

Reconnaissance Pb-Pb dating of single mineral phases by the step-leaching method: results from the Caledonides of East Greenland

Kristine Thrane

Reconnaissance Pb-Pb step-leaching analyses have been carried out on garnet and kyanite from the Krummedal supracrustal sequence in East Greenland, yielding respectively Neoproterozoic and Caledonian ages. These data support previous analyses suggesting that the Krummedal supracrustal sequence, widespread in southern parts of the East Greenland Caledonides, was affected by both an early Neoproterozoic and a Caledonian thermal event. Titanite and apatite fractions from the underlying crystalline basement rocks were analysed in order to obtain metamorphic ages, as a contrast and supplement to the numerous existing protolith ages on orthogneisses. The titanite yielded a date of 486 ± 15 Ma which, if interpreted as a true age, is older than the usual range of Caledonian ages in East Greenland. The significance of this date is uncertain, but one possibility is that it reflects extension and subsidence taking place prior to Caledonian collision. The apatite, in contrast, yielded a very young Caledonian date of 392 ± 24 Ma that may reflect the cooling of the basement gneisses to $< 500^\circ\text{C}$ subsequent to collision.

Keywords: Caledonian, East Greenland, geochronology, Neoproterozoic, step-leaching

Geological Survey of Denmark and Greenland, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark. Present address: Geological Institute, University of Copenhagen, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark. E-mail: Kthrane@geol.ku.dk

The Pb-Pb step-leaching (PbSL) method of Frei & Kamber (1995) makes it possible to date a range of rock-forming minerals that are normally difficult to date due to the low parent to daughter isotope ratios. Stepwise leaching of the mineral phases increases the data spread in uraniumogenic ($^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$) and thorogenic vs. uraniumogenic ($^{208}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$) diagrams, and as a consequence the precision of Pb/Pb isochrons is improved (Frei *et al.* 1997). Another advantage of the method is that the corresponding uraniumogenic and thorogenic Pb ratios of the different leach solutions can be observed, and a signature of Pb-containing microscopic mineral inclusions revealed. Leach solutions that do not follow a linear pattern in the $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram reveal sources with different Th/U ratio from that of the host mineral. If all the analyses fall on a linear trend

in the uraniumogenic diagram then the mineral inclusions are in isotopic equilibrium with the host mineral.

Investigations by the PbSL method were undertaken on selected samples collected during the 1997 and 1998 Geological Survey of Denmark and Greenland expeditions to the Kong Oscar Fjord region (72° – 75°N) of the East Greenland Caledonides (Henriksen 1998, 1999). The study area (Fig. 1) is made up of major Caledonian thrust sheets displaced westwards across foreland windows (see also Higgins & Leslie 2004, this volume; Thrane 2004, this volume). The thrust sheets incorporate Archaean and Palaeoproterozoic orthogneiss complexes overlain by a thick late Mesoproterozoic – early Neoproterozoic metasedimentary succession known as the Krummedal supracrustal sequence; the latter is structurally overlain by the Neoproterozoic Eleonore Bay Supergroup and Tillite

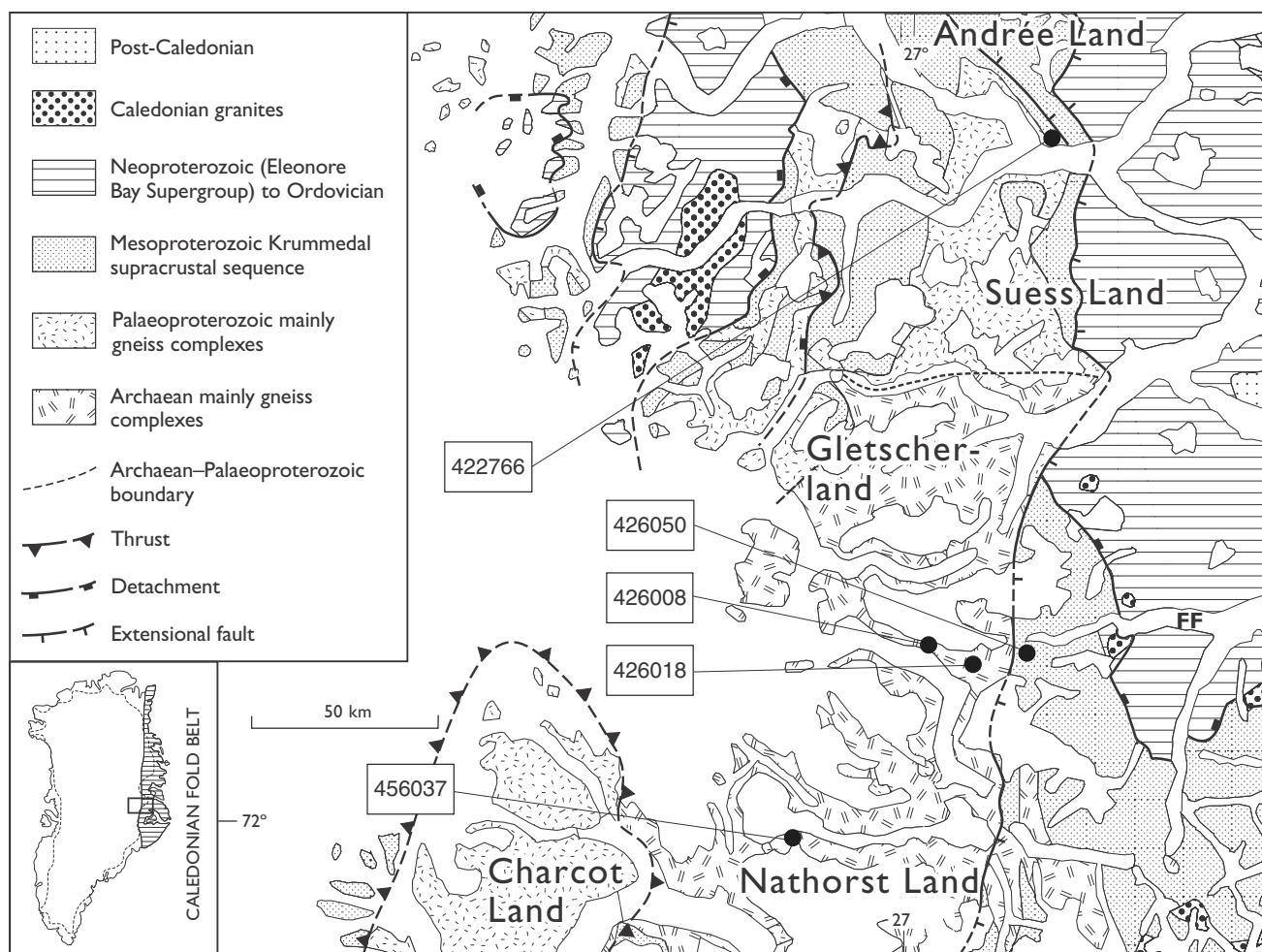


Fig. 1. Simplified geological map of the study area in the East Greenland Caledonides, with sample localities discussed in the text. Supracrustal rocks of Palaeoproterozoic age in Charcot Land are included with the Palaeoproterozoic gneiss complexes. **FF**, Forsblad Fjord.

Group, and Lower Palaeozoic rocks. These rock units have been variably reworked during the Caledonian orogeny.

Samples

In this study, PbSL analyses were carried out on garnet and kyanite from samples 426050 and 422766 of the late Mesoproterozoic – early Neoproterozoic Krummedal supracrustal sequence (Kalsbeek *et al.* 2000), with the objective of constraining the age of metamorphism which produced these minerals. In addition, PbSL analyses were undertaken on titanite from a garnet amphibolite (426037) and a gabbroic gneiss (426018), and on an apatite fraction from a tonalitic basement gneiss (426008). The latter three samples all derive from the crystalline basement complex under-

lying the Krummedal supracrustal sequence (Fig. 1), and the aim was to determine metamorphic ages for the mineral phases in the samples. Whole-rock Pb analyses were also carried out on samples 426008, 426018 and 426050.

Zircon grains from the crystalline basement complex in the study area analysed by ion microprobe have hitherto only yielded Archaean and Palaeoproterozoic magmatic ages. Although the rocks form parts of Caledonian thrust sheets and have undergone extensive Caledonian deformation and metamorphism, so far not a single Caledonian age has been obtained from zircon (Thrane 2002). While Caledonian K-Ar mineral ages have previously been recorded from all rock types in the study area (e.g. Rex & Higgins 1985), the spread in ages and uncertainties inherent in the method is indicative only of a metamorphic overprint of approximately Caledonian age.

Table 1. Sample data stepwise dissolution procedures

Sample	Weight mg	Step 1	Time min.	Step 2	Time min.	Step 3	Time hrs	Step 4	Time hrs	Step 5	Time hrs	Step 6	Time hrs	Step 7	Time hrs
426050 Garnet	236	Mix	10	4.4N HBr	45	8.8N HBr	3	8.8N HBr	24	conc. HF	48	conc. HF	260	8.8N HBr	290
426050 Kyanite	97	Mix	10	4.4N HBr	45	8.8N HBr	3	8.8N HBr	24	conc. HF	48	conc. HF	260		
422766 Kyanite	719	Mix	30	1.0N HBr	60	4.0N HBr	3	8.8N HBr	6	8.8N HBr	12	conc. HF	24	conc. HF	340
426018 Titanite	195	Mix	10	4.4N HBr	45	8.8N HBr	3	8.8N HBr	24	conc. HF	48	conc. HF	260		
426037 Titanite	71	Mix	10	4.4N HBr	90	8.8N HBr	3	8.8N HBr	24	conc. HF	50	conc. HF	340		
426008 Apatite	139	50% mix + 50% H ₂ O	10	50% mix + 50% H ₂ O	60	1.0N HBr	3	1.5N HBr	3	8.8N HBr	3	7N HNO ₃	9		

Mix = 1.5N HBr – 2N HCl 12:1 mixture. All steps except number 1 were left on the hotplate during the dissolution time.

Methods

For the samples analysed in the present study, a 200 mm sieve fraction of each mineral separate was purified by hand-picking. The samples were digested in a series of steps using procedures documented in Table 1; the method used was modified after that of Berger & Braun (1997) and Frei *et al.* (1997). The purified Pb was loaded on Re filaments with silica gel and H₃PO₄, and the isotopic ratios analysed on the VG sector 54-IT instrument at the University of Copenhagen. Most analyses were performed using the Faraday multi-collector; a few steps that contained very little Pb were analysed with the single collector (ion counting Daly detector). Fractionation of Pb was monitored by repeated analyses of the NBS 981 standard (values of Todt *et al.* 1993) and amounted to 0.103 ± 0.016 ‰/amu. The calculations of regression lines follow the method of Ludwig (1999). Errors quoted are 2σ .

Five to seven acid-leach steps were undertaken on each mineral separate. Whole-rock Pb and PbSL isotope data are listed in Table 2 and plotted in Figs 2–5.

PbSL results

Krummedal supracrustal sequence

The late Mesoproterozoic – early Neoproterozoic Krummedal supracrustal sequence is widely distributed in the southern part of the East Greenland Caledonides between 70° and 74°N (Fig. 1; Higgins 1988).

Sample 426050 was collected from the Krummedal supracrustal sequence south of innermost Forsblad Fjord, close to the faulted contact with the crystalline basement complexes (Fig. 1). The general metamorphic grade of the Krummedal supracrustal sequence is amphibolite facies, and the sample consists of quartz + plagioclase + K-feldspar + garnet + biotite + kyanite + sillimanite + amphibole + muscovite + titanite. The garnet and biotite represent early phases, while kyanite is a later phase that overgrows the deformation fabric of the biotite. Kyanite and K-feldspar crystallised at the same time, demonstrating that the rock has been exposed to high *P–T* conditions; during cooling, sillimanite, titanite and secondary biotite crystallised, and part of the kyanite was consumed during formation of muscovite.

Garnet and kyanite were analysed by PbSL (Fig. 2). Seven steps were performed on the garnet; all the steps, together with the whole-rock analysis, fall on a linear array in the ²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb diagram

Table 2. Pb-Pb step leaching (PbSL) data

Sample	Phase	Step	$^{206}\text{Pb}/^{204}\text{Pb}$	$\pm 2 \sigma^*$	$^{207}\text{Pb}/^{204}\text{Pb}$	$\pm 2 \sigma^*$	$^{208}\text{Pb}/^{204}\text{Pb}$	$\pm 2 \sigma^*$	r_1	r_2
426050	Wr		19.39	0.01	15.65	0.01	38.91	0.03	0.96	0.93
426008	Wr		14.32	0.01	14.61	0.01	38.51	0.03	0.93	0.92
426018	Wr		17.10	0.04	15.13	0.04	37.76	0.09	0.99	0.98
426050	Grt	1	23.34	0.64	16.01	0.44	39.09	1.08	1.00	1.00
426050	Grt	2	29.02	0.75	16.34	0.43	43.66	1.14	0.97	0.98
426050	Grt	3	69.99	1.99	18.74	0.53	116.25	3.30	1.00	1.00
426050	Grt	4	272.79	6.53	32.93	0.79	436.00	10.43	1.00	1.00
426050	Grt	5	99.56	1.31	20.49	0.27	44.90	0.59	1.00	1.00
426050	Grt	6	139.41	0.74	23.99	0.13	57.17	0.31	1.00	1.00
426050	Grt	7	152.05	4.39	24.48	0.71	87.67	2.53	1.00	1.00
426050	Ky	1	19.53	0.06	15.66	0.05	38.17	0.11	0.99	0.98
426050	Ky	2	20.45	0.14	15.70	0.11	38.52	0.27	0.99	1.00
426050	Ky	3	24.26	0.23	15.82	0.15	47.05	0.44	0.99	0.99
426050	Ky	4	34.83	0.16	16.42	0.08	65.68	0.31	0.99	0.99
426050	Ky	5	20.00	0.02	15.70	0.02	38.09	0.05	0.95	0.94
426050	Ky	6	33.13	0.19	16.49	0.10	38.81	0.22	0.99	0.99
422766	Ky	1	18.23	0.05	15.49	0.04	37.96	0.10	0.99	0.98
422766	Ky	2	19.92	0.16	15.64	0.12	40.81	0.32	0.99	1.00
422766	Ky	3	42.22	0.52	16.75	0.21	82.30	1.03	0.97	0.98
422766	Ky	4	171.43	19.09	24.12	2.69	326.96	36.41	1.00	1.00
422766	Ky	5	137.46	5.87	22.08	0.95	258.40	11.04	1.00	1.00
422766	Ky	6	20.59	0.04	15.70	0.03	38.60	0.07	0.98	0.97
422766	Ky	7	27.19	1.02	16.16	0.61	39.21	1.48	1.00	1.00
426018	Tit	1	16.50	0.02	15.09	0.02	37.40	0.04	0.95	0.95
426018	Tit	2	19.47	0.05	15.27	0.04	38.22	0.11	0.99	0.99
426018	Tit	3	104.74	1.13	20.29	0.22	56.20	0.61	1.00	1.00
426018	Tit	4	152.44	0.53	22.89	0.08	65.29	0.23	0.99	0.99
426018	Tit	5	120.05	0.35	20.97	0.06	56.99	0.17	0.99	0.99
426018	Tit	6	122.84	0.92	21.14	0.16	57.72	0.43	1.00	1.00
426037	Tit	1	16.53	0.22	15.11	0.20	37.11	0.50	1.00	1.00
426037	Tit	2	20.87	0.09	15.30	0.07	40.03	0.18	0.99	0.99
426037	Tit	3	76.66	1.92	18.21	0.46	46.56	1.17	1.00	1.00
426037	Tit	4	69.70	1.09	17.90	0.28	48.30	0.76	1.00	1.00
426037	Tit	5	36.53	0.18	16.15	0.08	41.79	0.21	0.99	0.99
426037	Tit	6	36.78	0.27	16.18	0.12	41.76	0.31	1.00	1.00
426008	Apa	1	27.93	0.06	15.36	0.04	40.96	0.09	0.99	0.99
426008	Apa	2	37.36	0.04	15.95	0.02	39.13	0.05	0.97	0.96
426008	Apa	3	38.28	0.03	15.91	0.01	38.70	0.04	0.93	0.85
426008	Apa	4	38.68	0.08	16.08	0.03	38.73	0.08	0.99	0.98
426008	Apa	5	64.84	0.94	21.41	0.31	35.92	0.52	1.00	1.00

Wr = whole-rock, Grt = garnet, Ky = kyanite, Tit = titanite, Apa = apatite.

* Errors are two standard deviations absolute (Ludwig 1988).

$r_1 = ^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ error correlation (Ludwig 1988).

$r_2 = ^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ error correlation (Ludwig 1988).

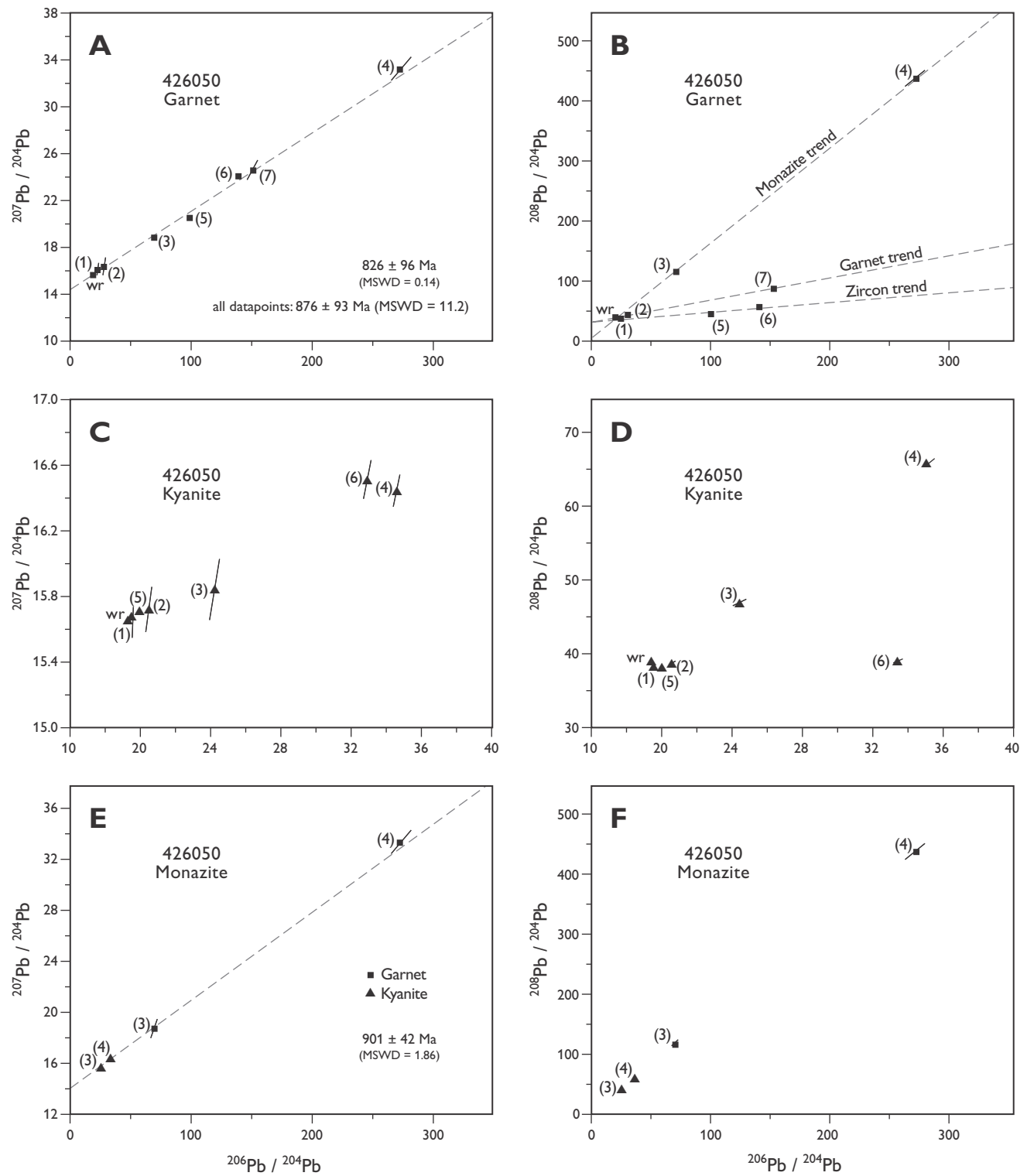


Fig. 2. Uranogenic ($^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$) and thorogenic vs. uraniumogenic ($^{208}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$) Pb isotope diagrams with PbSL data from step-leaching experiments on garnet (A, B) and kyanite (C, D), from mica schist sample 426050 (Krummedal supracrustal sequence). E and F are steps representing monazite inclusions within the garnet and kyanite.

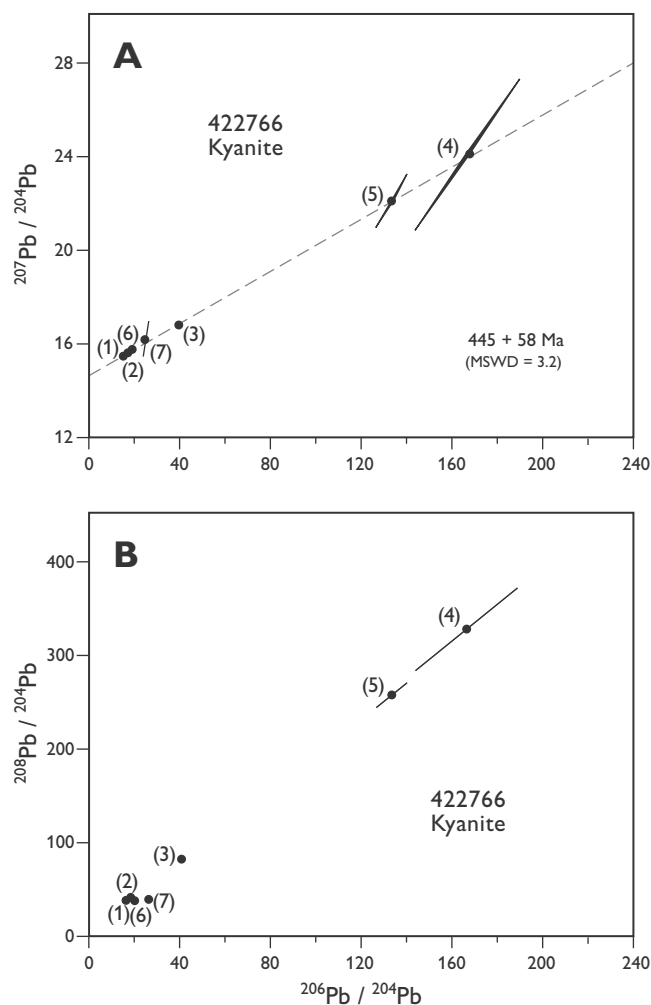


Fig. 3. Uranogenic ($^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$) and thorogenic vs. uraniumogenic ($^{208}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$) Pb isotope diagrams with PbSL data from step-leaching experiments on kyanite, from mica schist sample 422766 (Krummedal supracrustal sequence).

(Fig. 2A) yielding a $^{207}\text{Pb}/^{206}\text{Pb}$ date of $876 \pm 93 \text{ Ma}$ ($\text{MSWD} = 11.2$). The $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 2B) reveals the presence of mineral inclusions in the garnet. The different Th/U ratios of the host mineral and the inclusions may explain the large MSWD value of the errorchron. Steps 3 and 4 have very high Th/U ratios, interpreted as representing monazite inclusions ($\text{Th}/\text{U} > 3$; DeWolf *et al.* 1996). All the monazite is leached out in step 4, causing the observed drop in the Th/U ratio. The very low Th/U ratio in steps 5 and 6 is characteristic of zircon leach steps ($\text{Th}/\text{U} < 1$; DeWolf *et al.* 1996). All the zircon is dissolved in step 6. Step 7 was undertaken because of the red colour of the residue after step 6, showing that garnet was still present.

The only leach steps dominated by garnet are the two first, where all the most primitive Pb is extracted,

and step 7. These three steps together with the whole-rock analysis yield an isochron date of $826 \pm 96 \text{ Ma}$ ($\text{MSWD} = 0.14$). The large error of the date is due to the low precision of step 7.

The same procedure was carried out on kyanite, and again there is evidence for the presence of both monazite and zircon inclusions (Fig. 2D). Steps 3 and 4 are dominated by monazite, and step 6 by zircon. Three steps (1, 2 and 5) are interpreted as representing kyanite, but while the individual analyses are very precise they do not form a sufficiently wide spread in the Pb ratios to yield a precise date. The Pb whole-rock analysis and the kyanite-dominated steps define a slope which yields an isochron date of $1219 \pm 790 \text{ Ma}$ ($\text{MSWD} = 0.24$). Given the large uncertainty, this date does not yield any useful chronological information. The monazite-dominated steps from the garnet (3 and 4) and the kyanite (3 and 4) plot on a linear trend in both the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams (Fig. 2E, F). The four monazite steps yield an isochron date of $901 \pm 42 \text{ Ma}$ ($\text{MSWD} = 1.86$).

The monazite and garnet dates are in general accordance with the ion microprobe analyses of metamorphic zircon rims from the Krummedal supracrustal sequence that have yielded Neoproterozoic ages around 940 Ma (Thrane *et al.* 1999a, b; Kalsbeek *et al.* 2000). The cores of detrital zircons from the same study yielded ages ranging from c. 1100 to 1900 Ma, and it therefore serves no practical purpose to calculate an age from the zircon steps, as these will represent a mixture of ages.

Sample 422766, also derived from the Krummedal supracrustal sequence, was collected by J.C. Escher and K.A. Jones in the southern part of Andrée Land, very close to the contact with the structurally underlying crystalline basement (Fig. 1). The sample contains garnet and kyanite crystals up to 5 cm in diameter.

The kyanite was analysed by PbSL, while the garnet was considered too altered to justify analysis. Seven steps were undertaken on the kyanite, and the analyses represent an almost perfect leaching pattern (Fig. 3); all fall on a linear array in both the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagrams, except for step 7 which has a lower $^{208}\text{Pb}/^{204}\text{Pb}$ ratio that probably indicates the presence of zircon inclusions. A $^{207}\text{Pb}/^{206}\text{Pb}$ date of $437 \pm 62 \text{ Ma}$ ($\text{MSWD} = 2.6$) is obtained using all the steps, while if step 7 is excluded a date of $445 \pm 58 \text{ Ma}$ ($\text{MSWD} = 3.2$) is obtained. The large error is due to the analytical error of steps 4 and 5.

Crystalline basement

The East Greenland Caledonian orogen is dominated by major thrust sheets of reworked orthogneiss complexes. The crystalline basement is divided into an Archaean terrain to the south of 72°50'N and a Palaeoproterozoic terrain to the north (Fig.1; Thrane 2002).

PbSL analyses on titanite from a metagabbroic gneiss (426018) in the Archaean crystalline basement complex west of innermost Forsblad Fjord (Fig. 1) were undertaken. This gabbroic gneiss has yielded a Sm-Nd model age (t_{DM}) of 3.25 Ga (Thrane 2002). The whole-rock analysis has the same Pb ratios as step 1, indicating that the whole-rock and titanite are in equilibrium. The six leach steps together with the whole-

rock analysis yield an isochron date of 504 ± 48 Ma (MSWD = 1.81). However, the $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 4B) suggests that the titanite contains small amounts of monazite inclusions, which result in slightly elevated Th/U ratios for steps 3 and 4 compared with the titanite trend. If steps 3 and 4 are excluded, an isochron date of 486 ± 15 Ma (MSWD = 0.16) is obtained (Fig. 4A).

Titanite from a sheared garnet amphibolite (426037) cutting the basement gneisses of Nathorst Land (Fig. 1) was also analysed. All six data points define an isochron date of 335 ± 140 Ma (MSWD = 0.11; Fig. 4C); the large error of the date is due to the limited spread in the data points, as well as the large analytical errors of steps 3 and 4. In the $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram (Fig. 4D) the analyses show an unusual

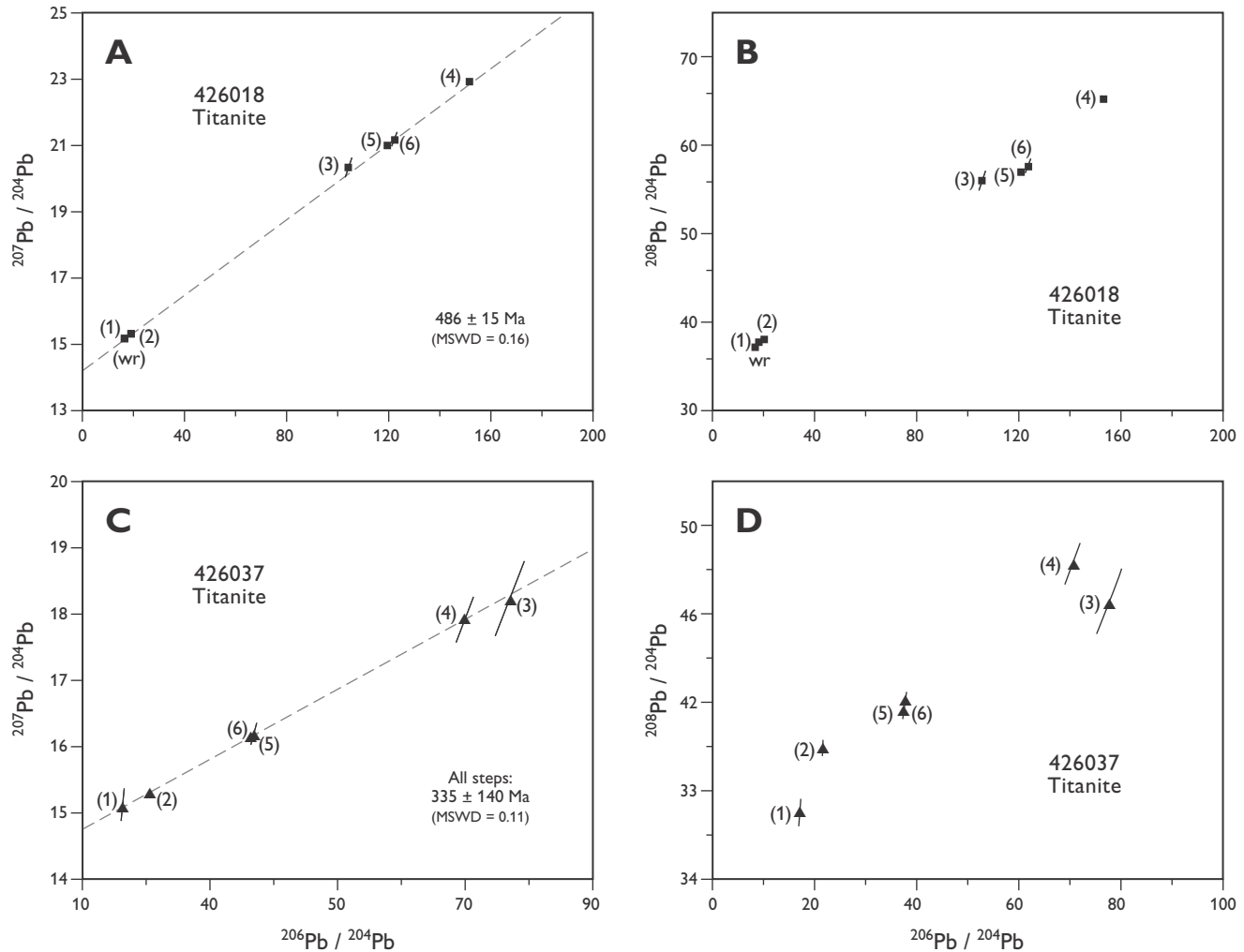


Fig. 4. Uranogenic ($^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$) and thorogenic vs. uranium ($^{208}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$) Pb isotope diagrams with PbSL data from step-leaching experiments on titanite from a gabbroic gneiss in the basement (A, B; sample 426018) and a garnet amphibolite (C, D; sample 426037).

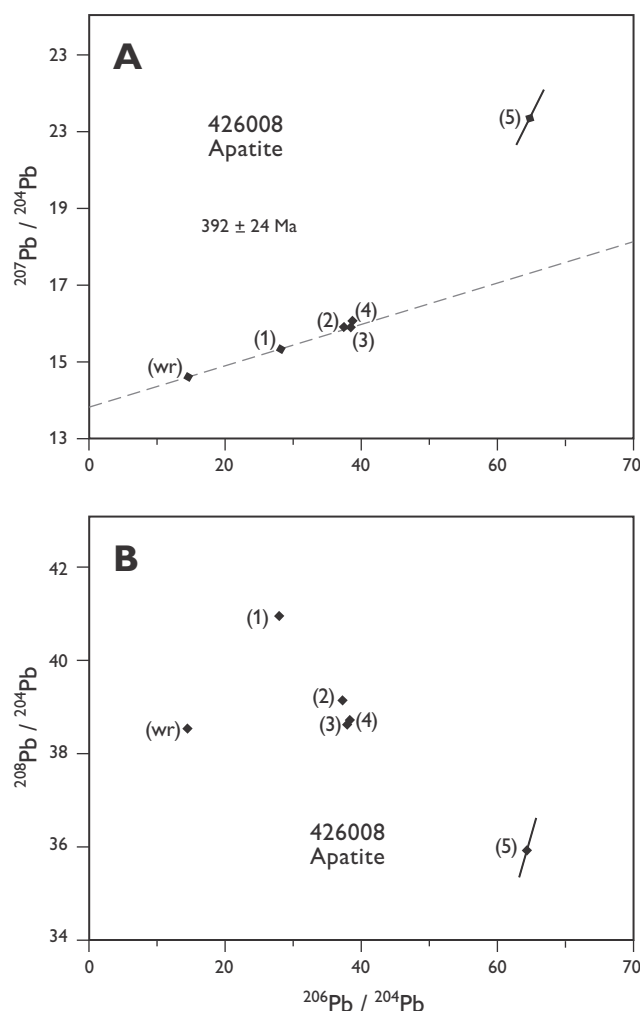


Fig. 5. Uranogenic ($^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$) and thorogenic vs. uranium ($^{208}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$) Pb isotope diagrams with PbSL data from step-leaching experiments on apatite from a tonalitic basement gneiss (sample 426008).

pattern: step 2 has an elevated Th/U ratio compared to the general trend while step 3 has a lower Th/U ratio. These features cannot be explained by the presence of monazite and zircon inclusions. If steps 2 and 3 are excluded from the isochron an even less precise date of 309 ± 230 Ma (MSWD = 0.03) is obtained.

Apatite from a tonalitic basement gneiss (426008) collected west of innermost Forsblad Fjord (Fig. 1) was also analysed. Zircon crystals from this sample have yielded U-Pb ages of *c.* 2800 Ma (Thrane 2002). Apatite dissolves much more easily than silicate phases, so a weaker acid and shorter leaching times were used in this experiment. The analyses form a complex pattern (Fig. 5). Step 1 is too thorogenic to derive from apatite, and it is interpreted instead as influenced by allanite since this is very easily dissolved and has a

higher Th/U ratio than apatite. Step 2 is less thorogenic than step 1, but more so than step 3, and is therefore interpreted as a mixture between allanite and apatite. Step 3 is the only step dominated by apatite. The only possible way to obtain a date is thus by combining the whole-rock analysis and step 3, which yields a date of 392 ± 24 Ma (Fig. 5A). Step 1 falls on the isochron, while step 2 falls slightly above, demonstrating that the two mineral phases were almost in equilibrium, with the presumed allanite being slightly older corresponding to its higher closure temperature. In the $^{208}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram it seems that both steps 3 and 4 are apatite steps, but in the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ diagram it is clear that step 4 is older and must be influenced by zircon inclusions which were leached out in the strong acid of step 5. The whole-rock analysis and step 5 yield a date of 2159 ± 46 Ma.

Summary and discussion

The analyses reported in this paper are the first PbSL analyses reported on rocks from the Caledonian orogen of East Greenland. All the samples have been analysed only once. Several of the dates obtained are not consistent with existing ages from the area, and some of the new dates are also somewhat controversial; replicate analyses should therefore be made for all the samples, to confirm that the dates are consistent, before any definite interpretations can be made. Thus different interpretations are presented in the discussion that follows.

The reliability of the PbSL method is still an open question. The main concern is the importance of the micro-inclusions contained in the mineral being analysed, and whether it is possible to be certain which combination of minerals is dissolved and affect the individual steps. This important point has not yet been resolved, and must be kept in mind when evaluating the new dates.

Supracrustal rocks

The PbSL study demonstrates that Neoproterozoic monazite and garnet are present in the Krummedal supracrustal sequence; evidence of Caledonian monazite has previously been reported (Kalsbeek *et al.* 2000). Zoned garnets have often been recorded (Elvevold & Gilotti 1999; Thrane *et al.* 1999b), of which

the outer rims are interpreted to be Caledonian whereas there has previously been doubt as to whether the cores were Neoproterozoic or early Caledonian. In contrast, the presence of Neoproterozoic kyanite has not been demonstrated in this study. Petrographically it is often difficult to determine to which mineral paragenesis the kyanite belongs, and thus it cannot be ruled out that some of the kyanite in parts of the Krummedal supracrustal sequence may be Neoproterozoic (Elvevold & Spears 2000).

Evidence of early Caledonian metamorphism in the crystalline basement?

The closure temperature for titanite is estimated by Dahl (1997, and references therein) to be in the range of 620–680°C, and by Cherniak (1993) in the range of 575–707°C, depending on the grain size. The titanite date of 486 ± 15 Ma for sample 426018, together with the date of the monazite inclusions, suggest that the crystalline basement did experience Caledonian medium to high-grade metamorphism.

No other ages of *c.* 486 Ma have yet been obtained in East Greenland. The age of the Caledonian collision in East Greenland is usually referred to the interval 430–425 Ma, on the basis of zircon ages from granite intrusions and the time of migmatite formation in the Krummedal supracrustal sequence (Watt *et al.* 2000; Kalsbeek *et al.* 2000, 2001). No comparable zircon ages have been recorded in the crystalline basement rocks in the study area, where evidence of the Caledonian overprint is restricted to imprecise lower concordia intercept ages ranging from 467 ± 18 Ma to 443 ± 25 (Thrane *et al.* 1999a). It is not possible to determine whether these lower intercept ages correspond to the 'traditional' East Greenland Caledonian range of events, or to a potential earlier event. In North-East Greenland Caledonian zircons have been recorded in some Palaeoproterozoic gneisses (Kalsbeek *et al.* 1993), which is in line with the assumption that the crystalline basement complexes of this northern region were more strongly reworked during the Caledonian orogeny.

It might be speculated that the titanite date of 486 ± 15 Ma is a cooling age, while the slightly older monazite micro-inclusions in the titanites could represent the peak of a collision event – comparable to the early Caledonian event in Scandinavia (Mørk *et al.* 1988; Andréasson 1994, 2000). However, this is not possible in East Greenland, since Ordovician carbonates were still

being deposited in the Iapetus-margin basin that lay east of the Laurentian crystalline basement at this time; there is no associated clastic input that would be expected if a collision had taken place nearby. The exceptionally thick Ordovician carbonate succession in East Greenland (Smith 1991) is indicative of a significant increase in the rate of subsidence, and it is possible that the *c.* 500 and 486 Ma dates are instead related to extension. The *c.* 430 Ma ages are thus still the best indication of the main Caledonian collision phase in East Greenland. Apatite, yielding the youngest Caledonian date of 392 ± 24 , could be interpreted to represent the time where the basement gneisses cooled to $< 500^\circ\text{C}$ (Dahl 1997).

Acknowledgements

The isotope data described in this paper were acquired at the Geological Institute, University of Copenhagen. Robert Frei is thanked for introducing and guiding me in the Pb-Pb step-leaching method. Jan C. Escher and Kevin A. Jones kindly provided sample 422766. Critical comments on the manuscript by Adam A. Garde, A.K. Higgins and Feiko Kalsbeek are greatly appreciated. This project was based on funding from the Danish Natural Science Research Council. Minik Rosing and Martin Whitehouse are thanked for reviewing the manuscript.

References

- Andréasson, P.G. 1994: The Baltoscandian Margin in Neoproterozoic – early Palaeozoic times. Some constraints on terrane derivation and accretion in the Arctic Scandinavian Caledonides. *Tectonophysics* **231**, 1–32.
- Andréasson, P.G. 2000: Finnmarkian deep-seated imbrication of a margin of Baltica: evidence from high-grade deformation zones in the Kebnekaise Mts., Swedish Caledonides. 24. Nordiske geologiske vintermøte, Trondheim, Norway, 6–9 January, 2000. Abstract volume. *Geonytt* **1**, 32 only.
- Berger, M. & Braun, I. 1997: Pb-Pb dating of apatite by a stepwise dissolution technique. *Chemical Geology* **142**, 23–40.
- Cherniak, D.J. 1993: Lead diffusion in titanite and preliminary results on the effects of radiation damage on Pb transport. *Chemical Geology* **110**, 177–194.
- Dahl, P.S. 1997: A crystal-chemical basis for Pb retention and fission-track annealing systematics in U-bearing minerals, with implications for geochronology. *Earth and Planetary Science Letters* **150**, 277–290.
- DeWolf, C.P., Zeissler, C.J., Halliday, A.N., Mezger, K. & Essene, E.J. 1996: The role of inclusions in U-Pb and Sm-Nd garnet

- geochronology: step-wise dissolution experiments and trace uranium mapping by fission track analysis. *Geochimica et Cosmochimica Acta* **60**, 121–134.
- Elvevold, S. & Gilotti, J.A. 1999: Reaction history of metapelitic rocks from Goodenough Land, East Greenland. In: Frederiksen, K.S. & Thrane, K. (eds): Second symposium on East Greenland geology, mainly Caledonian. Abstract volume. Danmarks og Grønlands Geologiske Undersøgelse Rapport **1999/21**, 31 only.
- Elvevold, S. & Spears, F.S. 2000: Garnet zoning and reaction history of anatectic pelites in the East Greenland Caledonides. 24. Nordiske geologiske vintermøte, Trondheim, Norway, 6–9 January, 2000. Abstract volume. *Geonytt* **1**, 62 only.
- Frei, R. & Kamber, B.S. 1995: Single mineral Pb-Pb dating. *Earth and Planetary Science Letters* **129**, 261–268.
- Frei, R., Villa, I.M., Nagler, T.F., Kramers, J.D., Przybyłowicz, W.J., Prozesky, V.M., Hofmann, B.A. & Kamber, B.S. 1997: Single mineral dating by the Pb-Pb step-leaching method: assessing the mechanisms. *Geochimica et Cosmochimica Acta* **61**, 393–414.
- Henriksen, N. 1998: North-East Greenland 1997–1998: a new 1:500 000 mapping project in the Caledonian fold belt (72°–75°N). *Geology of Greenland Survey Bulletin* **180**, 119–127.
- Henriksen, N. 1999: Conclusion of the 1:500 000 mapping project in the Caledonian fold belt in North-East Greenland. *Geology of Greenland Survey Bulletin* **183**, 10–22.
- Higgins, A.K. 1988: The Krummedal supracrustal sequence in East Greenland. In: Winchester, J.A. (ed.): Later Proterozoic stratigraphy of the northern Atlantic regions, 86–96. Glasgow and London: Blackie and Son Ltd.
- Higgins, A.K. & Leslie, A.G. 2004: The Eleonore Sø and Målebjerger foreland windows, East Greenland Caledonides, and the demise of the 'stockwerke' concept. In: Higgins, A.K. & Kalsbeek, F. (eds): East Greenland Caledonides: stratigraphy, structure and geochronology. *Geological Survey of Denmark and Greenland Bulletin* **6**, 77–93 (this volume).
- Kalsbeek, F., Nutman, A.P. & Taylor, P.N. 1993: Paleoproterozoic basement province in the Caledonian fold belt of North-East Greenland. *Precambrian Research* **63**, 163–178.
- Kalsbeek, F., Thrane, K., Nutman, A.P. & Jepsen, H.F. 2000: Late Mesoproterozoic to early Neoproterozoic history of the East Greenland Caledonides fold belt: evidence for Grenvillian orogenesis? *Journal of the Geological Society (London)* **157**, 1215–1225.
- Kalsbeek, F., Jepsen, H.F. & Nutman, A.P. 2001: From source migmatites to plutons: tracking the origin of ca. 435 Ma S-type granites in the East Greenland Caledonide orogen. *Lithos* **57**, 1–21.
- Ludwig, K.R. 1988: A computer program to convert raw U-Th-Pb isotope ratios to blank-corrected isotope ratios and concentrations with associated error-correlations. United States Geological Survey, Open File Report **OF-82-820**.
- Ludwig, K.R. 1999: Isoplot/Ex version 2.00: a geochronological toolkit for Microsoft Excel. Berkeley Geochronology Center, Special Publication **2**.
- Mørk, M.B., Kullerud, K. & Stabel, A. 1988: Sm-Nd dating of Svecofegites, Norrbotten, Sweden – evidence for early Caledonian (505 Ma) subduction. *Contributions to Mineralogy and Petrology* **99**, 344–351.
- Rex, D.C. & Higgins, A.K. 1985: Potassium–argon mineral ages from the East Greenland Caledonides between 72° and 74°N. In: Gee, D.G. & Sturt, B.A. (eds): The Caledonide Orogen: Scandinavia and related areas, 1115–1124. Chichester: John Wiley & Sons.
- Smith, M.P. 1991: Early Ordovician conodonts of East and North Greenland. *Meddelelser om Grønland Geoscience* **26**, 81 pp.
- Thrane, K. 2002: Relationships between Archaean and Palaeoproterozoic basement complexes in the southern part of the East Greenland Caledonides: an ion microprobe study. *Precambrian Research* **113**, 19–42.
- Thrane, K. 2004: Palaeoproterozoic age of the basement gneiss complex in the Charcot Land tectonic window, East Greenland Caledonides. In: Higgins, A.K. & Kalsbeek, F. (eds): East Greenland Caledonides: stratigraphy, structure and geochronology. *Geological Survey of Denmark and Greenland Bulletin* **6**, 57–66 (this volume).
- Thrane, K., Kalsbeek, F. & Watt, G.R. 1999a: Evidence for a Grenville event in the East Greenland Caledonian fold belt. In: Frederiksen, K.S. & Thrane, K. (eds): Second symposium on East Greenland geology, mainly Caledonian. Abstract volume. Danmarks og Grønlands Geologiske Undersøgelse Rapport **1999/21**, 37 only.
- Thrane, K., Watt, G.R., Kinny, P.D., Jones, K.A. & Escher, J.C. 1999b: Early Neoproterozoic breakup of Rodinia: SIMS U-Pb ages from the East Greenland Caledonides. *EUG 10, Terra Abstracts* **4**, 119 only.
- Todt, W., Cliff, R.A., Hanser, A. & Hofmann, A.W. 1993: Recalibration of NBS lead standards using a ²⁰²Pb + ²⁰⁵Pb double spike. *Terra Abstracts* **5** (Supplement 1), 396 only.
- Watt, G.R., Kinny, P.D. & Friderichsen, J.D. 2000: U-Pb geochronology of Neoproterozoic and Caledonian tectonothermal events in the East Greenland Caledonides. *Journal of the Geological Society (London)* **157**, 1031–1048.