oxides and elements only) before leaching

GEUS No.	**SiO_2** wt%	**TiO_2** wt%	**Al_2O_3** wt%	**Fe_2O_3** wt%	**MnO** wt%	**MgO** wt%	**CaO** wt%	**K_2O** wt%	**P_2O_5** wt%	**V** wt%	**Cr** wt%	**Nb** wt%	**La** wt%	**Ce** wt%	**Th** wt%
2003302	2.65	66.20	1.45	23.97	0.48	0.40	0.08	0.05	0.32	1010	672	979	571	1294	246
2003303	0.88	65.47	1.28	27.65	0.96	0.44	0.01	0.00	0.16	663	405	999	40	65	30
2003304	0.78	59.53	0.92	35.98	0.38	1.07	0.06	0.01	0.13	1098	1022	1463	209	426	185
2003305	2.28	59.58	1.83	29.99	2.46	0.44	0.04	0.03	0.18	397	90	2395	159	346	299
2003306	1.33	64.71	1.24	26.21	0.94	0.61	0.10	0.00	0.12	915	6002	897	71	160	74
2003307	1.94	59.04	0.96	34.74	2.34	0.32	0.01	0.03	0.14	442	278	1267	72	144	87

Table 6. Semi-quantitative to quantitative ICP-MS analysis of selected leached elements of effluents from leaching experiments

Solution	**T** °C	**GEUS** **No.**	**Si** wt%	**Ti** wt%	**Al** wt%	**Fe** Wt%	**Mn** wt%	**Mg** wt%	**Ca** wt%	**K** wt%	**P** wt%	**V** wt%	**Cr** wt%	**Nb** wt%	**La** wt%	**Ce** wt%	**Th** wt%
20% H2SO4	130	**2003302**	0.008	0.706	0.147	1.160	0.008	0.010	0.030	0.003	**0.017**	0.036	0.013	0.001	0.003	0.012	0.004
10% oxalic acid	20	**2003302**	0.029	0.740	0.161	1.290	0.007	0.012	0.030	0.003	**0.013**	0.045	0.015	0.003	0.002	0.010	0.004
20% H2SO4	130	**2003303**	0.005	0.588	0.163	0.194	0.019	0.005	0.012	0.000	0.011	0.004	0.003	0.001	0.001	0.001	0.000
10% oxalic acid	20	**2003303**	0.006	1.060	0.194	0.332	0.028	0.007	0.010	0.001	0.008	0.005	0.003	0.002	0.001	0.001	0.000
10% HCl	130	**2003304**	0.016	0.488	0.096	0.911	0.018	0.046	0.029	0.003	0.002	0.005	0.008	0.000	0.004	0.007	0.007
20% HNO3	130	**2003304**	0.015	0.099	0.097	0.285	0.002	0.040	0.032	0.003	0.003	0.001	0.007	0.000	0.004	0.009	0.007
20% H2SO4	130	**2003304**	0.008	0.589	0.076	0.809	0.015	0.033	0.019	0.002	**0.008**	0.005	0.009	0.001	0.003	0.005	0.005
10% oxalic acid	20	**2003304**	0.026	1.650	0.124	1.230	0.029	0.075	0.029	0.004	**0.009**	0.010	0.013	0.006	0.002	0.004	0.006
10% oxalic acid	130	**2003304**	0.014	1.610	0.076	1.030	0.024	0.052	0.026	0.003	**0.010**	0.008	0.010	0.005	0.002	0.004	0.001
10% HCl	130	**2003305**	0.018	0.760	0.114	1.170	0.144	0.002	0.003	0.002	0.001	0.016	0.003	0.000	0.002	0.006	0.021
20% HNO3	130	**2003305**	0.015	0.125	0.116	0.480	0.023	0.001	0.002	0.002	0.001	0.012	0.003	0.000	0.005	0.012	0.022
20% H2SO4	130	**2003305**	0.008	1.142	0.084	1.440	0.193	0.002	0.001	0.000	0.002	0.014	0.002	0.005	0.001	0.003	0.018
10% oxalic acid	20	**2003305**	0.022	2.740	0.112	1.470	0.233	0.005	0.002	0.002	0.006	0.016	0.003	0.017	0.001	0.003	0.012
10% oxalic acid	130	**2003305**	0.023	3.890	0.115	1.590	0.286	0.004	0.003	0.002	0.007	0.016	0.004	0.024	0.002	0.005	0.015
20% H2SO4	130	**2003306**	0.009	0.440	0.097	0.710	0.018	0.009	0.045	0.000	0.011	0.015	0.013	0.001	0.002	0.003	0.002
10% oxalic acid	20	**2003306**	0.024	0.453	0.085	0.582	0.015	0.008	0.034	0.001	0.005	0.015	0.012	0.002	0.001	0.003	0.002
10% HCl	130	**2003307**	0.012	0.783	0.118	1.160	0.117	0.006	0.003	0.004	0.001	0.003	0.002	0.000	0.001	0.003	0.003
20% HNO3	130	**2003307**	0.013	0.081	0.128	0.166	0.006	0.005	0.003	0.004	0.001	0.001	0.002	0.000	0.002	0.004	0.003
20% H2SO4	130	**2003307**	0.009	1.982	0.084	2.120	0.238	0.005	0.002	0.002	-0.001	0.004	0.003	0.005	0.001	0.001	0.003
10% oxalic acid	20	**2003307**	0.021	2.340	0.135	0.995	0.137	0.007	0.003	0.004	0.004	0.004	0.003	0.008	0.001	0.001	0.003

Conclusions

The investigations so far show that phosphorus is mainly incorporated into ilmenite during alteration. The Australian Bemax ilmenite ore is an exception, as the phosphorus content seems to be inherited from the source rock. The phosphorus content is typically low in fresh ilmenite from bed rock samples and in the unaltered cores in altered ilmenite grains from various depositional environments. However, in the altered parts of ilmenite the phosphorus content increases as the titanium content increases. Phosphorus increases particularly in the parts of ilmenite where the crystal structure is lost during alteration (i.e. the leucoxene altered parts), whereas the pseudorutile altered parts are relatively increased in impurities due to the leaching of iron. Also the amounts of other impurities (Al, Si and Ca) increase with the degree of alteration. The amount and type of impurities in the ilmenite grains vary with the ilmenite ore type and probably reflects the surrounding environment during alteration. The amount of magnesium and manganese present in the ilmenite grains also varies with ore type but reflects inherited differences in the source rocks.

The first analysed Bemax ilmenite ore samples showed varying total phosphorus contents from CCSEM, which did not match the varying XRF results. Measurements by XRF performed at DuPont lab. and by CCSEM at GEUS were repeated on new, carefully spilt samples in order to verify if these differences originated from problems with the first sampling method. Small differences between the XRF and CCSEM results exist, but they are not large enough to explain the poor behaviour of Bemax during production. Element mapping showed that silicate intergrowths are more common in the BEMAX ore compared to the other Australian ilmenite ores (Iluka and Doral), which may be due to different source areas. The Bemax ore probably comes from the Murray Basin in eastern Australia, where they have their source in Palaeozoic and Proterozoic rocks, whereas Iluka and Doral ores are from Western Australia and have their source in Archaean rocks.

CCSEM data compiled for selected areas, like India, Madagascar and Denmark, also show that increased titanium content typically is followed by increased phosphorus content. However, the ilmenite ore of commercial interest should have high titanium content, but low amounts of phosphorus. Ilmenite from Cretaceous–Jurassic deposits from Bornholm, Denmark, and Miocene lignite deposits in Poland are characterised by high titanium and low phosphorus contents. This indicates that especially fresh water deposits rich in ilmenite may be the best potential ilmenite ores.

Comparison of the CCSEM and XRF methods on precisely split samples show that CCSEM generally gives a higher phosphorus result than the XRF method. This apparent anomaly indicates a small systematic error between the CCSEM and XRF methods. Comparison between electron microprobe analysis and CCSEM on the same ore types shows a reasonably good correlation.

Phosphorus can be leached out of ilmenite with several acid types (HCl, HNO_3, H_2SO_4, $C_2H_2O_4$), of which oxalic acid seems to be the most effective. However, as phosphorus is brought into solution, other elements such as titanium, iron and other trace elements are also leached out. Natural leaching of ilmenite in tropical soil (from southern Madagascar) produces titanium-rich coronas that contain increased amounts of impurities, including phosphorus, even though this alteration product is rutile. The synthetically formed rutile investigated in this study has at least as high (or higher) phosphorus content as its original ilmenite ore, suggesting that synthetic rutile will not show improved behaviour during production.

Recommendations

A. Comparative studies of ilmenite alteration during weathering in non-marine environments and continued alteration in the marine environments to verify the hypothesis that in non-marine environments altered ilmenite has high titanium and low phosphorus content.

B. TEM (transmission electron microscopy) studies of leached phosphorus-bearing ilmenite to confirm the crystallinity or structure of the supposed apatite, alumino-phosphates or alumino-sulphate-phosphates. When the exact phosphorus minerals are known it will be easier to evaluate the conditions that favour their formation.

C. Measurement of additional trace elements in more samples, especially those having low phosphorus and a problematic behaviour during production (i.e. a poor Scott rank).

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