DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2003/98

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Summary

Three colour fractions of ilmenite representing different degrees of alteration were dissolved and analysed for U and Pb isotopic composition using the multi-collector, magnetic sector ICPMS at the Danish Lithosphere Centres Axiom laboraty. The aim of the study was to date the formation of pseudorutile possibly containing more U than the unaltered ilmenite.

The results show that the black, grey and light separates define a Pb^{207}/Pb^{206} age on 1187.7 ± 7.1 Ma, and an U-Pb age of 1250.2 ± 1.6 Ma. It was found that the ilmenites contain inclusions of zircon and that ilmenite separates further contain single grain zircons. As the content of U is very high in zircons compared to ilmenite/leucoxene, it is concluded, that the age found reflects the average age of the zircons rather that the age of the ilmenite transformation to pseudorutile/leucoxene. This is surported by the observation that the above mentioned ages lies within the age range previously found using Pb/Pb dating of the zircons in the sample.

Further, indications of Pb loss approx. 44 Ma was found as the lower intercept of the discordia diagram. This may be caused by leaching of the zircons in the exogenic environment. Accordingly, it may still be possible to date the timing of extensive leaching of the heavy mineral suite. However, further testing is needed in order to constrain this approach.

Introduction

When prospecting for deposits rich in altered ilmenite, it is of interest to understand the timing of the alteration process. Is it generally an in situ process altering the ilmenite in place as assumed eg. for the Trail Ridge deposit or it can be accumulation of ilmenite altered during earlier sedimentary cycles.

The aim of the present pilot project was to place constraints on the timing of alteration of ilmenite in the sediments that form the deposits at Voerslunde belonging to the Miocene Odderup Formation.. Ilmenite alteration is here understood as the process during which $Fe2O3$ is leached from oxidized ilmenite grains with subsequent formation of pseudorutile and formation of leucoxene. The hypothesis was that the pseudorutile was either formed during the Miocene, ie. immediately prior to or after the deposition of the beach sands in Voerslunde, or, alternatively, that the altered grains represent redeposited Mesozoic sediments of eg. Jurasic age. The rationale behind this latter hypothesis is that the Miocene sediments contain Jurassic spores and pollen, suggesting, that erosion of Jurassic sediments occured due to uplift in Skagerak (to the NE of Jutland) during the Laramic phase of the Alpine orogeny. Further, it is found, that the Mesozoic sands is characterised by high-grade ilmenite, which again may form the bulk of the altered ilmenite found at Voerslunde.

Earlier dating study of the zircon population of the same sample shows that zircon ages form groups, with one distinct group at 1000-1175 Ma, and a broad group at 1200-1800 Ma, and a few grains of yet older ages (Fig. 1) (Rasmussen & Knudsen, 2001).

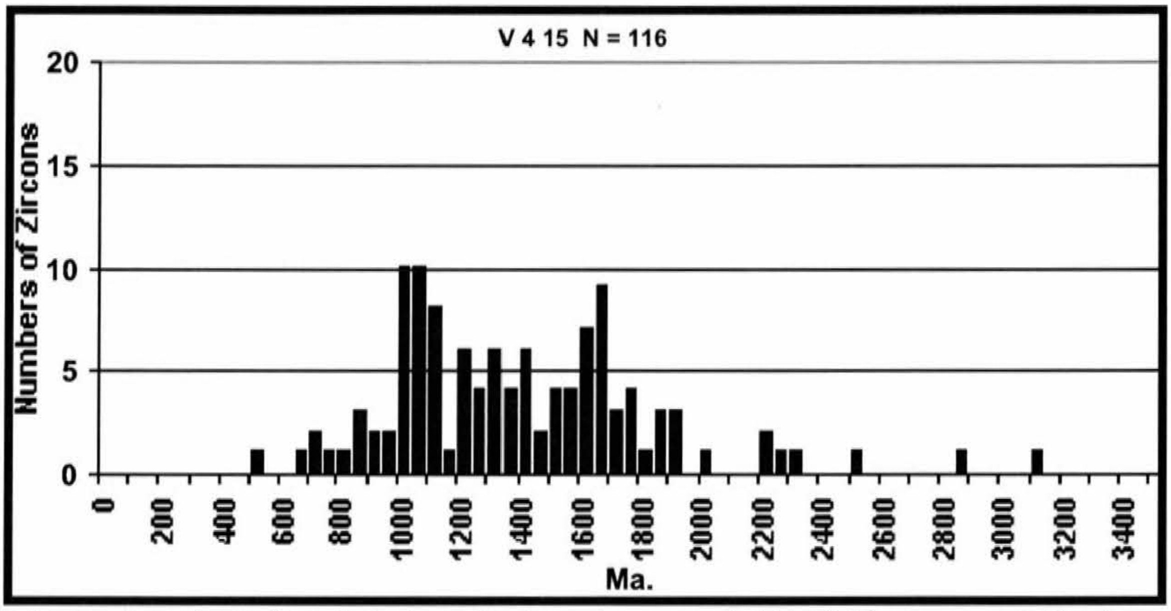

Fig. 1 *Age distribution of single grain zircon from sample V4-15 (Rasmussen & Knudsen, 2001).*

Analytical rationale

The method is based on the following assumptions;

1) During the leaching process of oxidized ilmenite to leucoxen, uranium is built into the lattice of leucoxene.
2) The unleached ilmenites contained no radioactive uranium.
3) Pb is excluded from leucoxene during its formation.
4) The colour of the Ti-oxide minerals reflects their Ti contents, so that the transition from unleached ilmenite (low Ti) to leucoxene (high-Ti) results in a colour transition from black to pale grey, respectively.
5) The separates are pure and do not contain other minerals.

Leucoxene (s.l.) was separated from sample V4-15 M heavy mineral concentrate, using a Frantz magnetic separator and heavy liquid. Finally, the leucoxene fraction was purified by hand picking under microscope and futher divided into three colour fractions, black, grey and light. Each fraction weighed ca. 100 milligrams.

The first attempt to date the leucoxene formation was based on laser ablation ICPMS technique. Ten grains from each fraction were mounted on carbon tape and analysed by laser ablation ICPMS (GEUS Quadropole ICPMS laboratory) for its content of U and Pb. While the analyses showed that there was not enough radiogenic Pb in the grains to yield a meaningful U/Pb age, the results indicated that there was enough radiogenic Pb for conventional U/Pb age dating on mineral separates. Thus, the three colour fractions, each about 100 milligrams, were exposed to several very strong acids and hot bombs for more than tree weeks until all material finally was dissolved.

Results of U-Pb dating

The three dissolved colour fractions were then analysed using the multi-collector, magnetic sector ICPMS at the Danish Lithosphere Centres Axiom laboraty. The results are given below in Table 1, and demonstrated in Figures 2, 3, 4 and 5.

The results show that the black, grey and light separates define a Pb^{207}/Pb^{206} age on 1187.7 ± 7.1 Ma, and an U-Pb age of 1250.2 ± 1.6 Ma. We regard the Pb^{207}/Pb^{206} age to be the most reliable, because the all Pb isotopes chemically behave identically and the age is calculated iteratively from the Pb^{207}/Pb^{206} ratio and is therefore not affected by Pb loss.

	U ppm	Pb ppm	206/204 Pb	207/204 Pb	208/204 Pb	207/206 Pb	207/206 age	206Pb*/238U=
Leux light	60,9	125,6	20,939	15,769	39,567	0,75306	4835	0,03067
Leux Grey	195,8	195,8	26,352	16,209	44,864	0,61510	4544	0,08382
Leux black	112,7	15,2	83,169	20,728	41,467	0,24922	3180	0,06738

Table 1. *ICPMS analyses of the three colour separates of leucoxene (s.l.).*

The lower intercept on concordia in Figure 5 at 44 Ma. may indicate that the material analysed experienced a substantial Pb loss at some event in the Eocene. The result is thus consistent with the provenance study made on zircons (Rasmussen & Knudsen. 2000) that show one of the source areas has an age of 1100-1250 Ma. This age, however, is unlikely to reflect the formation of leucoxene, that is, the leaching of Fe2O3 from oxidized ilmenite.

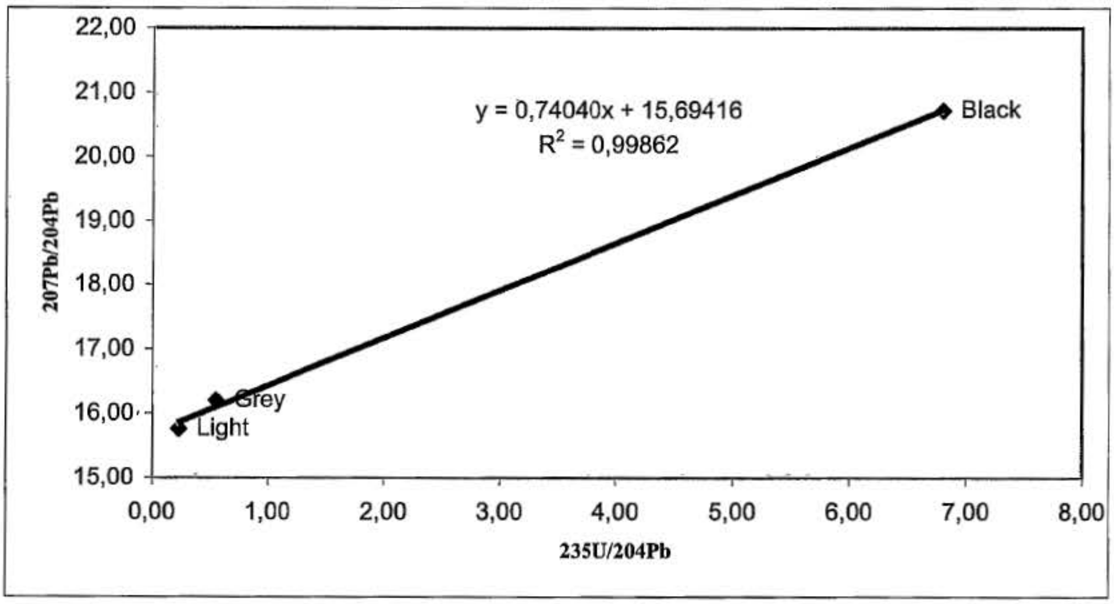

Figure 2. *The U/Pb age compared with the Pb/Pb age indicate loss of Pb from the system. (Model 3 Solution on 3 points. Age = 563 ± 200 Ma. Initial 207/204=15.7 ± 1.4. MSWD = 395, Probability = 0.000. Initial 207/204 variation =0.29 (2s). Assuming 0.5 and 0.1% errors, 0.99 err corr).*

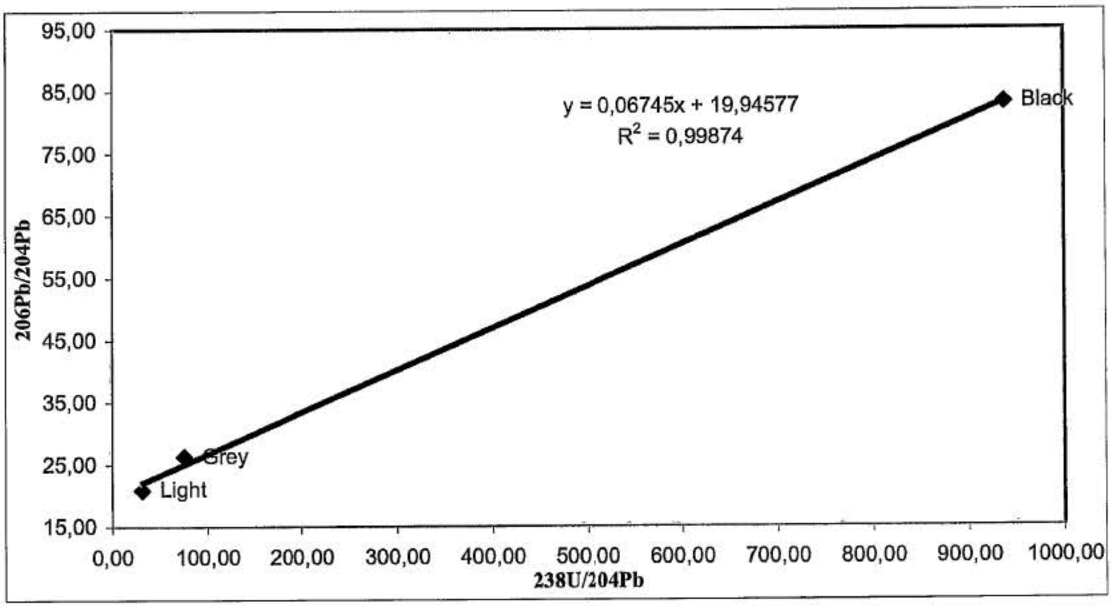

Figure 3. *The U/Pb age compared with the Pb/Pb age indicate loss of Pb from the system. (Model 3 Solution on 3 points. Age = 421 ± 180 Ma. Initial 206/204=20 ± 17. MSWD = 34297, Probability = 0.000. Initial 206/204 variation =3.5 (2s) assuming 0.5 and 0.1% errors, 0.99 err corr).*

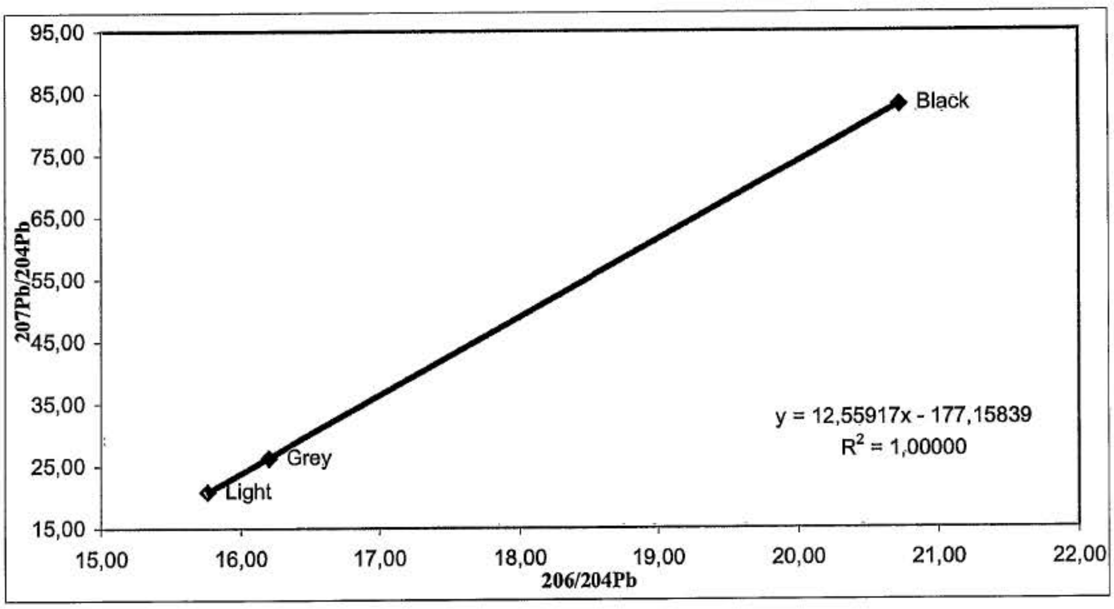

Figure 4. *The Pb/Pb age of 1187.7 ± 7.1 Ma is the most reliably, since the Pb/Pb age is insensitive to loss of U or Pb from the system. This is because the method is based on the Pb/Pb ratio alone. (Model 1 Solution on 3 points. Age = 1187.7 ± 7.1 Ma. w. decay-const errs:(±8.7 Ma). MSWD = 0.88, Probability = 0.35. Growth-curve intercepts at -548 and 1487 Ma assuming 0.1% errors and 0.99 err corr).*

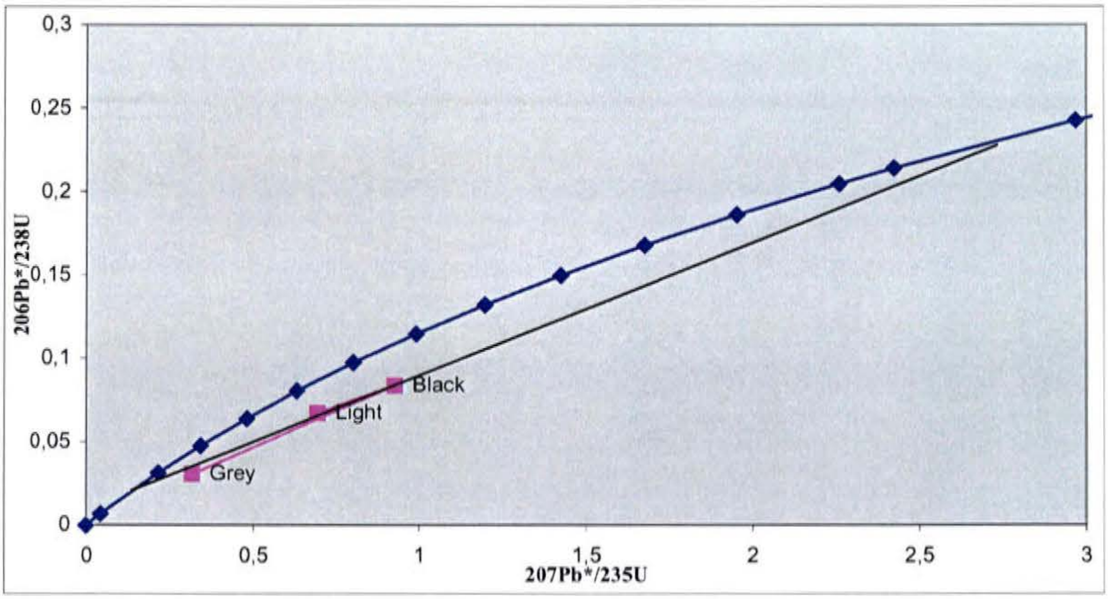

Figure 5. *The three colour separates fall on a line discordant with the undisturbed U-Pb growth curve (the concordia). This line, the discordia' has an upper intercept with the concordia at 1250.2 ± 1.6 Ma and a lower intercept at 44.17 ± 0.64. This indicates that the zircons may have experienced Pb loss during some event ca. 44 Ma. ago. (Model 1 Solution without [with] decay-const. errs on 3 points. Lower intercept: 44.17 ± 0.64 [±0.66] Ma. Upper intercept: 1250.2 ± 1.6 [±5.6] Ma. MSWD = 1.4, Probability of fit = 0.23 assuming 0.5% 2sd errors and 0.99 error corr).*

Origin and significance of the Pb-Pb age

In order to investigate the significance of the 1187.7 Ma age, the remaining grains of the three colour separates were mounted in epoxy and polished. Using the electron microbe (Jeol Superprobe at Geological Institute, University of Copenhagen), the three fractions were investigated by back-scatter imaging and wave-dispersive analysis. In all three colour separates, it was found that the leucoxene grains contained inclusions of zircon (Figs. 6 and 7).

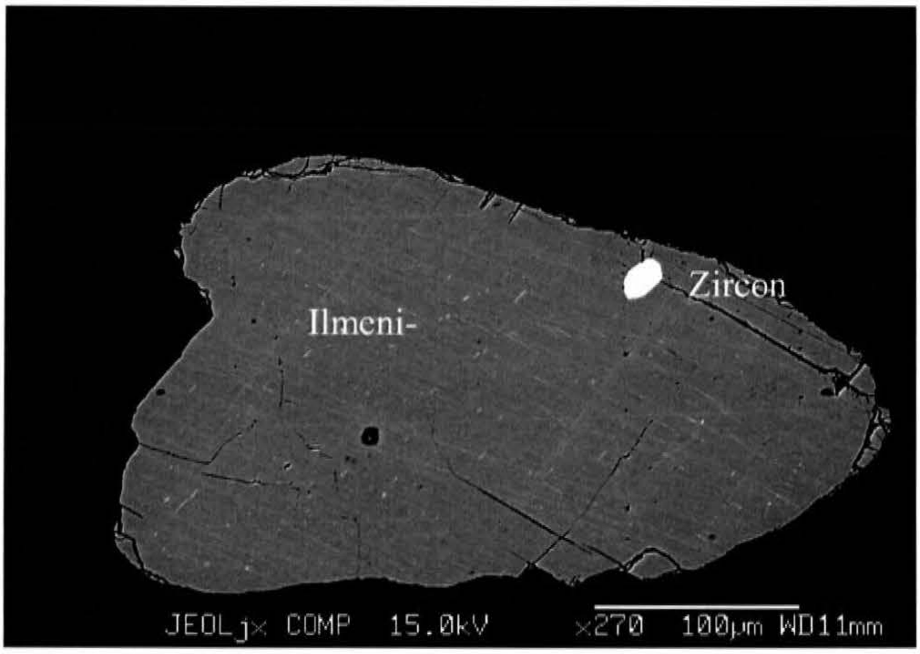

Fig. 6. *Ilmenite grain #5 from black coloured mineral fraction. Zircon inclusion is about 20 micron in diameter. Fine exsolutions of hematite and blebs of Nb enrichment probably stems from cooling of the original igneous ilmenite.*

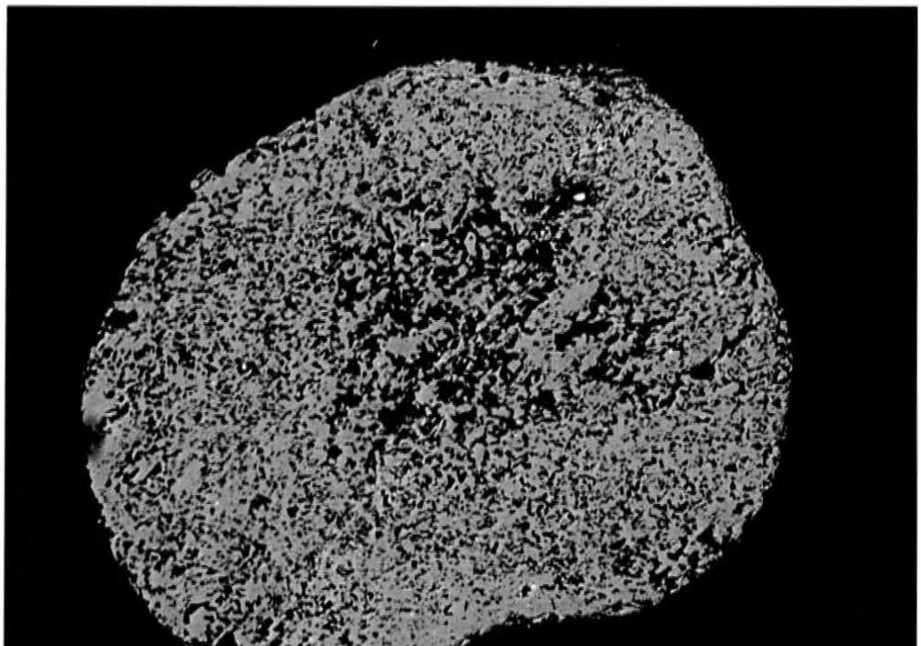

Fig. 7. *Pseudorutile grain #1 in light coloured mineral fraction. Small zircon inclusion is 2-3 micrometer in diameter. The spongy texture of the pseudorutile stems from advanced degree of leaching of hematite and its hydrous product goetite which were formed during an oxidation process of the original ilmenite grain.*

Since uranium partitioning into zircon is much higher than into ilmenite, the zircon inclusions are likely to host the majority of the uranium in the entire grain. Therefore, the requirements 2) given above is not met, and the decay of uranium and growth of lead commenced at the time of formation of the ilmenite grain, and a Pb-Pb or U-Pb date reflects this event and not the time of Fe2O3 leaching and rutile formation. During the course of microprobe analysis, it was further found that in addition to the zircon inclusions in leucoxene (s.l.), all three colour fractions contained single grain zircons (Fig. 8), in conflict with requirement 5) of above. Thus, in terms of the bulk inventory of zircon in the mineral separates, single grain zircons will account for the vast majority of this mineral. The consequence of this finding is that the Pb-Pb age of 1187.7 Ma given above is largely defined by the zircons found in the three colour mineral separates. This in turn means that the obtained Pb-Pb age has no bearing on the leaching process that lead to the formation of leucoxene.

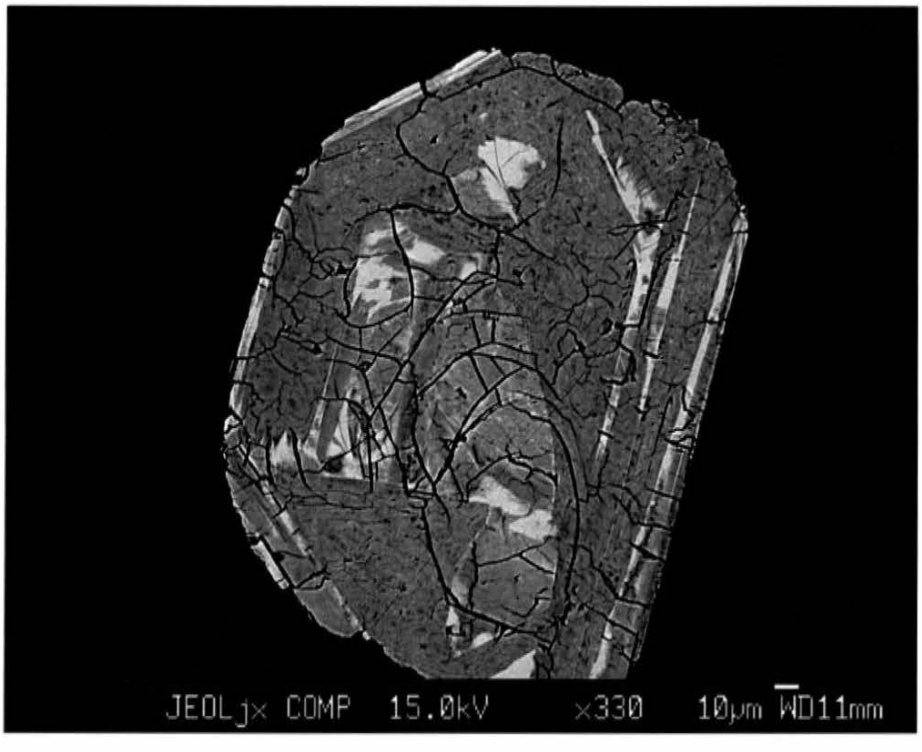

Fig. 8. *Euhedral zircon grain #4 in black coloured mineral fraction.*

Pb-loss and U-Pb ages

Some additional and valuable information can be extraced from the U-Pb analysis. It was stated above that the position of the data points below the concordia in Fig. 5, which gives the undisturbed U-Pb growth curve, shows that the measured material suffered some loss of Pb during its history. Since the three colour separates fall on a line with an upper intercept with the growth curve concordant with the Pb-Pb age, this line is a discordia, and the lower intercept can be interpreted as the timing of the event that resulted in Pb-loss of the single grain zircons. This age of 44.17 ± 0.64Ma places the event in the Eocene. Considering the relatively short time span between this age and the time of deposition of the Odderup Fm. in the Miocene, it appears reasonable to assume that the leucoxene (s.l.) and the zircons have travelled together during this period. The extensive leaching episode recorded by the lead loss of the single grain zircons, may accordingly be linked to the leaching of the ilmenite grains that resulted in the formation of leucoxene.

Speculations on sites of leaching

This interpretation is in close accordance with the palaeoclimatic data, which shows that the Eocene is a time of hot humid climate in Northern Europe. The Palaeocene and Eocene is also the time of continental breakup in the North Atlantic and the formation of one of Earths major large igneous provinces with immense volumes of erupted lavas. We envisage that such an environment lead to enhanced soil acidity in the onshore Scandinavian borderlands to the North Atlantic and deep alteration and leaching of onshore sedimentary packages.

The location of the onshore sediments in the Eocene must be some ways from the present position of the Miocene Odderup Fm. since in the early Palaeogene, the Danish subbasin was dominated by the deposition of marine carbonatious clays, reflecting a deep marine environment. Possible source regions and sites of leaching and leucoxene formation for the Odderup Fm. could be south Sweden, Finland , or, Poland. The zircon provenance study of Rasmussen and Knudsen (2000) suggests that the sediments were derived from the Baltic shield, including a strong signal from the Sveco-Norwegian orogeny (1200-900Ma). We speculate that the sediments were derived from these sources during the Caledonian orogeny and deposited somewhere in the south Sweden-Finland region, where it subsequently was leached by acidic surface water in the hot humid climate in the Eocene. During the Neogene uplift and shoreline regression, the leached sediments were transported in tidal facies westwards to reach it present location in the Miocene. The highly mature nature of the Odderup Fm. requires a long history of sediment transportation, thus agreeing with this hypothesis.

Suggestions to further work

If it is possible to date the leaching of the heavy mineral assemblage by the lower intercept of the discordia diagram, it is interesting. To test the critical age of 44.17 ± 0.64 Ma we need to do conventional zircon U/Pb age dating of the same sample.

The degree of Pb-loss is probably variable among the individual zircon grains, with the highest proportions lost from U-rich metamict grains. Another complication is, that the original age of the individual grains may vary considerably. Accordingly, attempts of dating individual grains may yield many different ages and accordingly a scatter on the upper intercept on the discordia. On the other hand this may not affect the lower intercept to a degree where the lead loss can not be seen. It appears worth testing.

References

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