DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2015/81

Changes in ilmenite composition during alteration and "leucoxenisation"

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GEOLOGICAL SURVEY OF DENMARK AND GREENLAND
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GEUS

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G E U S

Summary

Ilmenite is a Fe-Ti oxide mineral occurring in igneous and metamorphic rocks with a fairly high and variable content of Mn, Mg, Nb and Cr. When ilmenite is exposed to meteoric water in hot and humid conditions the mineral is altered and changes composition. In this process the elements Fe, Mn and Mg are leached out leading to formation of leucoxene rich in Ti.

Electron MicroProbe Analysis (EMPA) and X-ray mapping shows that the alteration of the ilmenite to leucoxene starts already when the host rock of the mineral is exposed to weathering in outcrop. The alteration is accompanied by introduction of a micro-porosity in the altered ilmenite seen e.g. as low totals in the analyses. EMPA and X-ray mapping shows that the chemical characteristics of this alteration are loss of Fe, Mn and Mg and introduction of elements such as Al, Si, Ca and P. Nb also increases in concentration due to the loss of Fe, Mn and Mg.

SEM studies and statistical analysis of large numbers of CCSEM data shows:

The patterns with increase in Si, Al and P during alteration seen in microprobe analysis of single grains can be reproduced when looking at very large set of CCSEM data (>10.000 grain analyses). It is further found, that when the altered ilmenite grains (leucoxene) are exposed to very intense alteration, the leucoxene recrystallizes and form grains with > 85 % TiO2. During this recrystallization process cleaner grains are produced and impurities such as Si, Al and P are gradually lost and the composition approaches that of pure rutile/anatase in the final stages of leucoxene formation.

The increase in content of e.g. P with Ti in the altered ilmenite i.e. the P/Ti ratio varies among the different localities.

Laser Ablation ICP-MS analysis shows:

Apart from the above mentioned increase in Al, Si, Ca and P with increasing degree of alteration, it is found that there is an increase in a number of other elements during the alteration. Increase in REE, U and Th together with P is interpreted as introduction of a monazite like component in the micro-pores in the altered ilmenite. The increase in Na and K with alteration is probably tied to precipitation of clay-minerals internally in the altered grains also responsible for the increase in Si and Al.

There is an increase in Pb and As during the alteration.

High-field-strength elements such as V, Zr, Nb, and Ta will generally follow Ti during geochemical processes, which is also the case during alteration of ilmenite, where these elements follow the Ti.

Content

1 Introduction

Ilmenite ($FeTiO_3$) occurs in igneous and metamorphic rocks with a variable content of elements like Mn, Mg, Nb and Cr depending on the environment in which the ilmenite was formed (McLimans et al 1995, Lloyd et al 1995). Unaltered ilmenite contains ca. 50 % FeO and 50 % TiO_2.

The TiO_2 content increases when ilmenite grains are subjected to leaching of iron, manganese and magnesium from the mineral grains in the sedimentary environment, a process that typically occur in hot and humid climates.

Ilmenite with elevated TiO_2 % is a more valuable ore because the amount of pigment that can be produced per ton of ilmenite is higher and the amount of waste generated as well as the consumption of chemicals is lower. However, the upgraded ores also contain elevated concentrations of impurities such as phosphorus or aluminum and the aim of this report is to investigate to what extent impurities get into the titanium ores during the alteration process that enhances the grade (% TiO_2) of the ore.

The information presented here is gathered by GEUS and DuPont in the project “Global Titanium” over the past 10 years.

1.1 Previous work

The classical description of alteration of ilmenite (Bailey et al, 1956) divides the alteration of ilmenite into three successive stages:

1. During the ***first stage*** ilmenite alters along fractures, grain boundaries, or internally to patchy intergrowths of ilmenite and an isotropic substance of lighter color and higher reflectivity than ilmenite is formed. This first stage is marked by progressive breakdown of the ilmenite lattice.
2. The ***second stage*** of alteration is reached when a grain has been completely transformed to an isotropic, amorphous iron-titanium oxide.
3. The ***third stage*** involves progressive alteration of this isotropic substance to leucoxene. In many grains the first, second and third stages overlap, so that the grains never consist solely of amorphous iron-titanium oxide. In any given part of a grain, however, ilmenite passes into the isotropic material prior to development of leucoxene.

The progressive alteration is accompanied by decrease in magnetic susceptibility and increase in the ratio of TiO_2 to iron oxides. The brown and white **leucoxene** of the third stage commonly consists of oriented finely crystalline aggregates. On the basis of XRD analyses Tyler & Marsden (1938) found that leucoxene is a microcrystalline form of rutile, anatase, or brookite.

Other authors (Temple 1966; Grey & Reid 1975; Dimanche & Bartholomé 1976) describe the transformation as a two stage process with formation of pseudorutile by iron diffusion out through the ilmenite crystal lattice in the first step with later rearrangement and precipitation of rutile in a porous network. Weibel (2003) describes the process in three stages: Ilmenite -> pseudorutile -> fine-grained leucoxene -> coarse leucoxene.

Frost et al (1983) found that when ilmenite is altered and the content of titanium increases the content of aluminum and silicium also increases. For compositions with Ti/(Ti+Fe) between 0.45 and 0.60 the impurity content is virtually independent of Ti/(Ti+Fe), and is very low (Al_2O_3 < 0,2 wt. % and SiO_2 < 0,05 wt. %). For compositions between those of rutile and pseudorutile, Frost et al (1983) found a direct correlation between the impurity contents and the Ti content of the alteration phase. The impurity levels increase with increasing Ti/(Ti+Fe) to about 3 wt. % Al_2O_3 and 1 wt. % SiO_2 for compositions close to TiO_2.

Mücke & Chaudhuri (1991) noted that elements like Al, Si, Cr, Ni, Ca increases with decreasing Fe+Mg+Mn. Increases in the Al_2O_3 and SiO_2 content with the alteration process is also noted by Hugo and Cornell (1991).

1.2 This work

A number of different techniques have been used to understand the chemical changes in ilmenite related to the alteration:

Electron MicroProbe Analysis (EMPA)

To study when and where the alteration of ilmenite start, a number of basement gneiss samples were collected from outcrop on Southeast Madagascar and Kerala in India where adjacent beach placers show elevated content of TiO_2 in the ilmenite. Further, ilmenite from saprolite (very deeply weathered basement) and placer deposits in Madagascar was analyzed. The composition of the ilmenite was analyzed using Electron Microprobe (University of Copenhagen) with a focus on the transition from unaltered to altered parts. A number of ilmenite grains from placer sand (ore) were analyzed also using EMPA to establish if there is a relationship between content of phosphorus and degree of alteration and the concentration of contaminants (Weibel, 2007; Weibel et al 2008).

XRF element mapping

Altered grains was studied using XRF element mapping in Scanning Electron Microscopy (SEM) at GEUS with a special emphasis has been put on the element phosphorus as this element is causing problems in some of Chemours reactors (Weibel, 2007; Weibel et al 2008).

Scanning Electron Microscopy

Ilmenite and leucoxene from a placer deposit at Keysbrook, Australia was studied using Scanning Electron Microscopy (SEM) at GEUS to understand leaching processes in ilmenite in the sedimentary environment.

Computer Controlled SEM (CCSEM)

Finally, CCSEM analysis of a large numbers of ilmenite grains from selected areas were processed using the statistical program SIROSOM to study if the processes observed in single grains can be understood as more global processes.

Laser Ablation ICP-MS

Placer ilmenite from a number of areas was analyzed using Laser Ablation ICP-MS (Thomas Zack, University of Göteborg) to study the relationship between the increase of TiO_2 in the grains during alteration with the behavior of different minor and trace elements in the grains during the leaching.

2 Electron Microprobe studies

The alteration of ilmenite is described from beach environment as mentioned above (Bailey et al, 1956; Temple, 1966; Grey & Reid, 1975; Dimanche & Bartholomé, 1976). The increase in titanium when iron is leached out is coupled with increase in Si and Al (Frost et al, 1983; Mücke & Chaudhuri, 1991; Hugo and Cornell, 1991).

To investigate where the alteration/leucoxenisation of ilmenite start and when the enrichment in e.g. phosphorus occur, samples were taken from exposed basement rocks in Madagascar and India (khondalite gneiss), from kaolinized weathering crust, saprolite and from sedimentary accumulations of ilmenite in beach placers. This work has partly been reported (Bernstein 2004 and Weibel et al, 2008) but the information's below from Madagascar has not been reported before.

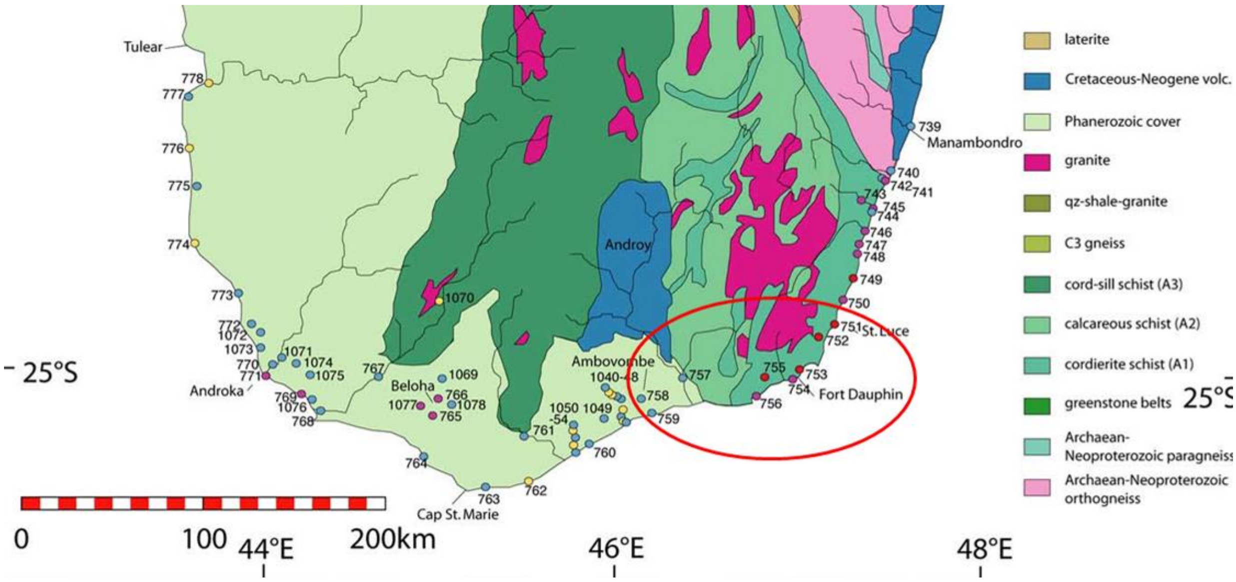
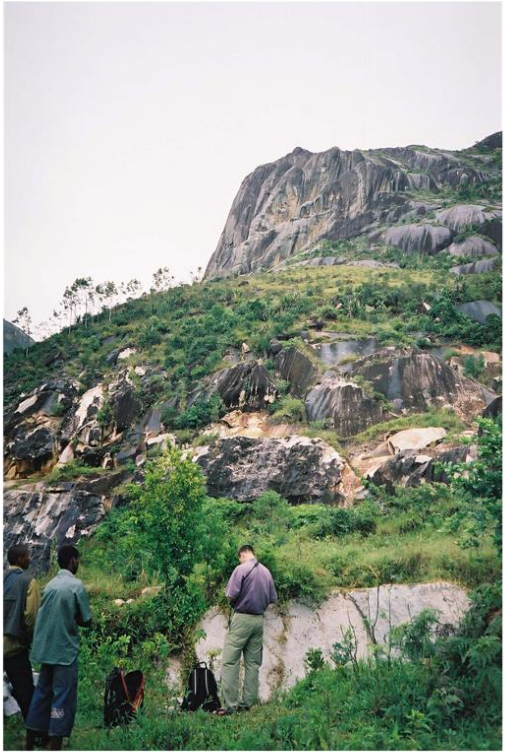


Figure 1 *Field-area in Madagascar. The bluish green colors on the map indicate paragneisses comparable to the Khondalites in Southern India.*

2.1 Basement outcrop on Madagascar

In the area near Fort Dauphin basement gneisses rise in hills and mountains 2-10 km onshore from the coast, and the rocks show evidence of deep chemical weathering (Figure 2).



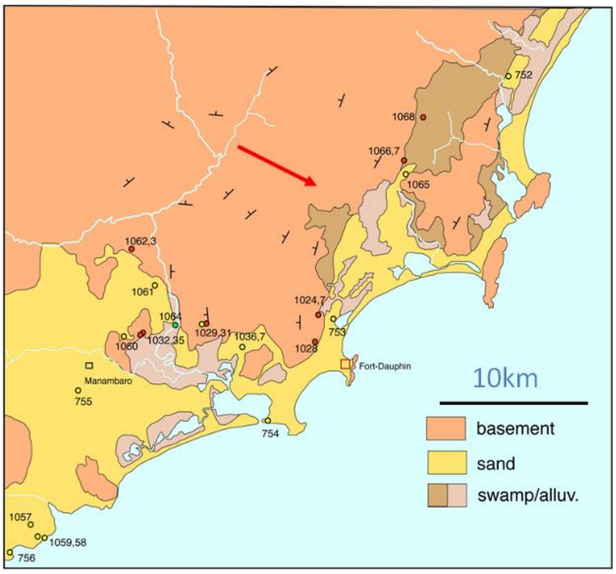
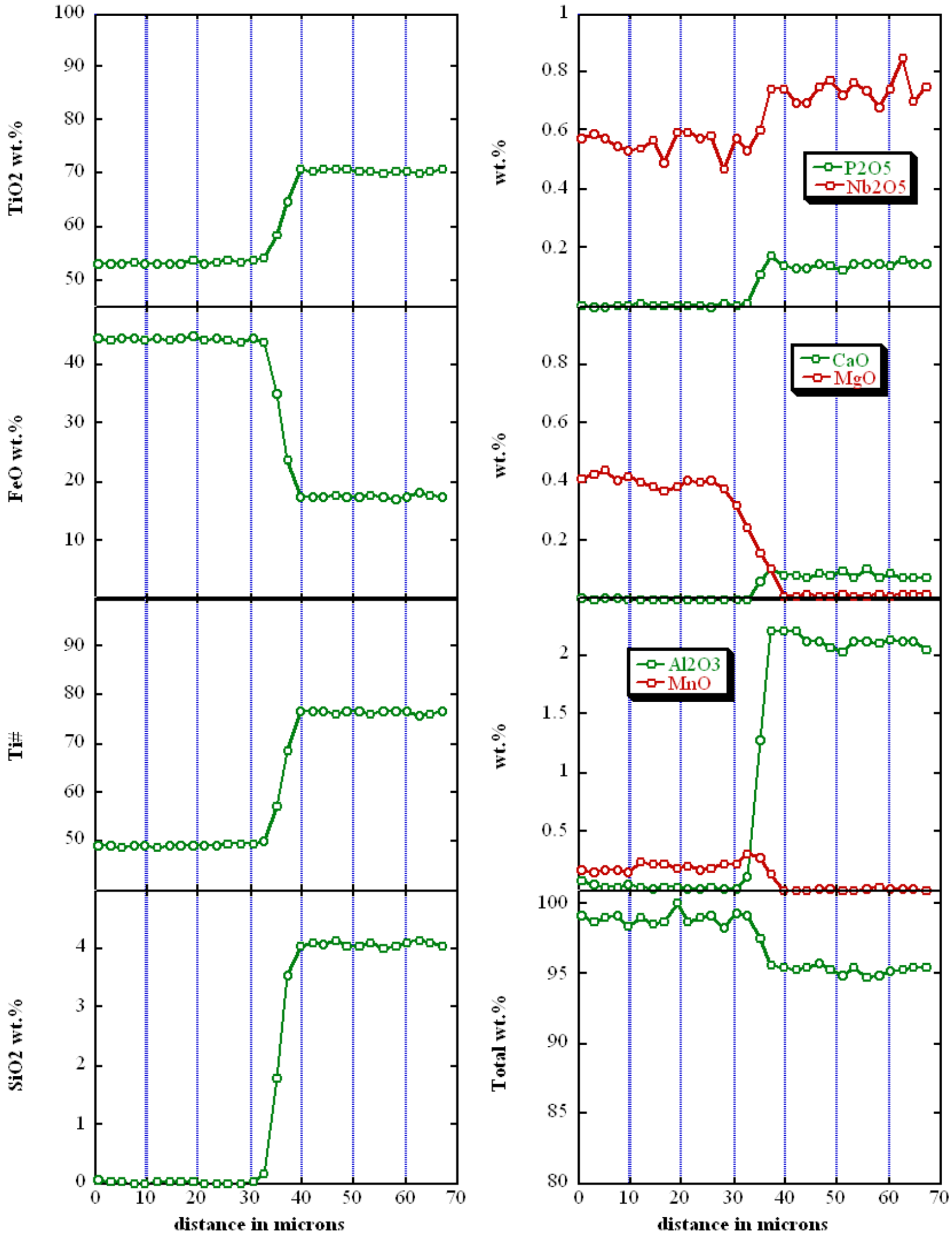


Figure 2
Basement gneisses rising in hills and mountains 2-10 km onshore from the South-east coast of Madagascar around Fort Dauphin.

Figure 3 *Top of basement gneisses - kaolinized saprolite is removed by erosion. Sample 2001024 is from 2 cm altered surface and from fresh gneiss 2001025 is from 10cm below the surface. The outcrop is a typical etch surface, which is the alteration front of deep chemical erosion on Madagascar.*



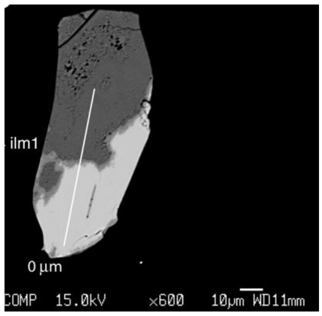


Figure 4

Sample 2001024 from Madagascar.

Backscatter image (upper right) of a small, partly leached ilmenite grain with a sharp transition between leached (dark) and unleached (bright) domains. Scale lower right is 10 µm.

Electron MicroProbe Analysis (EMPA) line scan (white line) analytical results are shown to the right. Distance in µm from 0 µm in the lower part of image.

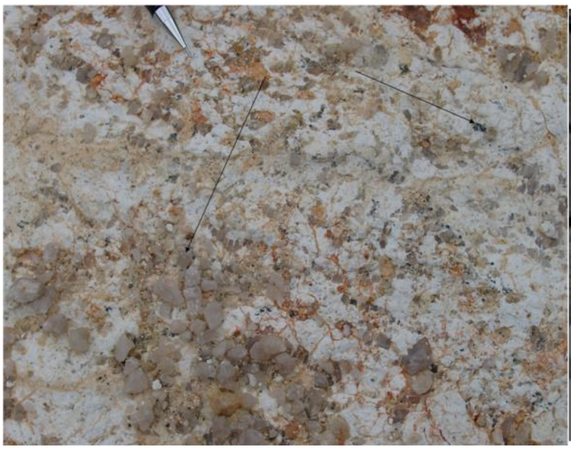
It can be seen that Si and Ti increases when Fe goes down (Figure 4 left column). In the right column it can be seen that P, Ca, Al and Nb are elevated in leached domain and that Mn and Mg decreases. The Total % also decreases (Figure 4 right bottom) in the altered domain indicating that the altered mineral grain is porous.

2.2 Deep kaolinisation of basement gneisses

Figure 5 *Deep kaolinisation of basement gneisses on Madagascar.*

The deep kaolinisation of basement gneisses has developed the rock into a saprolite with relic gneiss structures and the rusty bands on Figure 5 and 6 are altered garnet-rich bands.

Figure 6 *Relic gneiss structures in saprolite. Sample 2001034 is from this outcrop.*



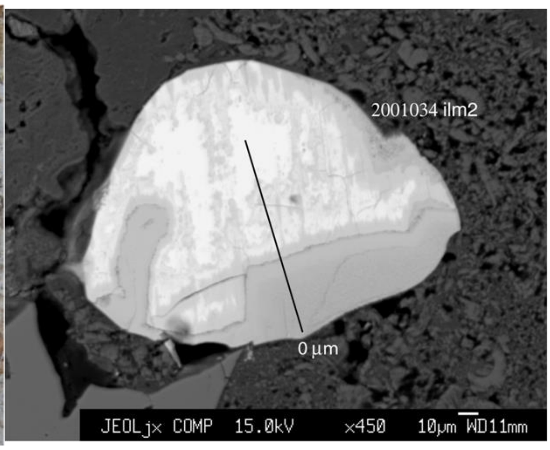


Figure 7 *Saprolite where only quartz and ilmenite has survived the kaolinisation process (left). To the right is a backscatter image of small, partly leached ilmenite grain. Position of EMPA line-scan is shown. Three domains are seen: 1) highly leached (gray) 2) moderately leached and 3) unleached (white). Sample 2001034.*

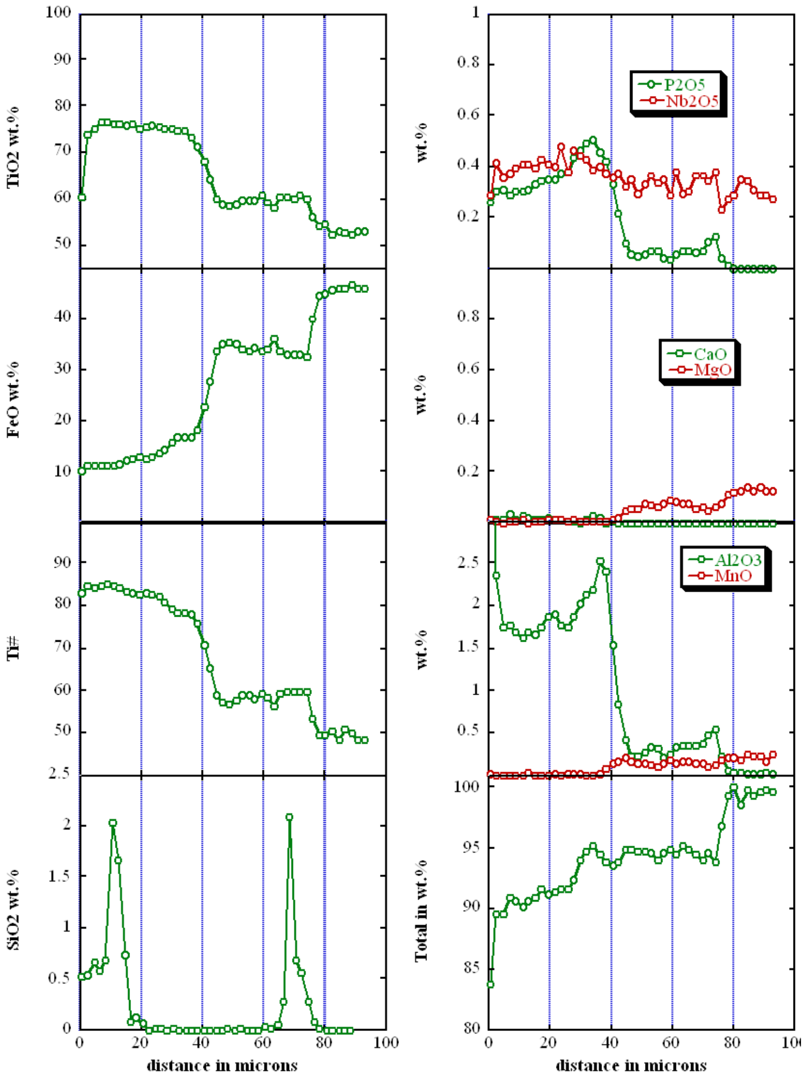


Figure 8

EMPA line-scan of 2001034.

The three domains can be recognized in the chemical profile over the grain. The unaltered ilmenite is to the right in this diagram with high Fe, Mg and Mn. The intermediate domain is also intermediate in Ti, Fe, Mg, P, Al and Total (porosity) relative to the very altered ilmenite (left).

Nb high throughout and showing a slight increase in the altered part

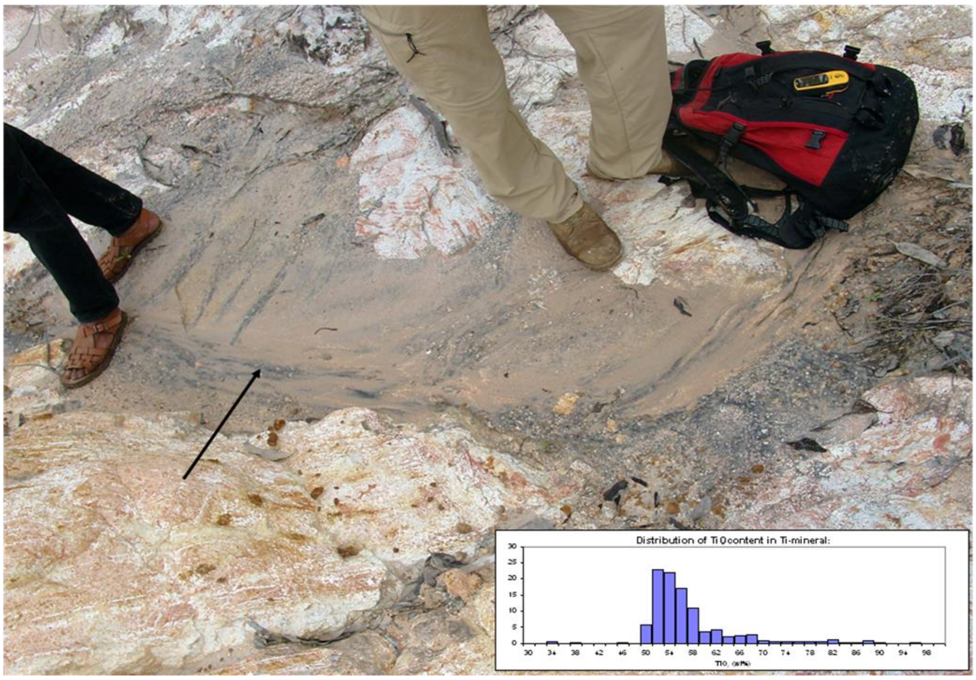
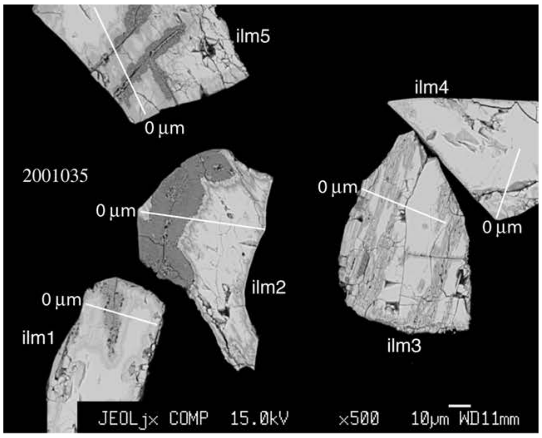


Figure 9 *Ilmenite in sediment rich in opaque mineral grains, derived directly from kaolinized gneiss. The CCSEM histogram (lower right corner, this sample 2001035,) show that moderately leached ilmenite with TiO_2 in the low 50'ties dominate.*



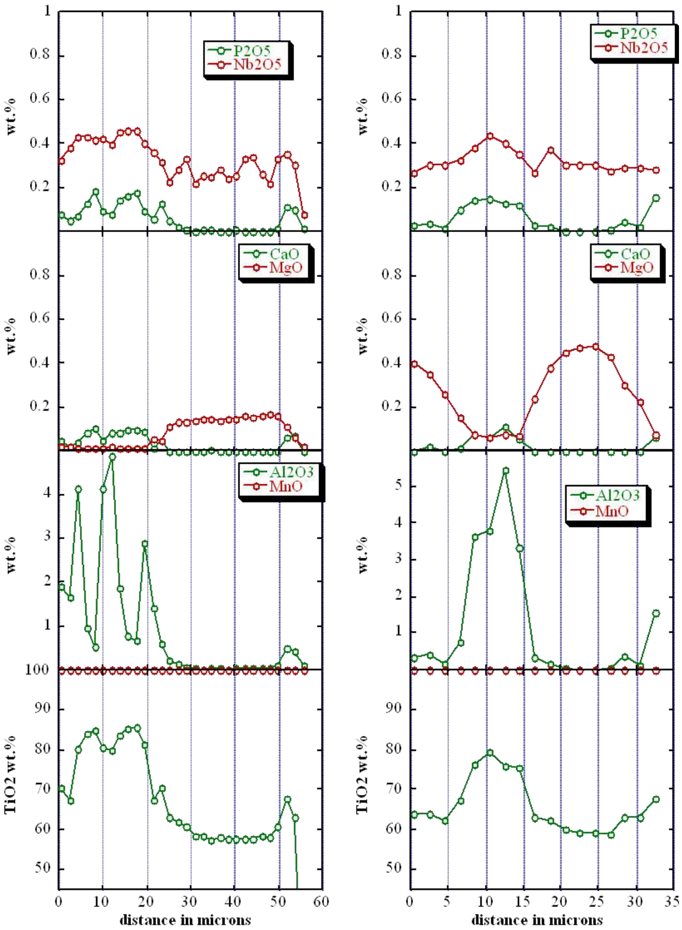
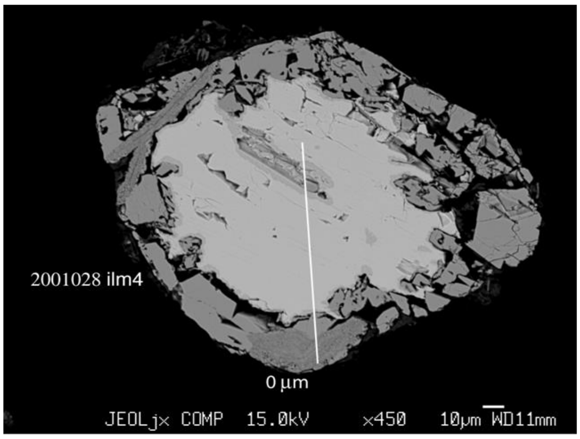


Figure 10 *Sample 2001035*

EMPA line-scans. Grains at various stages of leaching, all angular with no signs of transport.

Profile to the left represent ilm 3 profile to the right represent ilm 1.



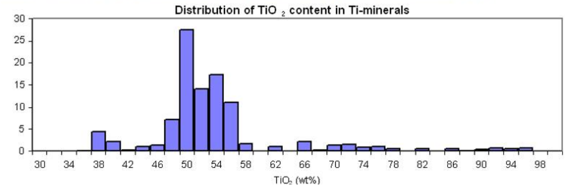


Figure 11 *Sample 2001028 is from this 15 cm wide crack between gneiss blocks, filled with black soil and gravel, rich in organic matter (left). Right image is a backscatter image showing the position of the line-scan (Figure 12) in ilmenite with alteration along the rim and in cracks.*

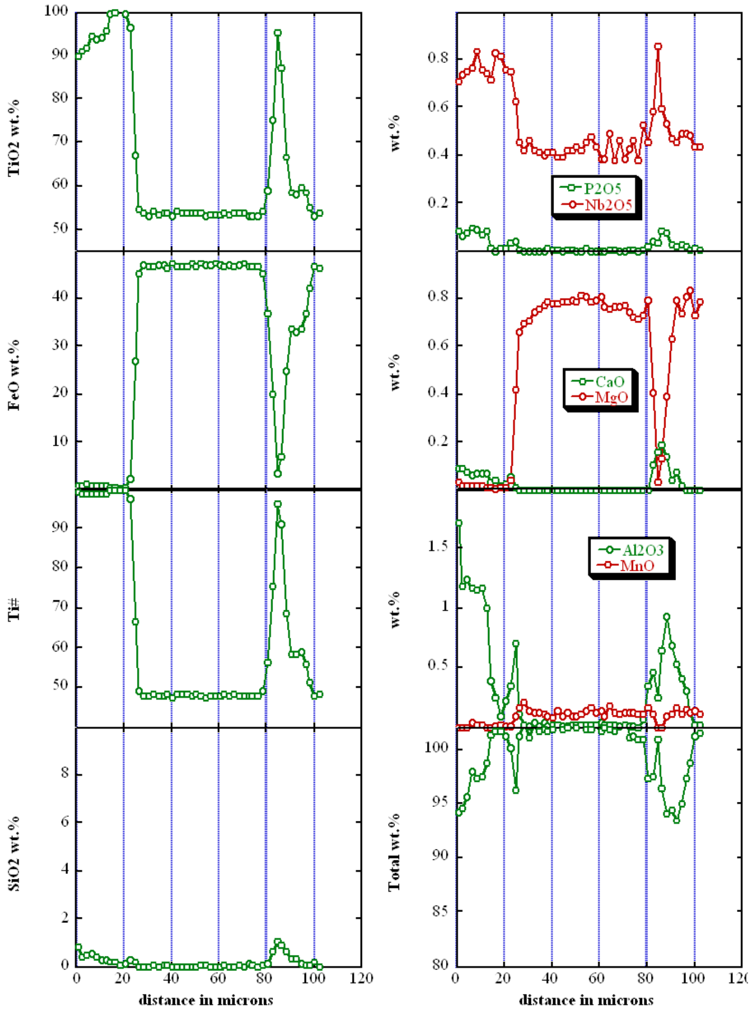


Figure 12

EMPA line-scan of sample 2001028.

Unaltered ilmenite core in a grain with a high TiO_2 rim and an altered crack in the interior. Nb is high initially (0,4 %) and the concentration is doubled in the altered rim equivalent to Ti indicating that Nb stays behind when Fe, Mg and Mn is leached.

Elements such as Al, Si, Ca and P increases much more than Nb from the unaltered core to the altered rim. This indicate that Al, Si, Ca and P must have been introduced from outside into the pore space generated by the loss of Fe, Mn and Mg.

The CCSEM histogram in lower left corner of Figure 11 show that moderately leached ilmenite with TiO_2 in the low 50'ties dominate.

2.3 Ancient dune with leached ilmenite on Madagascar

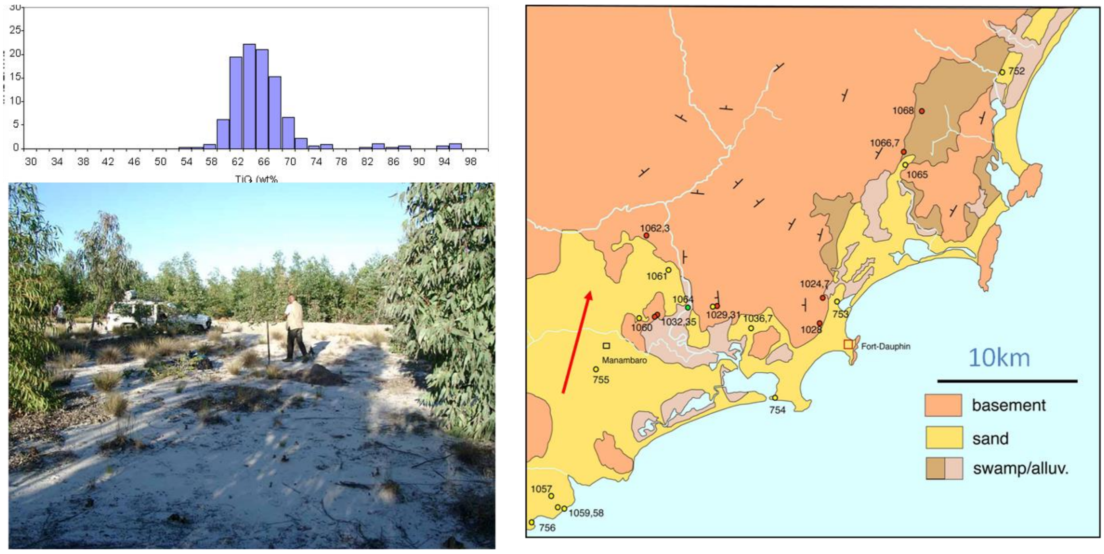
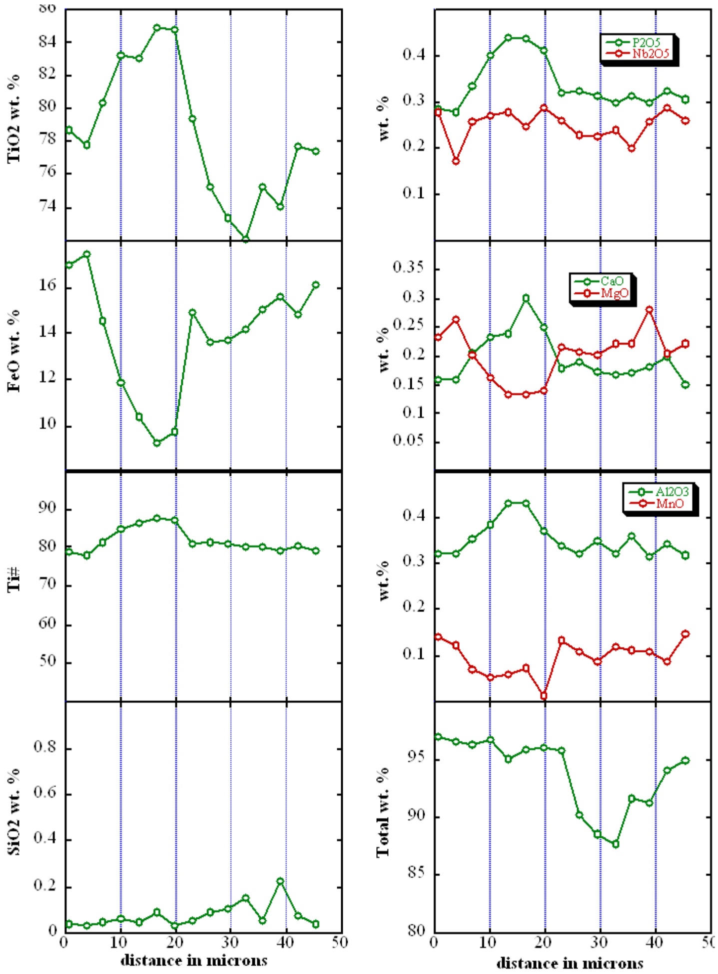


Figure 13 *Sample 2000755 - Ancient dune with leached ilmenite grains - no unleached ilmenite is found. The CCSEM histogram in upper left corner show that leached ilmenite with TiO_2 in the mid 60'ties dominate.*



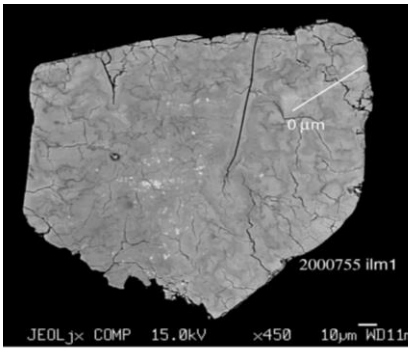
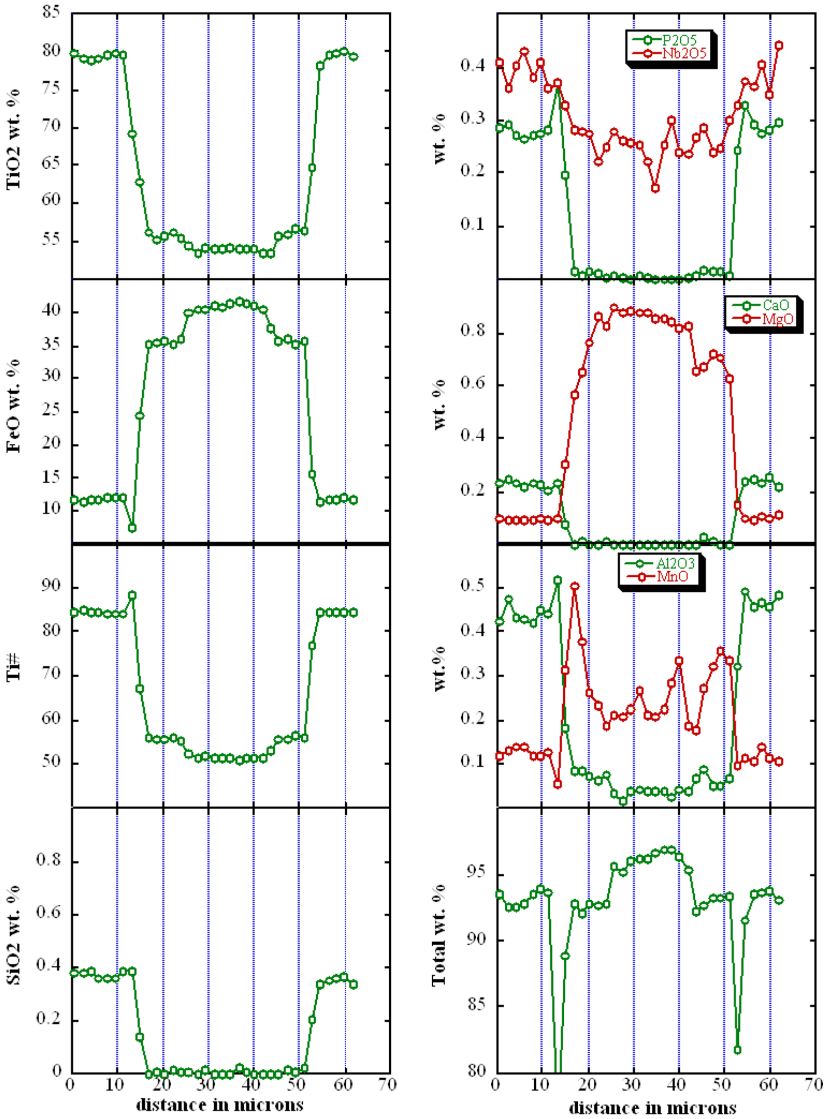


Figure 14 *Sample 2000755.*

The backscatter image (right) shows the position of the line-scan (left) on this patchy leucoxene with contraction cracks.

P, Ca and Al are high where Ti is high and Fe low.



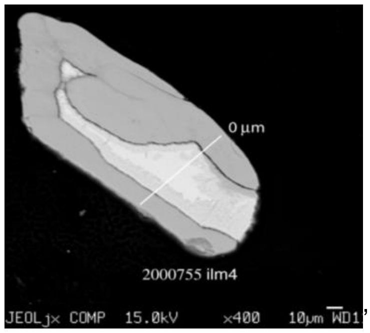


***Figure 15** Sample 2000755.*

Backscatter image (right) showing the position of the EMPA line-scan across unaltered ilmenite in the core, a slightly altered zone and highly leached leucoxene rim.

The profile (left) shows that P, Ca and Al are high where Ti is high and Fe low in the highly leached rims,

The Total % is low at the interface between the unaltered and the altered ilmenite.

The microprobe data from Madagascar and India show:

1. The alteration of the ilmenite to leucoxene starts already in outcrop.
2. The alteration is accompanied by introduction of micro-porosity below the resolution of the Scanning Electron Microscope (low totals).
3. The chemical characteristics of this alteration are loss of Fe, Mn and Mg and introduction of Al, Si, Ca and P from the outside.
4. Ti and Nb increase in concentration due to the loss of Fe, Mn and Mg.
5. The chemical changes seen in outcrop rock samples from Madagascar are similar to what can be found in outcrop rock samples from India (Kerala).
6. The chemical characteristics of the incipient alteration in ilmenite in outcrop are similar to the alteration found in ilmenite in the dunes at Madagascar.
7. The overall grade (% TiO_2) of the ilmenite in rivers draining the outcrops is elevated compared to unaltered hard-rock ilmenite but low compared to the placer ilmenite in Madagascar and Kerala. This indicates that the main alteration of the ilmenite happen near or at the coast.

2.4 Microprobe analysis of ore samples

Th… nt production were

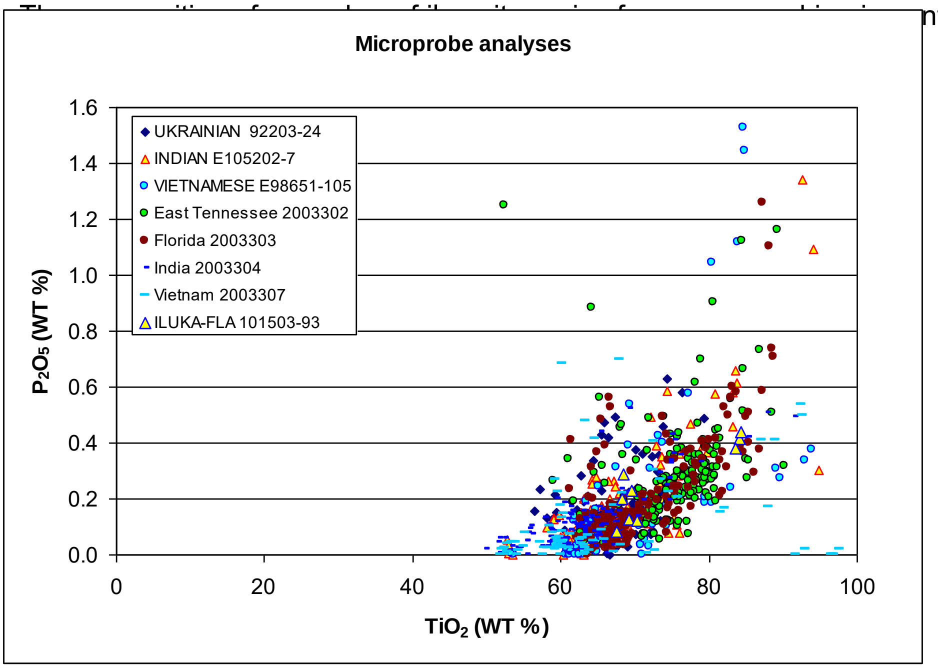


Figure 16 *P_2O_5 versus TiO_2 in ilmenite grains from ore samples from a range of different countries.*

There is an increase in phosphorus with increasing titanium (Figure 16) and grains with e.g.

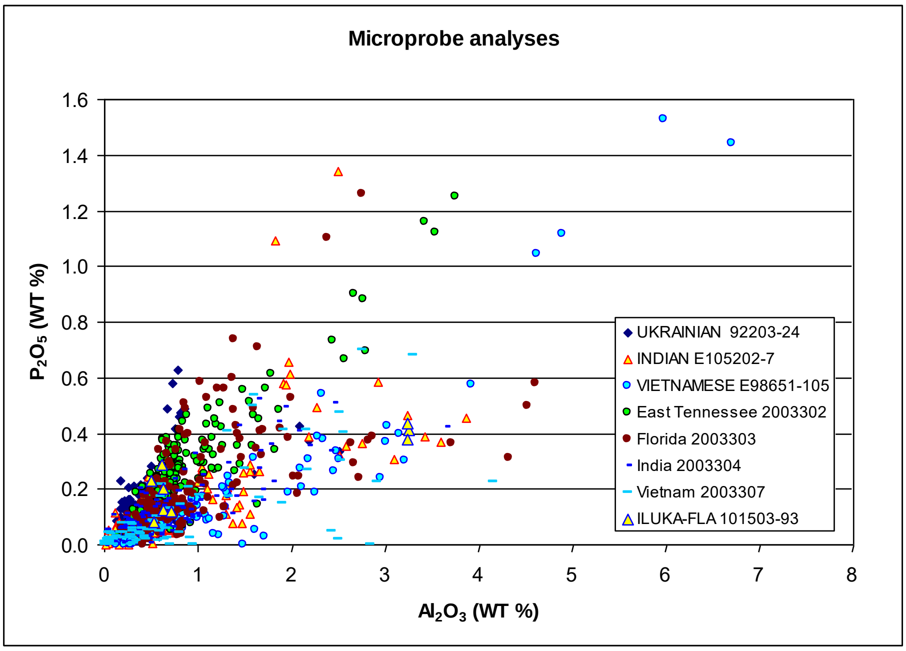


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Figure 17 *P_2O_5 versus Al_2O_3 in ilmenite grains from ore samples.*

There is also a relationship between Al and P in the ilmenite (Figure 17) but the ratio between P and Al varies among the different ores.

3 XRF mapping of altered ilmenite

One of the elements that may cause problems in the (DuPont) pigment production is Phosphorus and GEUS have been working with locating phosphorus in ilmenite ores (Weibel 2007; Weibel et al 2008). As part of this project altered ilmenite grains were subjected to X-ray mapping (Figure 18 and 19).

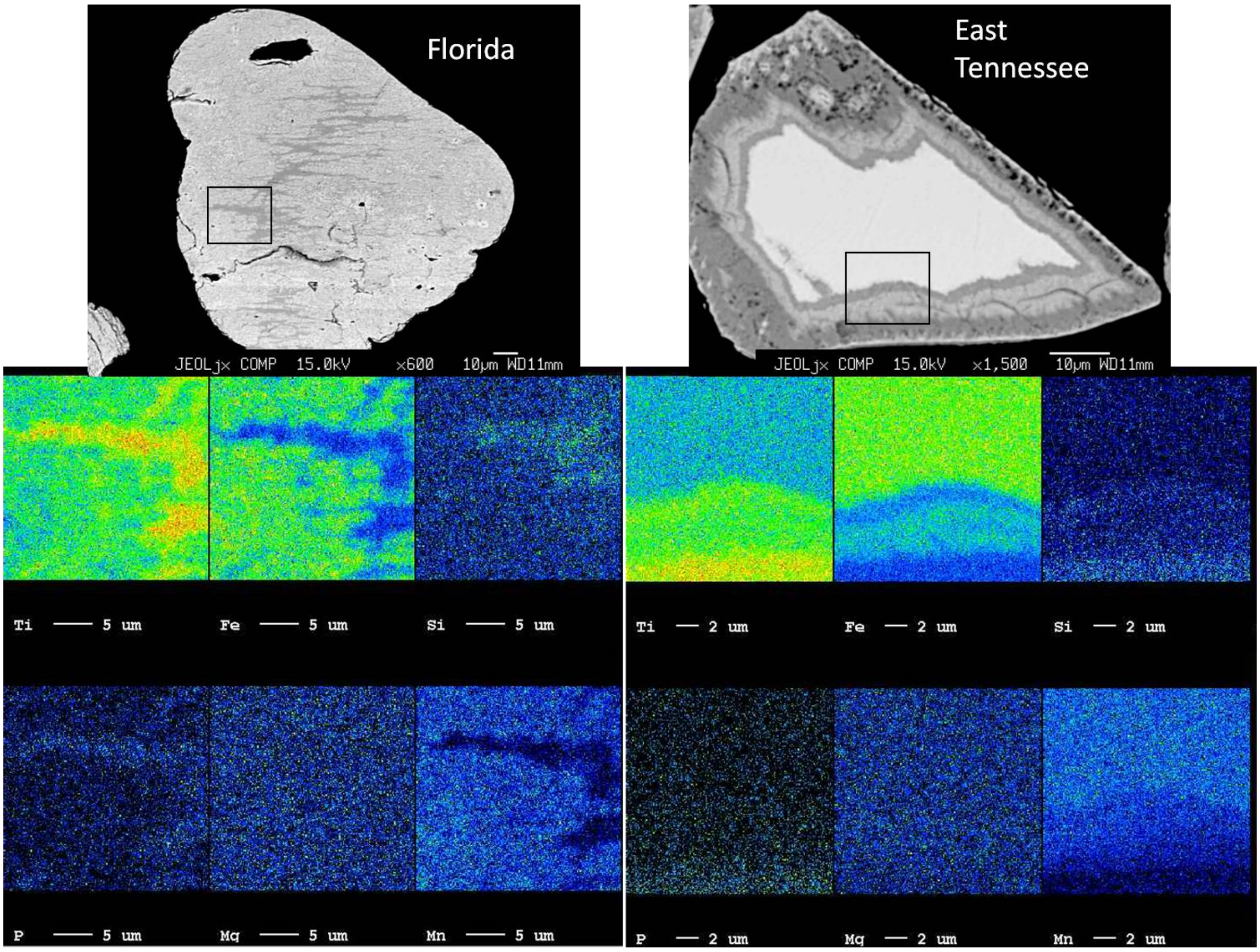


Figure 18 X-ray maps of altered ilmenite from USA (Weibel, 2007). There are 6 x-ray maps show the distribution of Ti, Fe, Si, P, Mg and Mn. The top greyscale image is electron backscatter image with a frame showing the location of the element map.

On Figure 18 it can be seen, that where Ti is high (orange) Fe is low (blue). This is where the ilmenite is altered and it can be seen that Mn follow Fe out during leaching. Furtner, it can be seen that that Si and P is elevated in the same structure/fracture from which Fe and Mn has been leached out (left). The ilmenite grain from East Tennessee (Figure 18 right) show a core of unaltered ilmenite (white on the top backscatter image) surrounded by a number of zones with low Fe and Mn and increase of Ti, Si and P simultaneous with the decrease in Fe and Mn.

In the samples from India (Figure 19) it is also seen that where Fe and Mn is leached out Ti, Si and P increases.

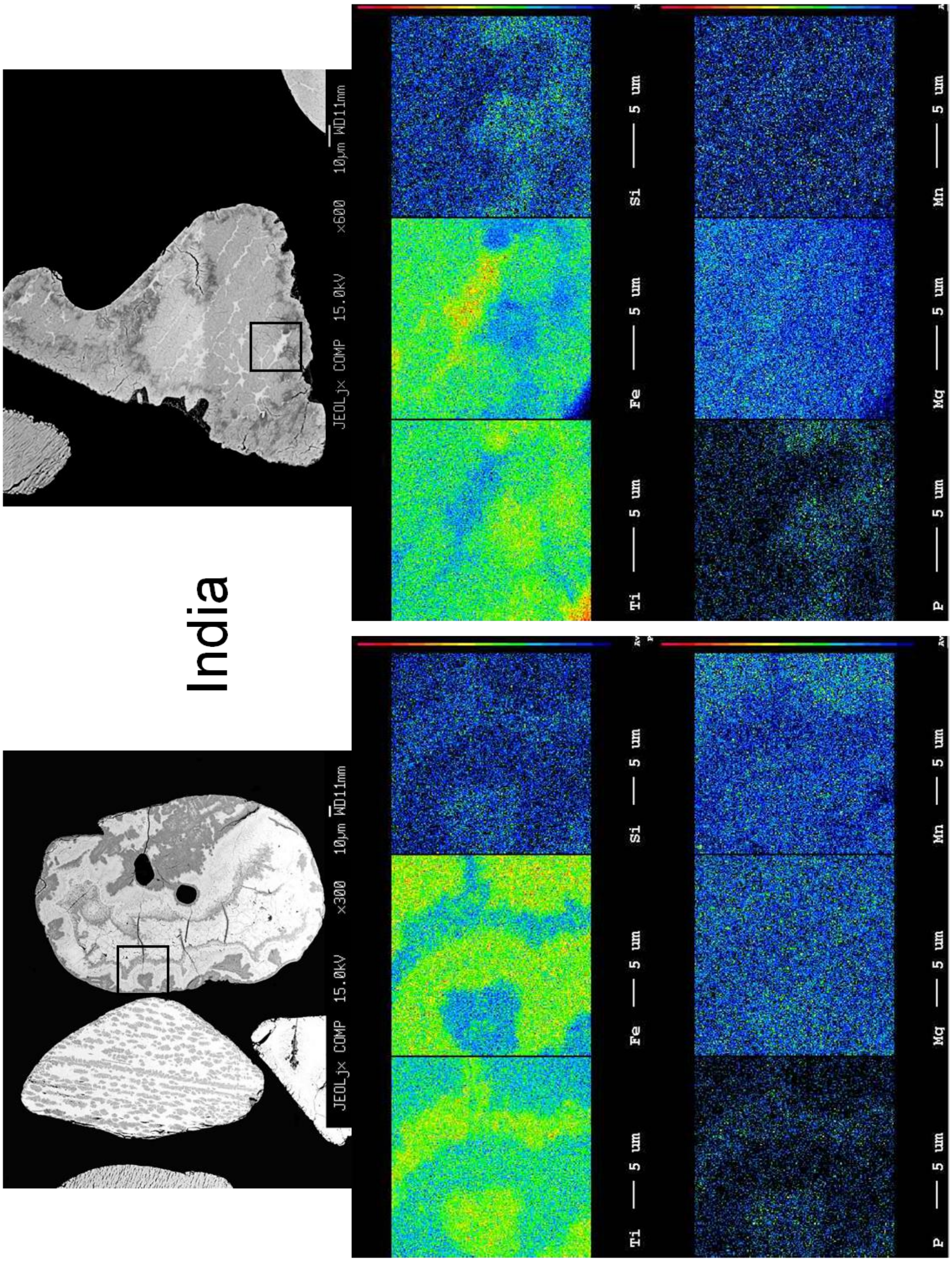


Figure 19 X-ray maps of altered ilmenite from India (Weibel, 2007).

4 SEM studies of Leucoxene from Keysbrook

Elevated aluminium contents in ilmenite and leucoxene ore from the Keysbrook deposit, Australia is in the range from 1.3 to ~3% Al_2O_3 is a problem in pigment production (Andrew Romeo pers. comm. 2013) and two samples were investigated to find out if the problem was presence of aluminium bearing minerals or if it is tied to crusts etc. that can be removed by processing. In order to understand the problem we:

- Performed CCSEM analysis on the two samples L70 and L88
- Studied the samples using the Scanning Electron Microscope
- Made a number of point EDX analyses in the leucoxene grains.

Figure 20
Location of Matilda Zircon's Keysbrook deposit.

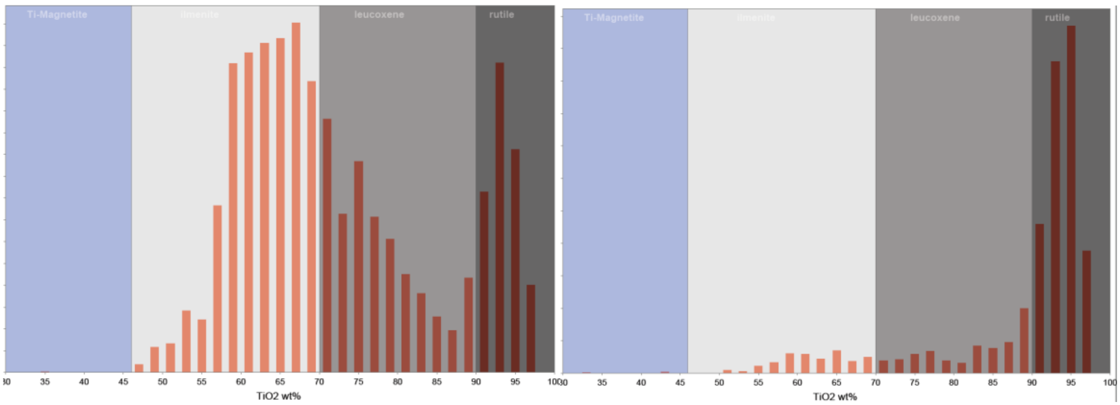


Figure 21 Histograms of the titanium content of the two samples derived using CCSEM. Sample L70 to the left and L88 to the right. X-axis scale is from 30 to 100 % TiO_2.

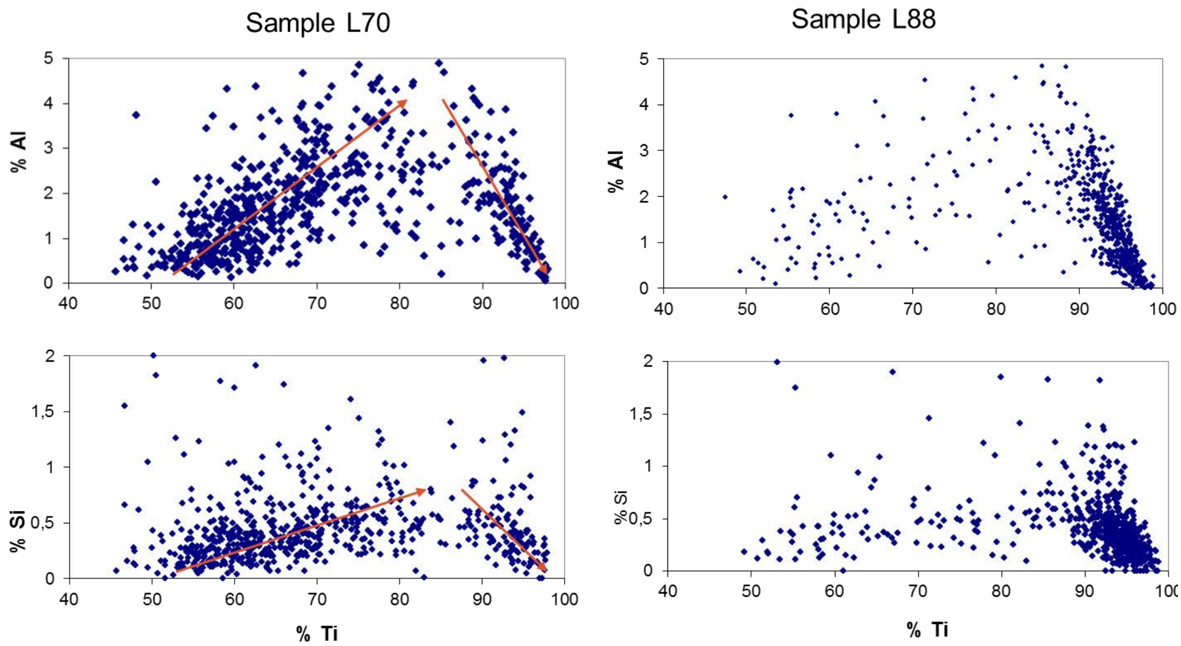


Figure 22 *% Al versus % Ti by CCSEM analyses of individual grains of the two samples from Keysbrooke. Only grains > 40 µ are shown.*

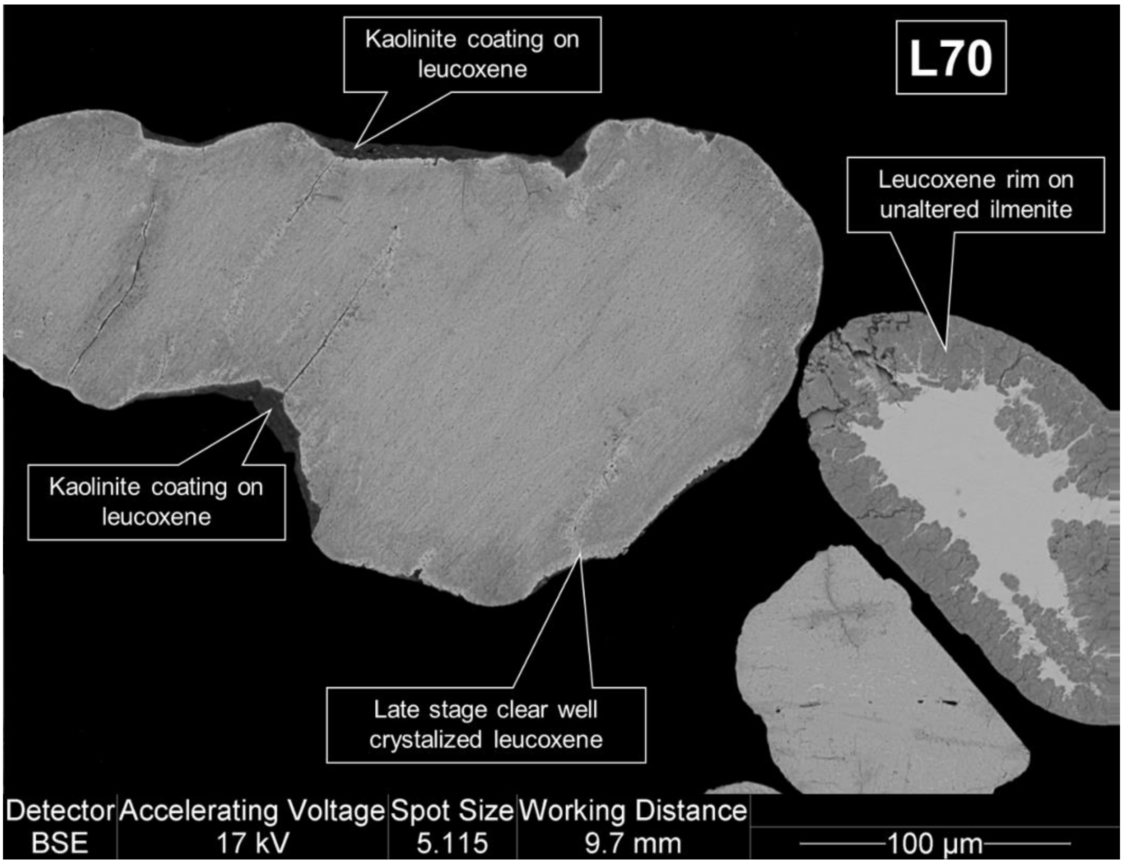
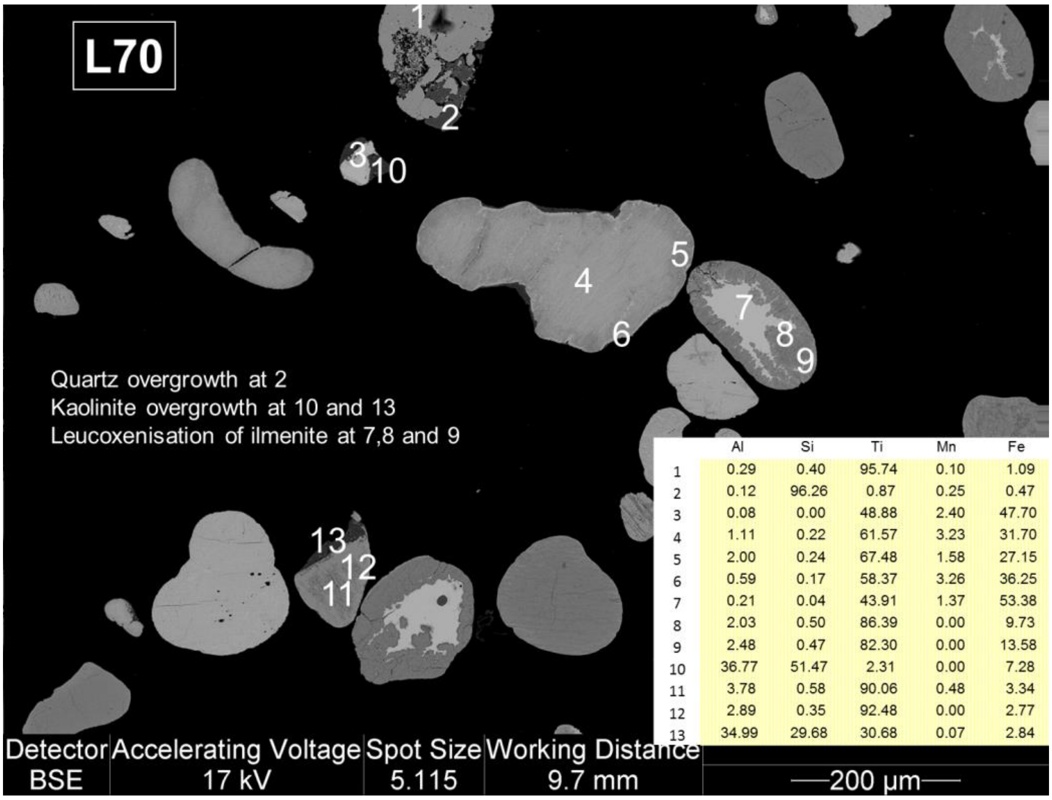
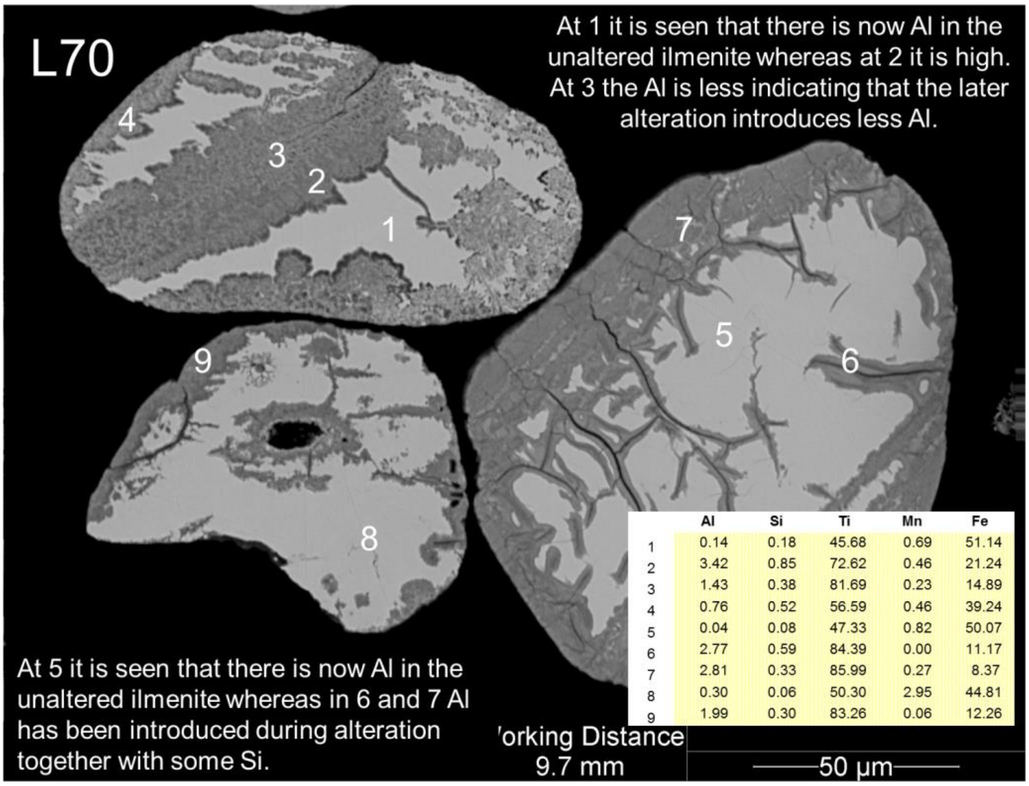


Figure 23 *SEM backscatter image of leucoxene from Keysbrooke (sample 70). Note the bright leucoxene/rutile rim on the large grain. Grains in the center are also shown on Figure 24.*



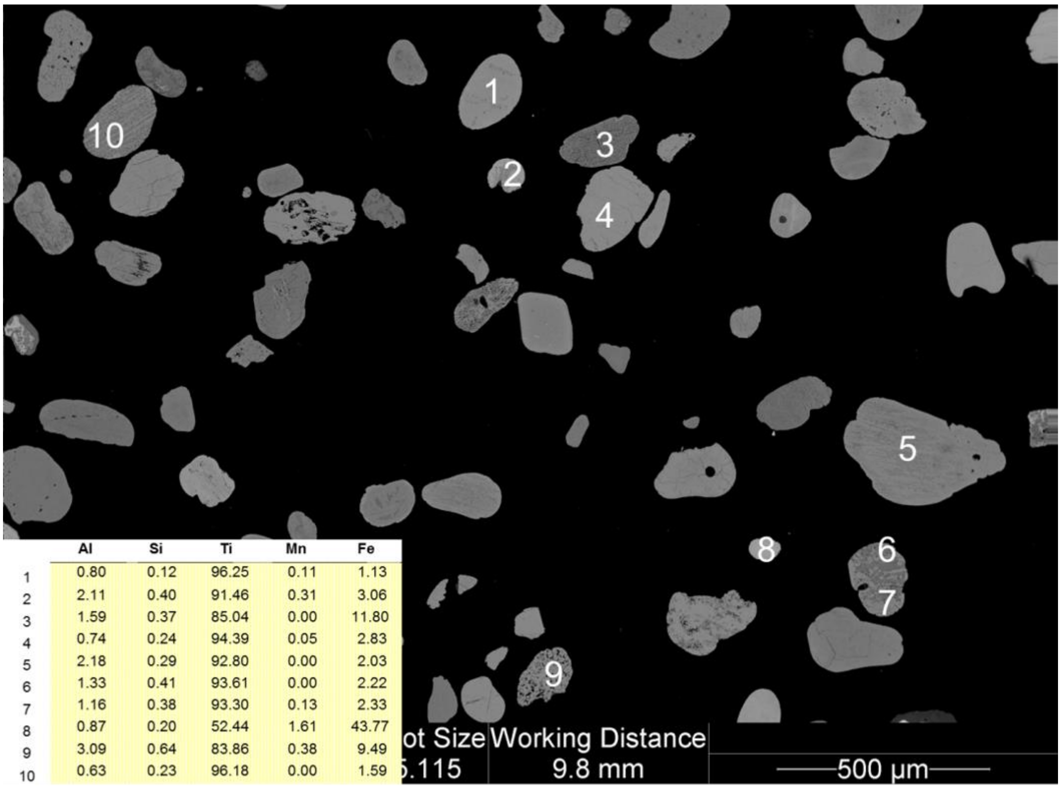
	Al	Si	Ti	Mn	Fe
1	0.29	0.40	95.74	0.10	1.09
2	0.12	96.26	0.87	0.25	0.47
3	0.08	0.00	48.88	2.40	47.70
4	1.11	0.22	61.57	3.23	31.70
5	2.00	0.24	67.48	1.58	27.15
6	0.59	0.17	58.37	3.26	36.25
7	0.21	0.04	43.91	1.37	53.38
8	2.03	0.50	86.39	0.00	9.73
9	2.48	0.47	82.30	0.00	13.58
10	36.77	51.47	2.31	0.00	7.28
11	3.78	0.58	90.06	0.48	3.34
12	2.89	0.35	92.48	0.00	2.77
13	34.99	29.68	30.68	0.07	2.84

Figure 24 *SEM backscatter image of leucoxene from Keysbrooke (sample L70). Compositions of the analysed points are given in the insert.*



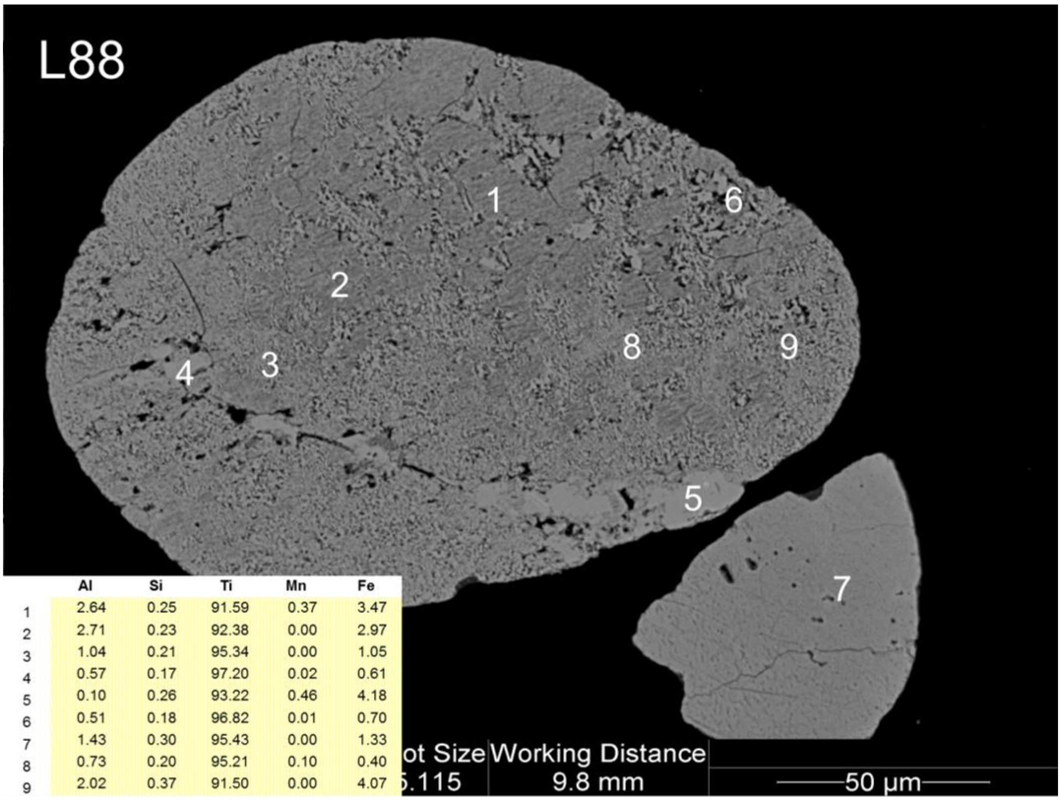
	Al	Si	Ti	Mn	Fe
1	0.14	0.18	45.68	0.69	51.14
2	3.42	0.85	72.62	0.46	21.24
3	1.43	0.38	81.69	0.23	14.89
4	0.76	0.52	56.59	0.46	39.24
5	0.04	0.08	47.33	0.82	50.07
6	2.77	0.59	84.39	0.00	11.17
7	2.81	0.33	85.99	0.27	8.37
8	0.30	0.06	50.30	2.95	44.81
9	1.99	0.30	83.26	0.06	12.26

Figure 26 *SEM backscatter image of leucoxene from Keysbrooke (sample L70).*



	Al	Si	Ti	Mn	Fe
1	0.80	0.12	96.25	0.11	1.13
2	2.11	0.40	91.46	0.31	3.06
3	1.59	0.37	85.04	0.00	11.80
4	0.74	0.24	94.39	0.05	2.83
5	2.18	0.29	92.80	0.00	2.03
6	1.33	0.41	93.61	0.00	2.22
7	1.16	0.38	93.30	0.13	2.33
8	0.87	0.20	52.44	1.61	43.77
9	3.09	0.64	83.86	0.38	9.49
10	0.63	0.23	96.18	0.00	1.59

Figure 24 *SEM backscatter image of leucoxene from Keysbrooke (sample L88).*



	Al	Si	Ti	Mn	Fe
1	2.64	0.25	91.59	0.37	3.47
2	2.71	0.23	92.38	0.00	2.97
3	1.04	0.21	95.34	0.00	1.05
4	0.57	0.17	97.20	0.02	0.61
5	0.10	0.26	93.22	0.46	4.18
6	0.51	0.18	96.82	0.01	0.70
7	1.43	0.30	95.43	0.00	1.33
8	0.73	0.20	95.21	0.10	0.40
9	2.02	0.37	91.50	0.00	4.07

Figure 25 *SEM backscatter image At 4, 5 and 6 the leucoxene is recrystallized into solid leucoxene with lower Al relative to earlier leucoxene.*

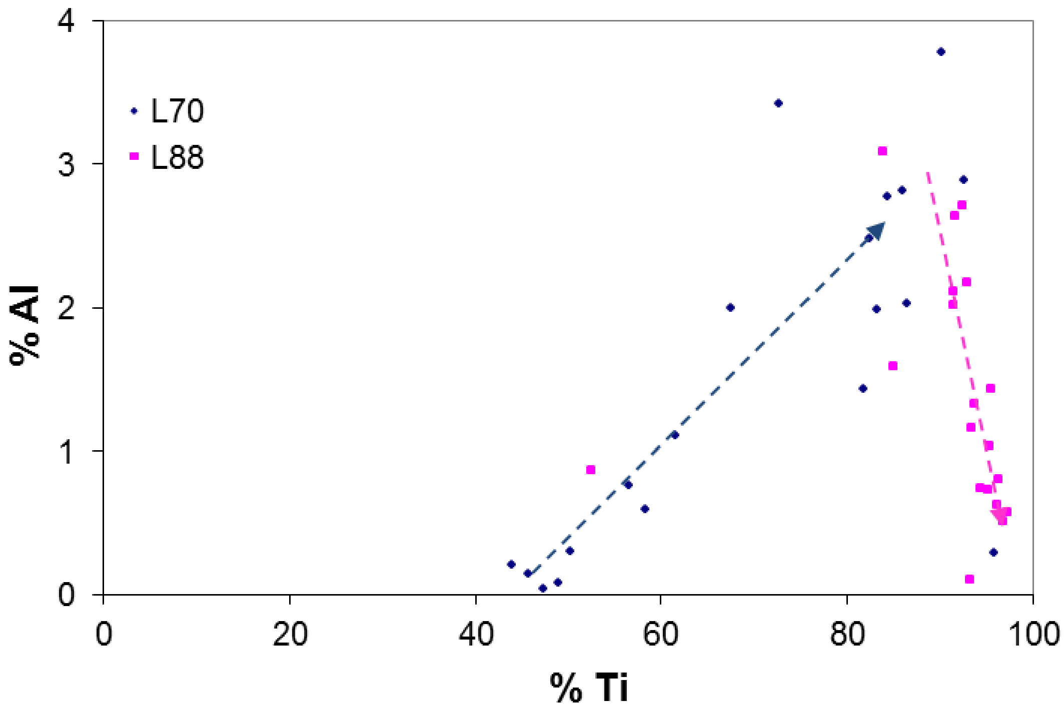


Figure 27 *Analytical data from the EDS system on the SEM from the grains shown on Figures 23 to 26.*

In sample L70 (blue dots on Figure 27) there is an increase in Al with Ti, whereas in L88 consisting of almost pure leucoxene with high Ti content, there is a decrease in Al with increasing Ti. The process of leucoxenization is much further advanced in sample L88 compared to L70. In sample L70 there is an overall increase in Al with Ti and increasing degree of leucoxenization.

The increase in Al followed by a decrease pattern is seen also on Figure 22.

The two trends may reflect two processes active during the alteration of ilmenite:

1. When the ilmenite is broken down and Fe, Mn and Mg are leached out, Al is incorporated (together with Si, Ca and P) in the space left behind as micro-porosity resulting in low totals in the microprobe data.
2. The form in which Al, Si, Ca and P is incorporated into the mineral may be as microcrystalline (sub-microscopic) mineral grains of e.g. kaolinite and apatite or monazite.
3. When this process continues, the pseudo-rutile is recrystallized into a more pure form with less Al, Si, Ca and P. This occurs on the surface of the leucoxene grains as well as along fractures.

The implications of this are that Al is incorporated in the leucoxene grains and can not be removed by physical processing.

5 Ilmenite alteration in Brazil

To test if the patterns described above can be identified in other areas, ca. 30.000 titanium mineral grains analyzed using CCSEM from three areas in Brazil have been extracted from the GEUS CCSEM database: the Rio Gurupi Area in Northern Brazil, the Recife area and the Salvador area. To understand the chemical variation in so many grains we applied a geo-statistical program called “Self Organizing Maps” or SiroSOM developed by CISRO in Australia to the CCSEM data. The principle in SiroSOM plots are that grains with common chemical features are assigned the same color and grains close to each other in the diagram are joined together so the size of the dots reflect the number of grains with similar chemistry aiming at generalizing the information in a way so it is easier to recognize the patterns in the data compositions (Löhr et al 2010).

CCSEM data represent rapid analyses where the accuracy and precision of each data-point is not very high. Each analysis represents average grain compositions incorporating inclusions, overgrowth and non-liberated grains. However, the advantage of the CCSEM analysis is the very large number of grain analyses making such analytical data well suited for geo-statistical analysis.

5.1 Rio Gurupi area, Northern Brazil

The Rio Gurupi area was the focus for DuPont exploration for a number of years because the composition of the ilmenite was found to be favorable for pigment production. The area is located in the tropics, the climate is humid and the combination of the hot and humid climate may be the reason why the ilmenite has been altered to the fairly high grade maybe in combination with reworking of previously altered ilmenite from Cretaceous sediments (Knudsen et al 2015).

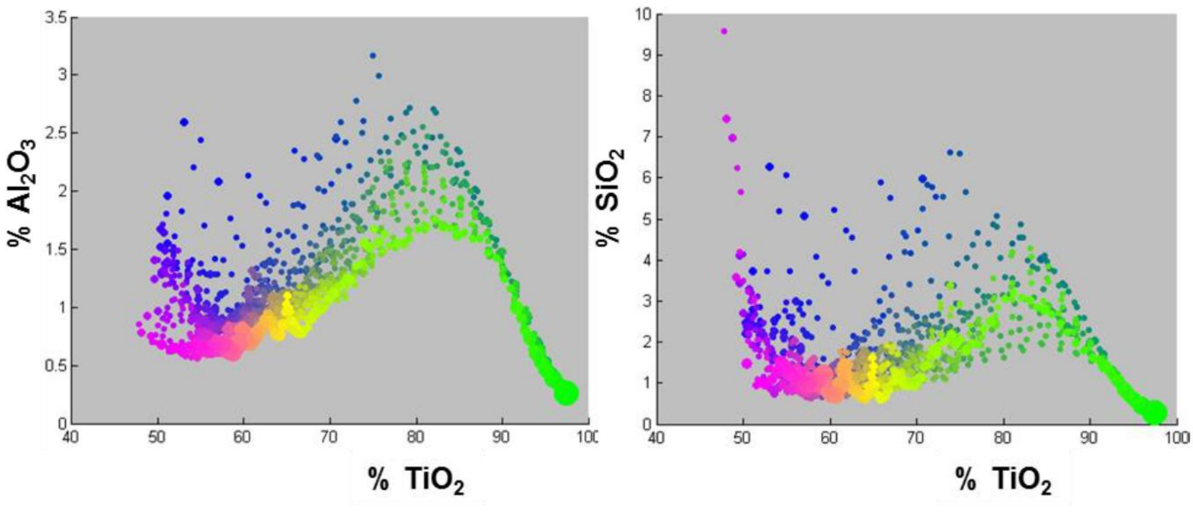


Figure 29 *Al_2O_3 and SiO_2 versus % TiO_2. SiroSOM plot of CCSEM analyses of 11567 individual grains from the Rio Gurupi Area, Northern Brazil.*

The blue dots (Figure 29) represent grains characterized by high SiO_2 and Al_2O_3 and low to intermediate TiO_2. The green dots represents high TiO_2 grains where the darker green dots has high SiO_2 and Al_2O_3 and the light green has lower SiO_2 and Al_2O_3. There is a relationship between TiO_2 and both SiO_2 and Al_2O_3 with an increase followed by a decrease in both elements just as it is seen in Figure 22 and 28. The peak in both SiO_2 and Al_2O_3 is about 80 % TiO_2.

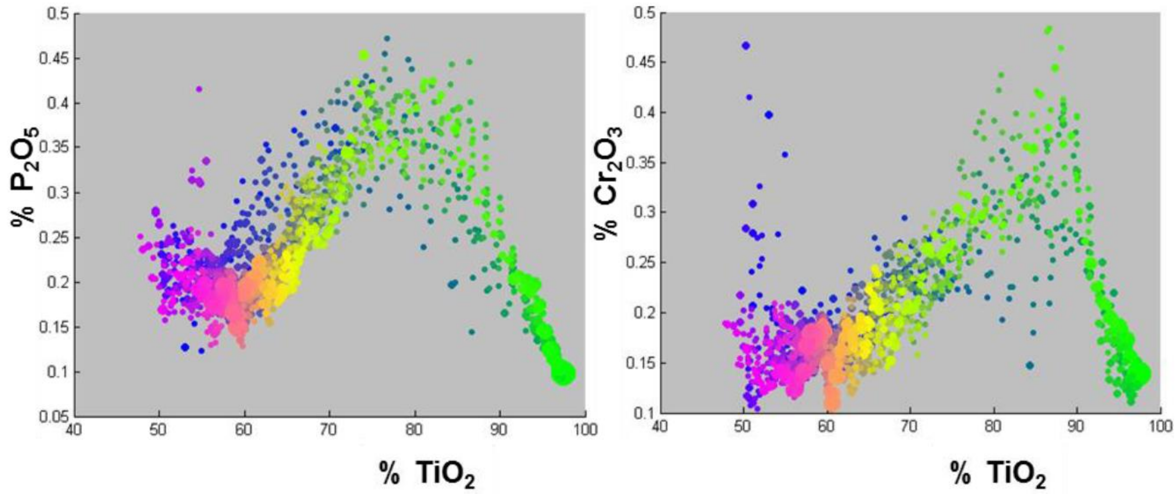


Figure 30 *P_2O_5 and Cr_2O_3 versus TiO_2 from CCSEM analyses titanium minerals from the Rio Gurupi Area.*

The relationship between TiO_2 and P_2O5 and Cr_2O_3 are shown in a similar way in Figure 30 and the relationship between TiO_2 and both P_2O_5 and Cr_2O_3 show a similar increase followed by a decrease as it is seen in Figure 29 with a peak in P_2O_5 about 80 % TiO_2.

5.2 Recife and Salvador areas

Samples were collected along the Brazil coast and analyzed using CCSEM to understand the compositional variation. In the following the samples from the Recife and the Salvador areas will be described.

When ilmenite is altered Ti increases whereas Fe and Mn decreases (Figure 31) in good agreement with the general understanding of the ilmenite alteration process. The yellow dots represent non liberated grains containing alumino-silicates and consequently high SiO_2 and Al_2O_3 (Figure 32). It can be noted, that the content of Mn decreases a bit faster than the content of Fe suggesting that Mn is leached out faster than Fe.

The colour coding is not the same in the figures from Belem and Recife/Salvador areas.

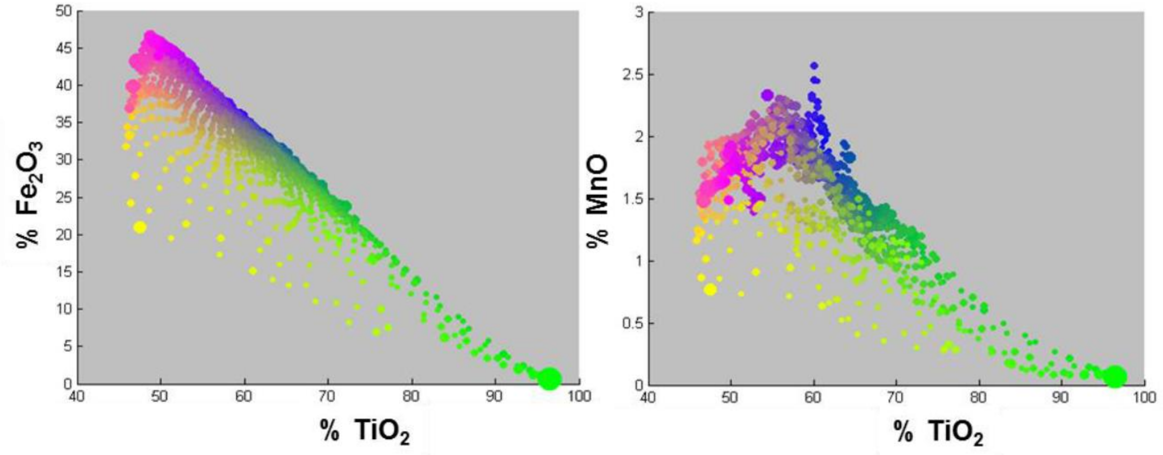


Figure 31 *MnO and Fe_2O_3 versus TiO_2 in titanium minerals from the Recife Area. The colouring is different from figures (29 & 30) but same as on Figs 32 and 33.*

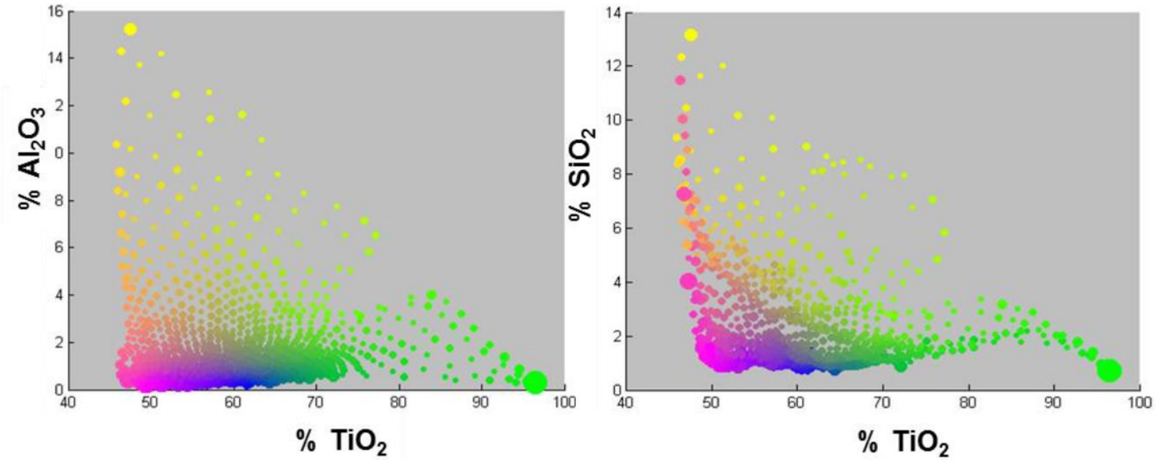


Figure 32 *Al_2O_3 and SiO_2 versus TiO_2 in titanium minerals from Recife Area.*

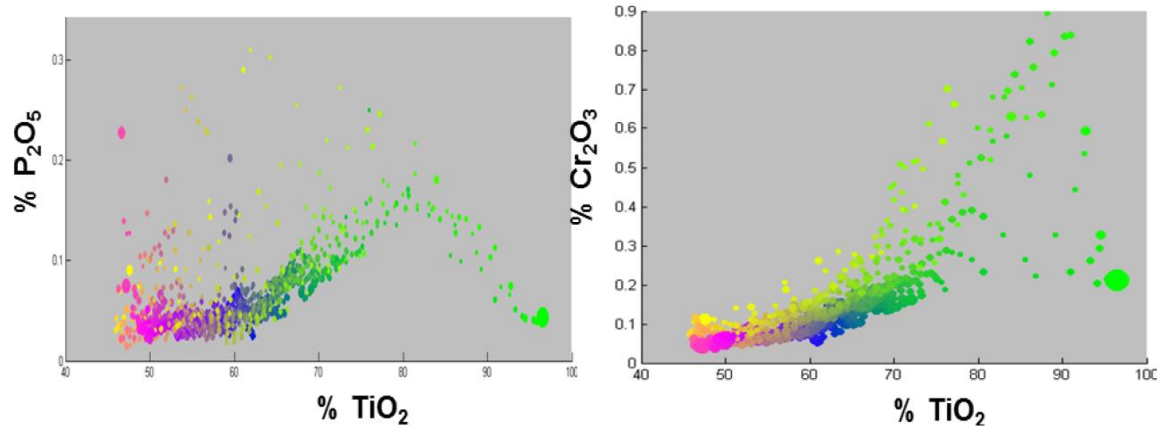


Figure 33 *P_2O_5 and Cr_2O_3 versus TiO_2 in titanium minerals from the Recife Area.*

From about 60 % the content of Al_2O_3 and SiO_2 as well as P_2O_5 increases with increasing TiO_2 which is in good agreement with the observations from both Madagascar and Australia described above. Further, there is a decrease in all three components when the TiO_2 exceeds ca. 80 to 85 %, which is also in good agreement with what is observed in the samples from Keysbrook, Australia and was explained as caused by recrystallization of the first generation of microcrystalline leucoxene into a more well crystallized and pure rutile/anatase.

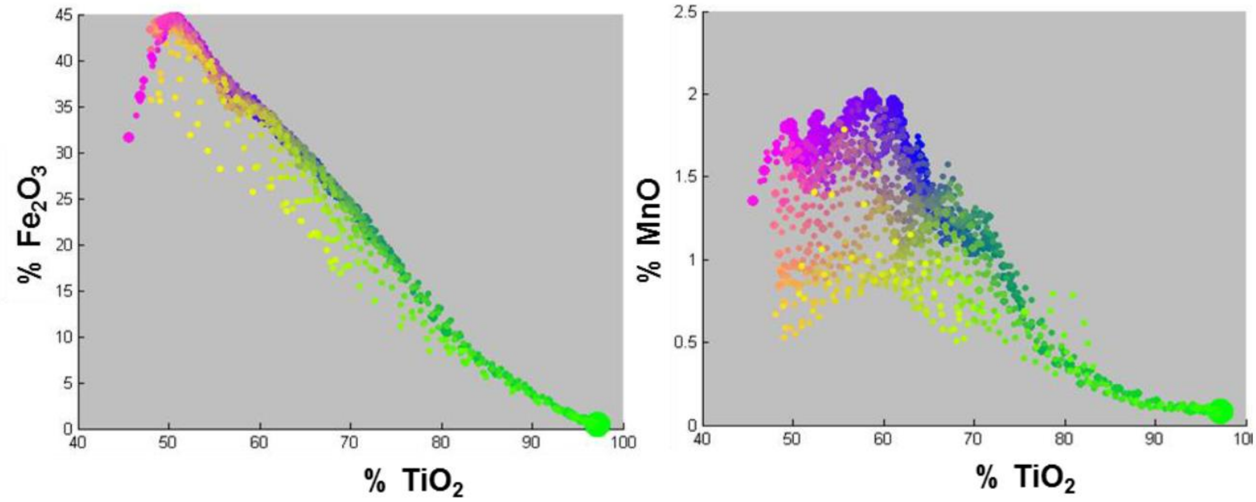


Figure 34 *MnO and Fe_2O_3 versus TiO_2 in titanium minerals from the Salvador Area.*

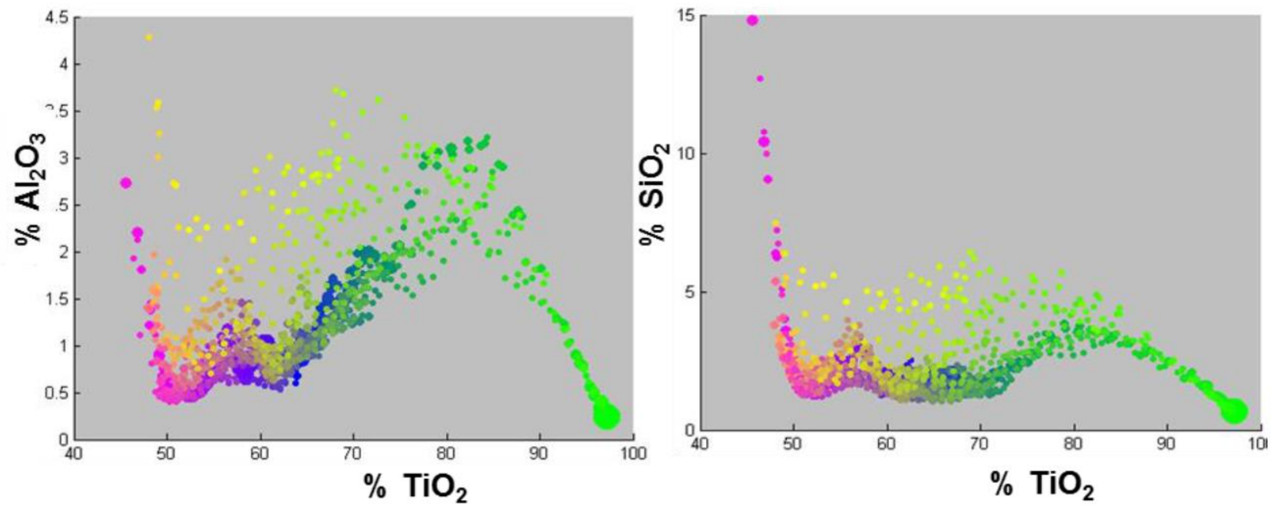


Figure 35 *Al_2O_3 and SiO_2 versus TiO_2 in titanium minerals from Salvador Area.*

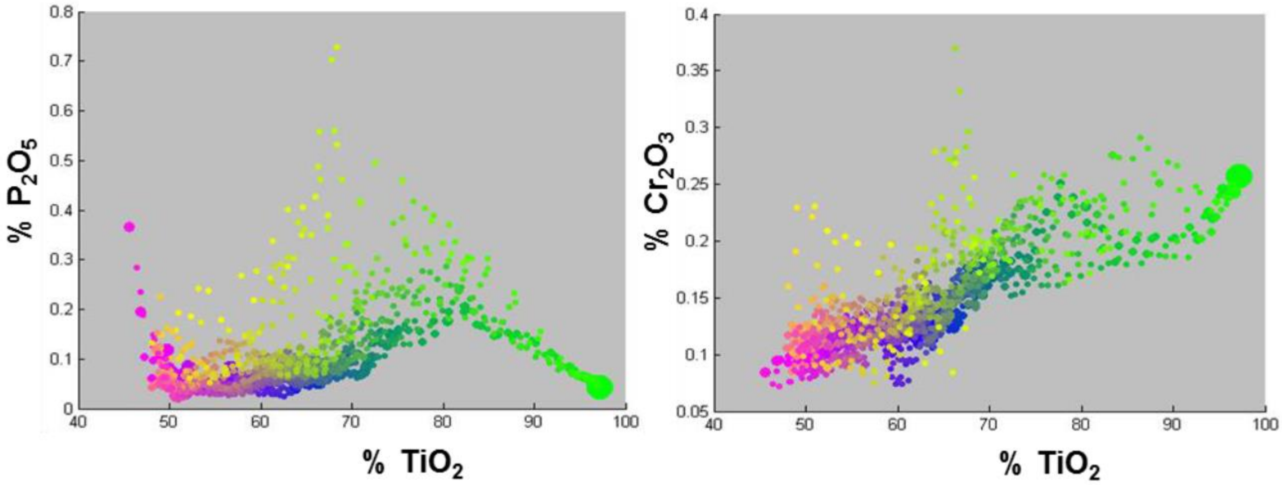


Figure 36 *P_2O_5 and Cr_2O_3 versus TiO_2 in titanium minerals from Salvador Area.*

There is an increase in the Cr_2O_3 content with increasing TiO_2. The increase is more than what can be explained by the (volume) loss of Fe, Mn and Mg. Cr must accordingly have been introduced into the mineral just as Al, Si and P. The very high TiO_2 (> 95%) grains are likely to be igneous and metamorphic rutile and the composition is not an effect of ilmenite alteration but indicate the composition of the metamorphic rutile (with respect to Cr_2O_3) which is ca. 0,25 % in Salvador and Recife but ca. 0,15 in Belem. The peak in Cr_2O_3 at ca 80 % TiO_2 is ca. 0,4 % in Belem whereas it is 0,8 % in Recife and 0,25 % in Salvador. The peak at ca 80 % TiO_2 in P_2O_5 is ca. 0,45 % in Belem whereas it is 0,15 % in Recife and 0,25 % in Salvador. This suggests that the geochemical conditions with respect to mineralisation of the leucoxene grains vary considerably among these areas.

6 Laser Ablation ICP analysis of altered ilmenite

Placer ilmenite in 5 samples from 1) Trail Ridge, Florida, 2) Miocene in Denmark, 3) Quaternary dunes in Madagascar, 4) recent beach in Northern Brazil and 5) Cretaceous sandstone in Brazil was analysed using Laser Ablation ICP-MS (LA-ICP-MS) by Thomas Zack, University of Goteborg. The purpose is to study the relationship between the increase of TiO_2 during alteration with the behaviour of different minor and trace elements in the grains during this process.

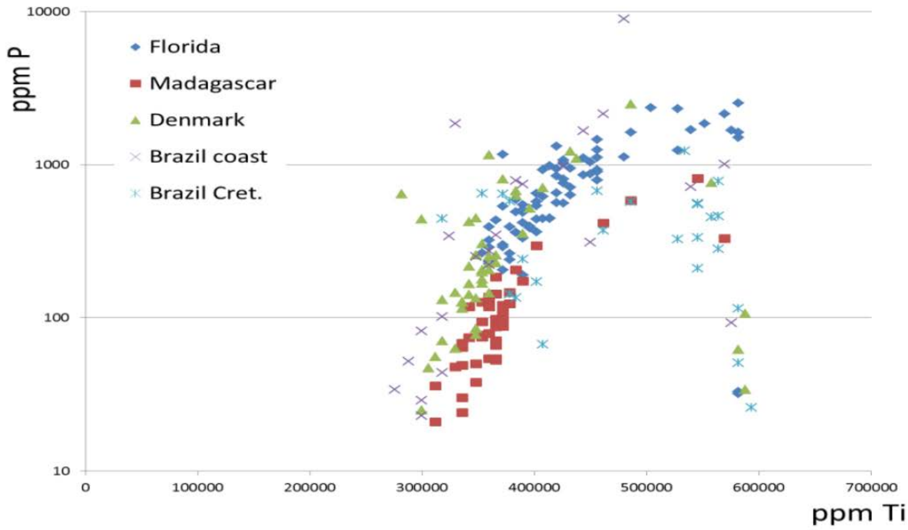


Figure 37 *P versus Ti in titanium minerals by LA-ICP-MS analysis. Values in ppm.*

The relationship between P and Ti as described in the previous sections is also seen in the LA-ICP-MS data. It can be noted that the ratio between P and Ti varies among the areas e.g. with high ratio in Denmark as compared to a lower P/Ti ratio in Madagascar.

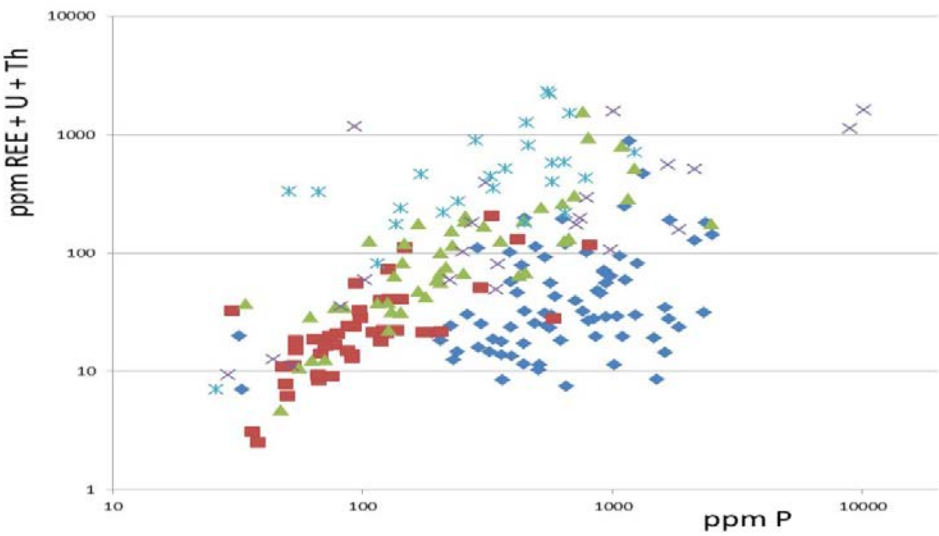


Figure 38 *REE + U + Th versus P in titanium minerals by LA-ICP-MS analysis. Values in ppm.*

The content of REE, U and Th increases with increasing P in most areas apart from Florida (Figure 38). REE, U and Th are present together in monazite and the relationship with P may suggest that a monazite component is introduced into the ilmenite during the alteration in the examples from Denmark, Mozambique and Brazil whereas in Florida the phosphate that is introduces has a different composition.

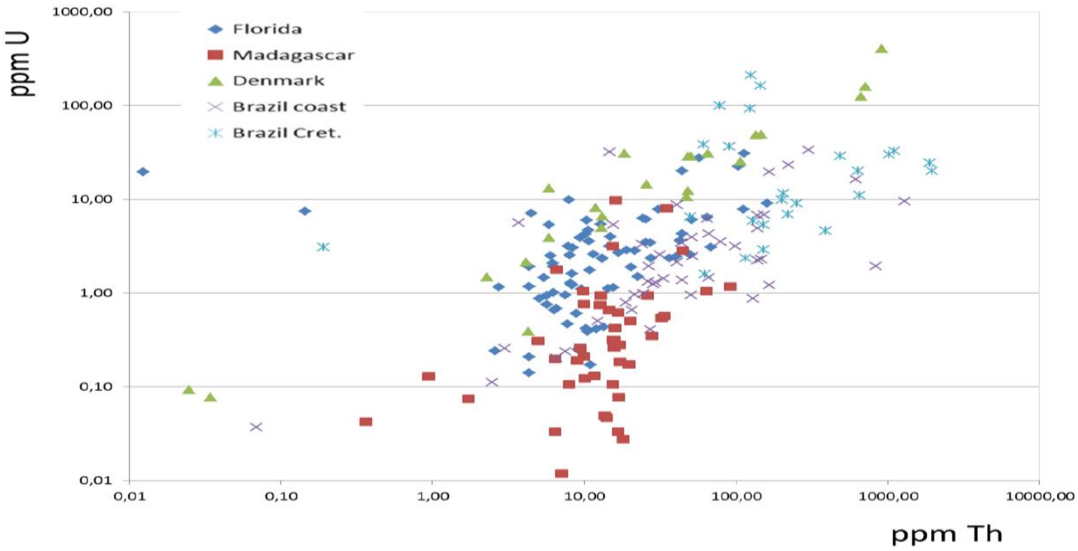


Figure 39 *Log Log plot of U versus Th in titanium minerals. LA-ICP-MS analysis.*

There is a large variation in the content of U and Th in the analysed grains (Figure 39) with an overall relation between the two elements. The ratio varies with a high U/Th ratio e.g. in Denmark as compared to Madagascar or Brazil coast. Precipitation of U is very dependent on oxygen fugacity and this ratio is likely to be related redox conditions in the environment where the leucoxene was formed. U concentration varies with Ti in different ways in the different areas (Figure 40).

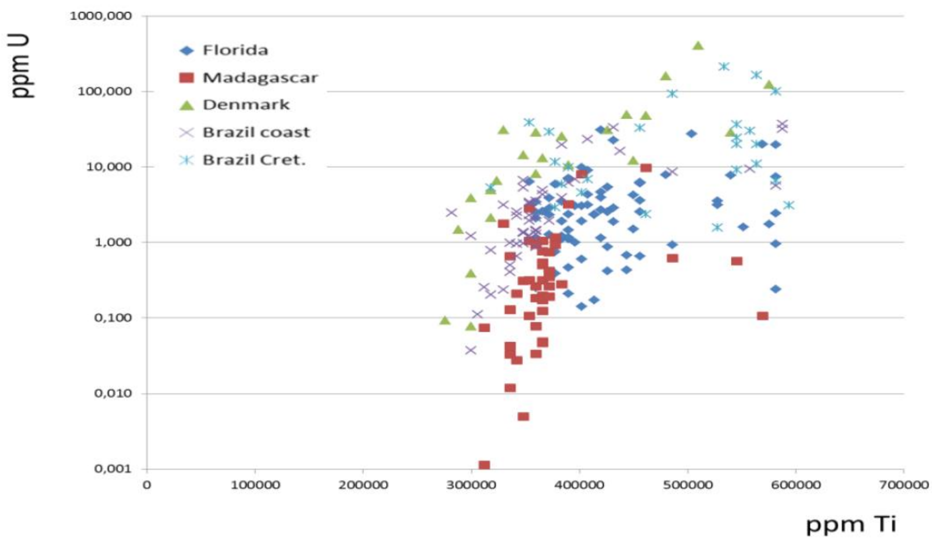


Figure 40 *U and Th versus Ti in titanium minerals. LA-ICP-MS analysis. Note that the vertical scale is logarithmic and span many orders of magnitude.*

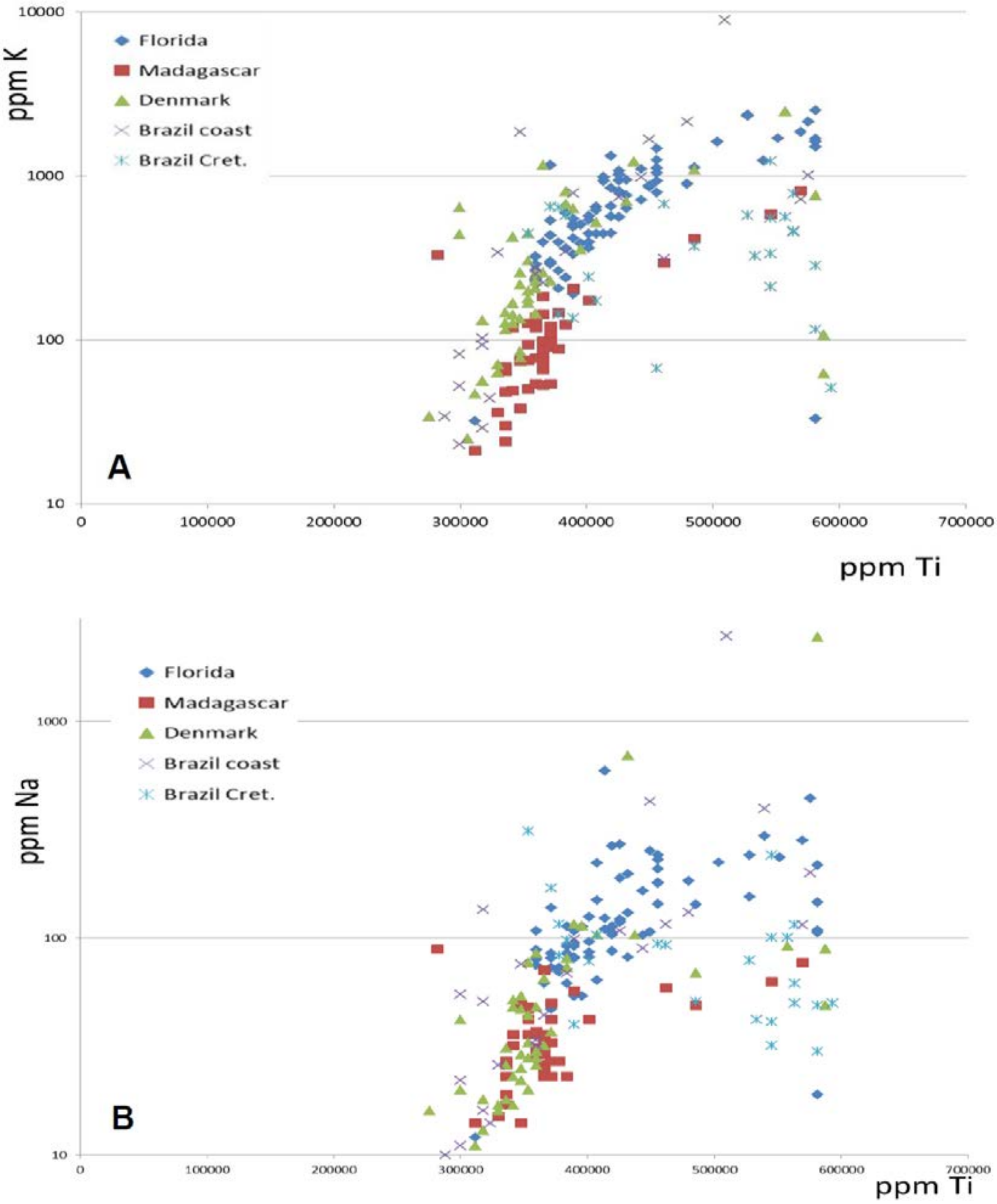


Figure 41 *K and Na versus Ti in titanium minerals. LA-ICP-MS analysis.*

The content of K and Na also varies with Ti during the alteration of ilmenite (Figure 41 A & B). This is likely to be caused by mineralization of the grains by clay minerals during this process as also indicated by the increase of Al and Si described above. The differences in the K/Ti and Na/Ti ratios are probably caused by differences in the composition of the clay minerals.

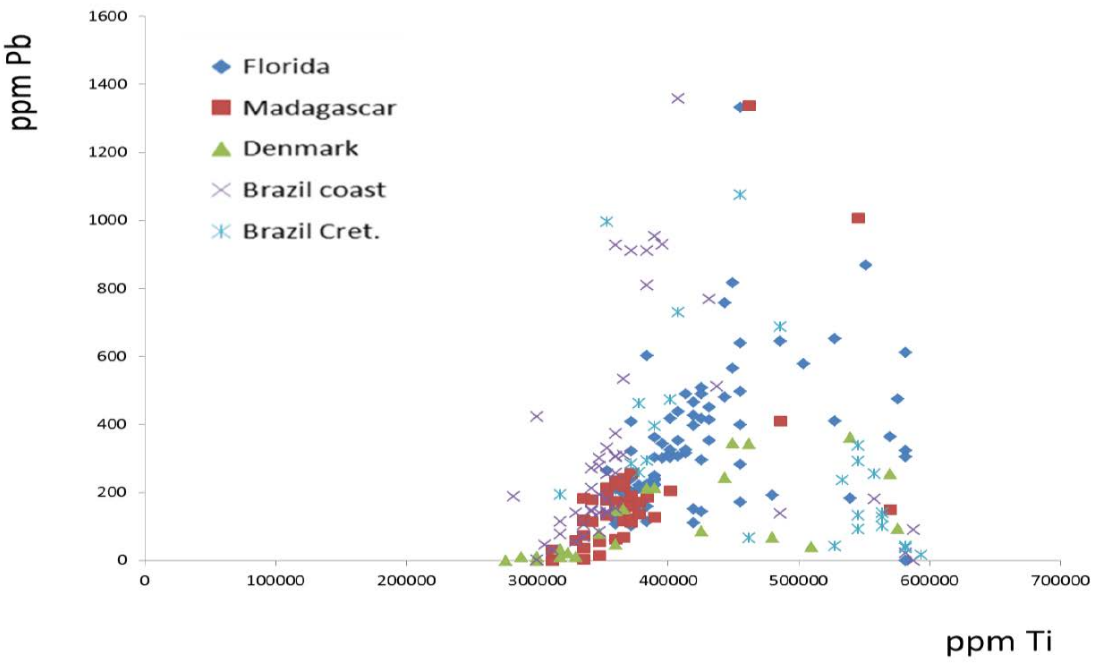


Figure 42 *Pb versus Ti in titanium minerals. LA-ICP-MS analysis.*

There is a relationship between Pb and Ti (Figure 42) as described with P above as well as between As and Ti (Figure 43). This indicates that Pb and As is also introduced into the leucoxene during alteration. The Pb/Ti and As/Ti ratios varies among the areas with e.g. high Pb/Ti ratio in at the Brazil coast as compared to e.g. Denmark.

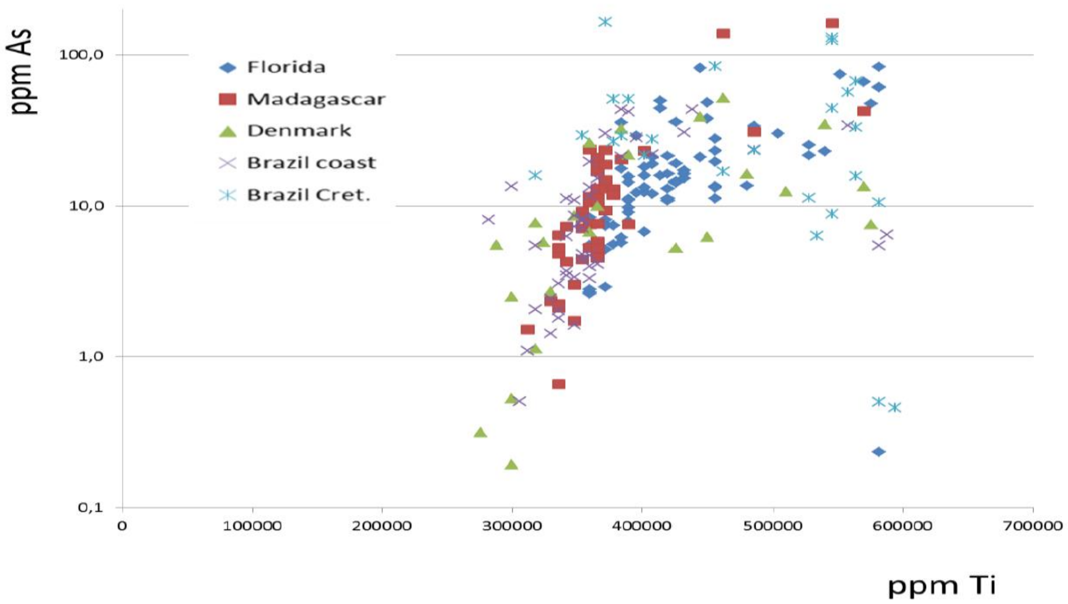


Figure 43 *As versus Ti in titanium minerals. LA-ICP-MS analysis.*

Cr is an element that is often already present in Ilmenite before alteration. However, the content increases with Ti and accordingly with alteration (Figure 44).

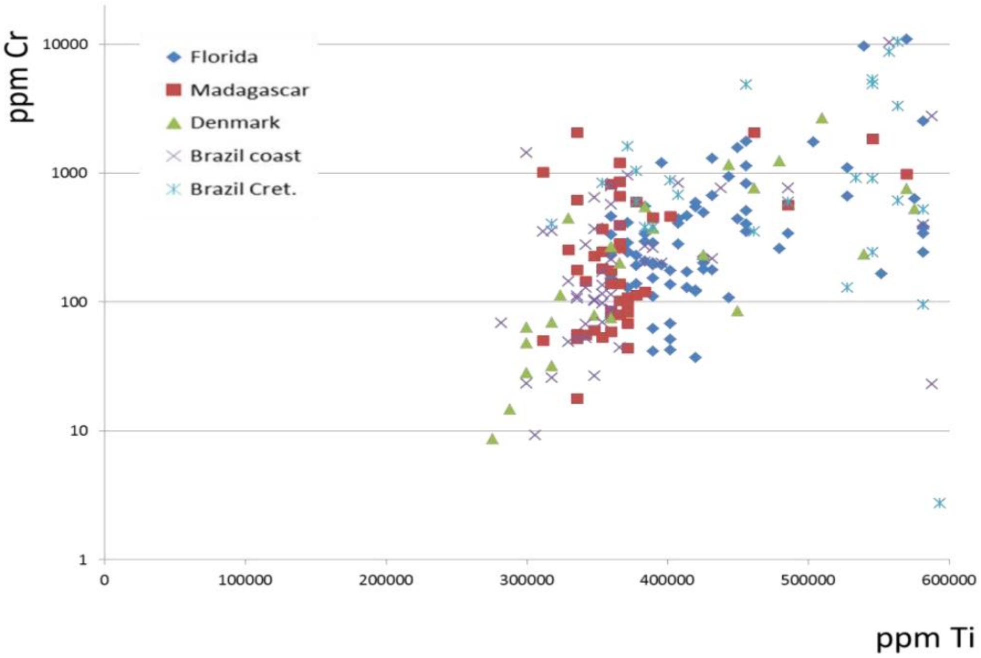


Figure 44 *Cr versus Ti in titanium minerals. LA-ICP-MS analysis.*

High-field-strength elements such as V, Zr, Nb, and Ta will generally follow Ti during geochemical processes. This is also the case during alteration of ilmenite where these elements neither decrease nor increase with increasing Ti (Figure 45). And they follow each other like Nb and Ta (Figure 46). There are slight differences in the Ta/Nb ratios which probably are due to differences in provenance.

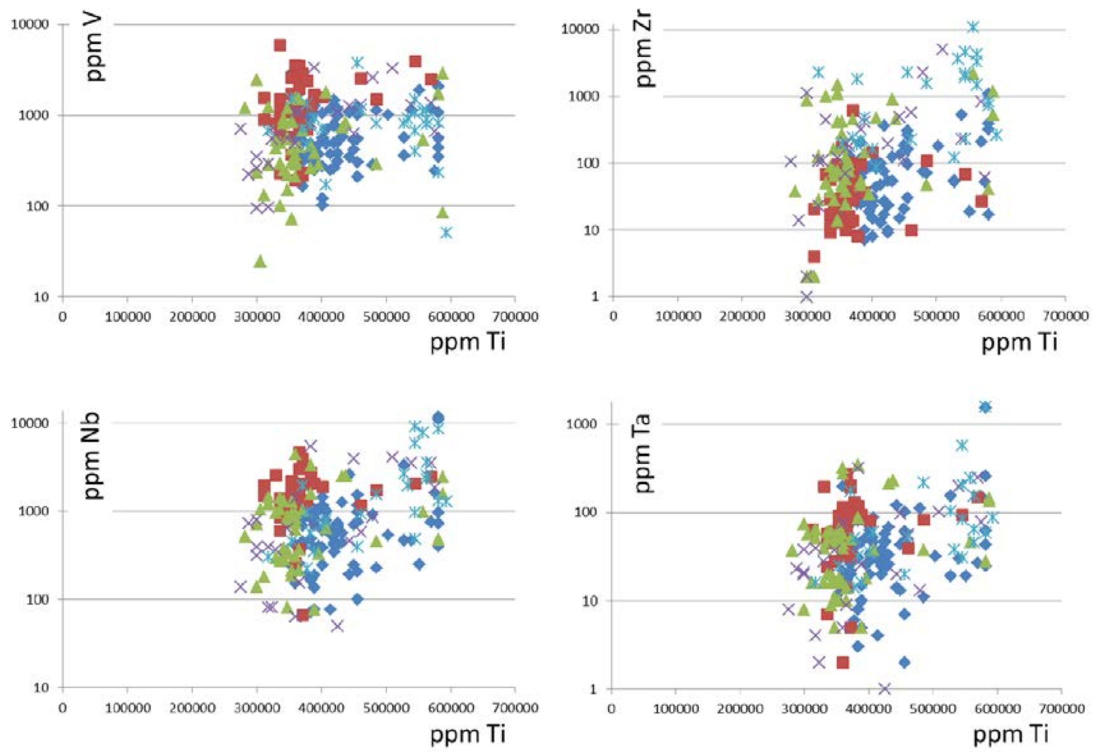


Figure 45 *V, Zr, Nb and Ta versus Ti in titanium minerals. LA-ICP-MS analysis.*

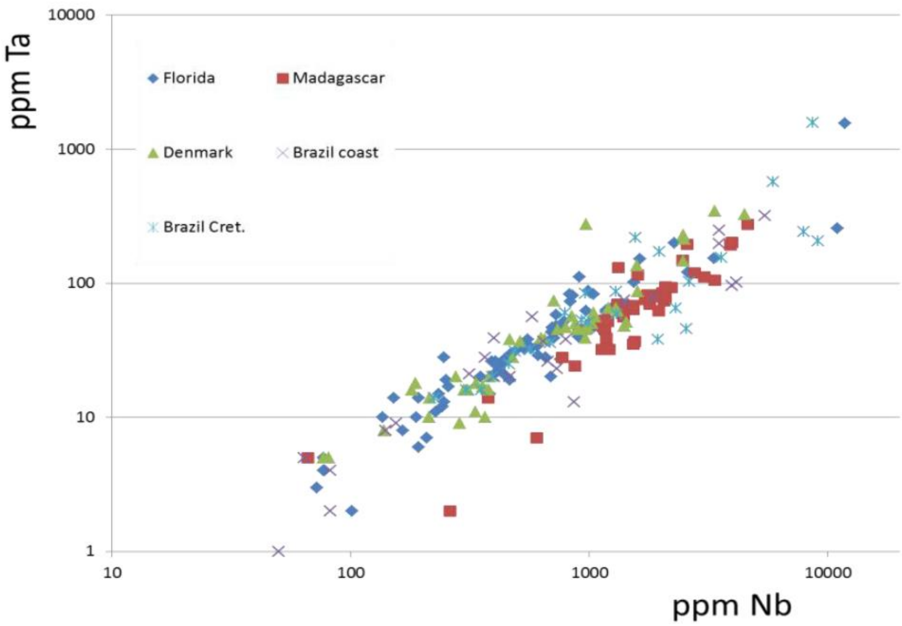


Figure 46 *Ta versus Nb in titanium minerals. LA-ICP-MS analysis.*

7 Conclusions

Ilmenite is a Fe-Ti oxide mineral occurring in igneous and metamorphic rocks with fairly high and variable contents of Mn, Mg, Nb and Cr. When ilmenite is exposed to meteoric water in hot and humid conditions the mineral is altered and changes composition. This process leads to formation of leucoxene and it has long been known that Fe, Mn & Mg is leached out during this alteration of ilmenite.

During the present work with the alteration processes in ilmenite it has been found that there are a global processes leading to increase in a number of elements:

Microprobe analysis and X-ray mapping shows

- The alteration of the ilmenite to leucoxene starts already in outcrop.
- The alteration is accompanied by introduction of micro-porosity (low totals).
- The chemical characteristics of this alteration are loss of Fe, Mn and Mg and introduction of Al, Si, Ca and P from the outside.
- Nb increase slightly in concentration due to the loss of Fe, Mn and Mg i.e. Nb follow Ti.
- The chemical changes seen in outcrop rock samples from Madagascar are similar to what can be found in outcrop rock samples from India (Kerala).
- The chemical characteristics of the incipient alteration in ilmenite in outcrop are similar to the alteration found in ilmenite in the dunes at Madagascar.
- The overall grade (% TiO_2) of the ilmenite in rivers draining the outcrops is elevated compared to unaltered hard-rock ilmenite but low compared to the placer ilmenite in Madagascar and Kerala. This indicates that the main alteration of the ilmenite happen near or at the coast.

SEM studies and statistical analysis of large numbers of CCSEM data shows:

The patterns with increase in Si, Al, P and Cr during alteration seen in microprobe analysis of single grains can be reproduced when looking at very large set (>10.000) of CCSEM data. It is further found, that when the altered ilmenite grains (leucoxene) are exposed to very intense alteration, the leucoxene recrystallizes and form grains with > 85 % TiO_2. During this recrystallization process cleaner grains are produced and the impurities are gradually lost and the composition approaches that of pure rutile/anatase.

The increase in content of e.g. P with Ti in the altered ilmenite i.e. the P/Ti ratio varies among the different localities.

Laser Ablation ICP-MS analysis shows:

The increase in content of e.g. P with Ti during the alteration of ilmenite as well as the variation in the P/Ti ratio varies among the different localities is confirmed by this technique. Further, it is found that there is an increase in a number of other elements during the alteration. Increase in REE, U and Th together with P is interpreted as introduction of a monazite like component in the altered ilmenite at many localities – but not in Florida where this relationship is not seen. There is an increase in Na and K with alteration probably tied to precipitation of clay-minerals also responsible for the increase in Si and Al.

There is an increase in Pb and As during the alteration.

High-field-strength elements such as V, Zr, Nb, and Ta will generally follow Ti during geochemical processes. This is also the case during alteration of ilmenite where these elements neither decrease nor increase with increasing Ti; and they follow each other e.g. with a strong correlation between Nb and Ta.

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