FINGERSEG, Fingerprinting Caledonian tectono-thermal events in South-East Greenland using low temperature U-Th/Pb and Ar/Ar Geochronology

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1. Introduction

The project FINGERSEG is a geochronology-based study funded by Geocenterbevilling 6- 2017. Aim of the project is to find evidence of Palaeozoic (i.e. Caledonian) tectono-thermal overprint on rock-samples collected in South-East Greenland. The collaboration between GEUS and the Geological Museum gave the possibility to analyse rock samples for U-Th/Pb and Ar/Ar age dating in order to investigate low temperature thermal events in South-East Greenland.

The reason to investigate for Caledonian-age events in South-East Greenland was due to a new analysis (Thomsen and Guarnieri pers. comm.) of detrital rutile obtained from a dropstone of red beds collected in the Ammassalik area (Lat. 66ºN) in South-East Greenland (Dawes, 1986). The rock analysed for detrital zircon showed Archaean to Palaeoproterozoic ages but the U-Th/Pb age of detrital rutile resulted in robust Silurian ages (ca. 430 Ma) in addition to a single Palaeoproterozoic rutile age at 1800 Ma. This surprising result came from an erratic rock, probably transported from the north-west, suggesting that such a type of rocks should be present nearby under the ice cap.

2. Background

Ordovician-Silurian rocks were discovered to the north in the Kangerlussuaq area (Lat. 68ºN) by Brooks et al. (1981) belonging to the Batbjerg intrusion that is surrounded by Lower Palaeozoic marbles and metasandstones (Fig. 1).

Evidence for Caledonian-age cooling events are shown by apatite fission tracks analysed on samples collected in the Skjoldungen and Ammassalik areas (Fig. 1) during the SEGMENT Project in South East Greenland (Guarnieri 2014; Guarnieri et al. 2014; Green et al. 2014; Kolb et al. 2016). The data show clear Ordovician-Silurian cooling ages that can be interpreted as post-Caledonian exhumation.

Moreover, greenschist facies metasandstones were encountered during the ODP Leg 152 Hole 917A located offshore Skjoldungen (Lat. 64ºN) in South East Greenland (Fig. 1). The drill went through ca. 779 m of Tertiary basalts and then 10 cm of quartz-sandstones. After the quartz-sandstone the drill recovered 53.7 m of steeply dipping and metamorphosed (greenschist facies) sandstones and siltstones (Vallier et al. 1998). The authors interpreted the metasandstones as Upper Cretaceous in age and correlate it with the Kangerlussuaq Basin to the north.

The presence of un-metamorphosed quartz-sandstones between the metasandstones and the Tertiary basalts above, suggests that the greenschist facies event is not related to Tertiary activity but should be older (Caledonian?). In 2015 four samples from Leg 152/917A were requested to the ODP repository and analysed at GEUS for detrital zircon and rutile to estimate the maximum age of the rocks. Unfortunately no heavy mineral were found, thus the age is still unknown, however anticipated to be of Lower Palaeozoic age.

Fig. 1. Samples distribution from Skjoldungen-Ammassalik (SEGMENT project) and Batbjerg (red) and from ODP Leg 152 (green).

3. Analytical work

The following rock samples are available and considered to be analysed in FINGERSEG project:

• 4-6 Core samples from ODP Leg 152/917: Ar/Ar age dating of biotite/muscovite by Michael Storey at the Geological Museum's Argon Geochronology laboratory.

• 40 Basement rock samples from South-East Greenland: U-Th/Pb age dating of titanite/monazite/rutile/apatite (LA-ICPMS facility at GEUS);

• 10 Basement rock and metasediment samples from the Batbjerg area in Kangerlussuaq, East Greenland (collected by K. Brooks, available and stored at the Geological Museum): U-Th/Pb age dating of titanite/monazite/rutile/apatite (LA-ICPMS facility at GEUS).

• 10 Basement rock samples from Mont Forel-Glacier de France area in South-East Greenland (collected by the British Army in 2016 and stored at GEUS; see Fig. 1): U-Th/Pb age dating of titanite/monazite/rutile/apatite (LA-ICPMS facility at GEUS).

4. Methods

4.1 40Ar/39Ar dating

For 40Ar/39Ar age determination whole-rock mini-cores and biotite crystal separates were loaded into pits in aluminum irradiation disks. Each unknown was surrounded the neutron flux monitor Fish Canyon sanidine (FCs) with an assigned age of 28.201 (Kuiper et al., 2008). The irradiation disks were then wrapped in aluminum foil and encapsulated in a heat-sealed quartz glass tube. The samples were irradiated in the cadmium-lined in-core (CLICIT) facility at the Oregon State University TRIGA reactor for 9 hours. Argon isotopic analyses of the gas released by laser step-heating of the whole-rock mini-cores and biotite separates (Supplementary data) were made on a fully automated, high-resolution Nu Instruments Noblesse multi-collector noble-gas mass spectrometer (Nu Instruments) at the Natural History Museum of Denmark, using previously documented instrumentation and procedures (Storey et al., 2007, Rivera et al., 2011). The data are reported relative to the astronomically calibrated 40Ar/39Ar age of 28.201 Ma for the Fish Canyon sanidine monitor mineral (Kuiper et al., 2008).

4.2 U-Th/Pb dating

U/Pb geochronology was carried out by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) at GEUS. The U/Pb dating were performed in-situ on the same polished rock chip of sample 103R as for the Ar/Ar dating. Based on the AQM screening analysis, apatite mineral grains of preferably > 20 um in size were selected for the LA-ICPMS dating. The location of each apatite mineral grain as identified by the AQM and BSE images were transferred to the LA-ICPMS instrument by using a linear transformation matrix from the two coordinated frames, using six reference points, and thereby matching the position between the three (AQM + BSE images and LA-ICPMS instrument). A NWR 213 frequency-quintupled solid state Nd:YAG laser system from Elemental Scientific Lasers (ESL) mounted with a standard TV2 ablation cell was coupled to an ELEMENT 2 double-focusing single-collector magnetic sector-field ICPMS from Thermo-Fisher Scientific. The mass spectrometer is equipped with a new jet interface pump system, a detector amplifier, and employed Ni jettype sampler and standard H-type skimmer cones. Operating conditions and data acquisition parameters are listed in Appendix 1. Prior to loading, the chip section and standards were carefully cleaned with ethanol to remove possible surface contamination. To ensure stable laser output energy, the laser was heated prior to operation, providing a stable laser power and flat ablation craters. The mass spectrometer was run for at least one hour before analysis to stabilize the background signal. The ablated material was swept by the helium carrier gas and mixed with argon gas ca. 0.5 m before entering the mass spectrometer. The ICP-MS was optimized for dry plasma conditions through continuous linear ablation of the GJ-1 zircon standard. The signal-to-noise ratios for the heavy mass range of interest (i.e. 202Hg to 238U), emphasizing on 238U and 206Pb, were maximized, while simultaneously opting for the lowest element-oxide production level by minimizing the UO2/U ratio. To minimize instrumental drift, a standard-sample-standard analysis protocol was followed, bracketing 7- 8 samples by 4 standard measurements for each bracket. Standard analyses and results were validated by analyses of the natural apatite standards McClure (Schoene and Bowring 2006) and Durango (Chew et al. 2011), and the Plešovice (Slama et al. 2008) and GJ-1 (Jackson et al. 2004) zircon standards. All standards demonstrated an averaged age accuracy within 3% deviation (2σ) from reference values, and internal uncertainties of < 2-3% (2σ). Data processing was performed off-line using the software Iolite v. 2.5 (Paton et al. 2010, 2011) with the VizualAge data reduction scheme (Petrus & Kamber 2012). Data were corrected for background, session drift and down-hole isotopic fractionation by using GJ-1 as the primary reference material. Data was acquired from single spot analysis using a laser spot size of for the analyses of 25 µm. A laser fluence of ca. 3 J/cm2 and a pulse rate of 5 Hz was applied. Acquisition sequence included 30 s background measurement, then laser ablation on for 40 s, and finally washout for 40 s. Factory-supplied software was used for the acquisition of the transient data, obtained through automated running mode of pre-set analytical locations.

Apatite usually require common Pb correction. However, for apatites with a high proportion of common Pb, assumption that the common Pb ratio is invariant will mean that any error in the isotope ratios assigned to common Pb will result in a consistent bias, rather than a random, of the calculated 206Pb/238U and 207Pb/206Pb radiogenic ratios (Ludwig, 1998). Thus, using a ''SemiTotal–Pb/U isochron'' approach (Tera and Wasserburg, 1972), the background- and session-drift corrected ratios can be plotted on the Tera-Wasserburg concordia diagram without correction for common Pb. If (and only if) the true 206Pb/238U and 207Pb/206Pb radiogenic isotope ratios represent comparable dates, the non-common Pb corrected data will be dispersed along a line whose lower intercept with the concordia curve defines the age of the episode responsible for this line (Ludwig, 1998). This is the case for the apatite grains herein, and thus the lower intercept age reported here for the apatites is not corrected for common Pb, assuming that this intercept age denotes the U/Pb isotopic age of a specific geological event recorded by the apatite mineral grains. Diagrams and statistical information were produced through the software IsoplotR (Vermeesch 2018).

5. Results

5.1 U-Th/Pb and Ar/Ar age dating of rock samples from ODP Leg 152

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First evidence for Neoproterozoic rocks offshore South-East Green-

land

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ABSTRACT

Meta-sedimentary rocks recovered beneath Paleogene basalts near the base of the ODP Leg 152-917A offshore South-East Greenland were thought to be of Late Cretaceous age. This interpretation, however, has several inconsistencies as it requires a tectono-metamorphic event during the Cretaceous not recognized in the North Atlantic region, and the presence of a wide Mesozoic sedimentary basin that extended from SE-Greenland to the Rockall Plateau, for which there is currently no evidence. Here, we report a Neoproterozoic U/Pb apatite age of 905±21 Ma and a slightly younger ⁴⁰Ar/³⁹Ar isochron whole-rock age of 820±40 Ma for an altered tuff layer that occurs in the upper part of the meta-volcaniclastic sequence recovered from Hole 917A. The ⁴⁰Ar/³⁹Ar step-heating ages on biotite and whole-rock minicores from deeper in the Hole 917A yielded Paleoproterozic dates that cluster around 1950 to 1850 Ma, pointing toward a Paleoproterozoic source. The U/Pb apatite date is interpreted as the eruption age of the tuff layer, whereas the slightly younger whole-rock $40Ar^{39}Ar$ age is consistent with low-temperature greenschist alteration of volcanic glass and secondary mineral growth during sedimentary burial in an extensional regime. The ca. 905 Ma age for the tuff provides the first evidence for Neoproterozoic rocks offshore South-East Greenland and suggests a correlation between this sequence and the Torridon Group in the Hebridean Foreland of the Scottish Caledonides. The calc-alkaline nature of the volcaniclastic rocks and the

age of the tuff layer point toward a source area with arc-magmatism related to the Renlandian event of the Valhalla Orogeny.

1. Introduction

The South-East Greenland offshore area is dominated by the Paleogene volcanic province (Fig. 1), which is associated with the opening of the North Atlantic (Larsen & Saunders 1998). This province was the target for the ODP Leg 152 drilling and sampling of volcanic rocks for geochronology and geochemistry to improve our knowledge of the East Greenland Large Igneous Province (Larsen & Saunders 1998; Tegner et al. 1998; Storey et al. 2007). At site 917 of the ODP Leg 152 ~53.7 m of steeply dipping metasedimentary rocks was drilled beneath >800 m of Paleocene basalts (Vallier et al., 1998). Ten centimeters of quartz sandstone, probably of fluvial origin, was recovered between the basalt and metamorphosed sedimentary rocks (Vallier et al., 1998).

The onshore area along SE Greenland is characterized by the Archean North Atlantic Craton orthogneisses and supracrustal rocks together with Paleoproterozoic Nagssugtoqidian Orogen-related magmatic rocks and gneisses. In the Ammassalik area an early Mesoproterozoic batholith are documented (Kolb, 2014). North of Ammassalik, the nearest known Mesozoic sediments are located at Kap Gustav Holm and further north, where Cretaceous–Paleocene sedimentary rocks belong to the Kangerlussuaq Basin (Larsen et al., 1999). The basin consists of a ca. 1 km thick Cretaceous to Paleocene sedimentary succession (Larsen et al. 1999) onlapping Archean basement gneisses. The sedimentary rocks belong to the Kangerlussuaq Group and the volcano-sedimentary package to the Blosseville group (Soper et al. 1976; Nielsen et al. 1981). The basin and the inland area were covered by a thick pile of plateau basalts in the Early Eocene and overprinted by Paleogene magmatism related to the break-up of the NE-Atlantic Ocean.

The fluvial quartz-sandstone drilled in Core 917A, which unconformably overlies the metasedimentary package, is texturally immature and probably sourced from a deeply weathered basement terrane. Contacts between mineral grains are sharp and un-sutured, indicating

that minimal recrystallization occurred. This is also supported by unaltered micas and plagioclase feldspar grains with a high calcium content, of which some show well-developed twinning (Vallier et al. 1998). On the contrary, the metamorphic grade of rocks underneath the angular unconformity reached the lower end of the greenschist facies window, and which is considerably higher than the metamorphism of the basalts (Demant et al., 1998), This suggests an earlier and stronger metamorphic overprint that, in absence of a cleavage indicating a major folding event, was interpreted by Vallier et al. (1998) as tilting caused by rifting processes. They showed that the metasedimentary rocks were significantly deformed and overprinted compared to the quartz-sandstone, and concluded that they were metamorphosed, tilted, uplifted and eroded during the Late Cretaceous-Paleocene before the quartz sandstone was deposited and the basalt flows emplaced. The age of the metasedimentary package was not resolved, and these rocks were assumed to be analogues to the Cretaceous-Paleocene sediments of the Kangerlussuaq Basin (Fig. 1). In that basin the Lower Paleocene shoreface sandstone foresets of the Klitterhorn member of the Sediment Bjerge Formation are unconformably overlaid by fluvial sandstones of the Schjelderup member of the Vandfaldsdalen Formation (Larsen and Saunders, 1999; Larsen et al., 1999; Larsen et al., 2005; Larsen et al., 2016). In a recent paper Gerlings et al. (2017) correlated the metasedimentary sequence from LEG 152 to Aptian sediments dragged offshore Ammassalik representing the Mesozoic Ammassalik Basin to which they estimated a thickness of ca. 2 seconds (two-way time). The same sequence is suggested to be part of a wider area linked with the Hatton Bank-Rockall Plateau by Hitchen (2004).

In this paper we question the simple correlation between the metamorphic sequence and the Cretaceous succession indicating that the meta-volcaniclastic rocks belong to a Neoproterozoic sedimentary cycle possibly extending the Torridon basin of the Hebridean Foreland offshore South-East Greenland.

2. Method

2.a. Core sampling

The ODP Leg 152 site 917 is located on the South-East Greenland shelf approximately 50 Km offshore. The drill penetrated 821 m of Paleogene plateau basalts before reaching a thin layer (821.1 to 821.2 meters below sea bottom) of coarse-grained, quartz-rich sandstone of possible fluviatile origin, and of unknown age. Beneath this sandstone, steeply inclined, lowgrade metamorphic rocks were encountered at 821.2 to 874.9 (mbsb). Core 103R corresponds to the topmost part of the metasedimentary succession reached at a depth of 826.9 down to 831.5 (mbsb), while core 110R represents the bottommost part between 865.3-874.9 (mbsb). Four samples were selected for Ar/Ar dating from core 917A and provided by the ODP repository in Bremen. These are 103R: 80-115 cm, 104R: 62-98 cm, 108R: 44-91 cm and 110R: 22-80 cm (Fig. 2). For those samples were also prepared thin sections for petrographic analysis because previous work by Vallier et al. (1998) indicated the presence of volcanic glass and plagioclase minerals replaced by secondary minerals. Finally, sample 103R was selected for automate quantitative mineral mapping (SEM) to spot minerals for U/Pd dating that were too small for hand picking.

2.b. Automated quantitative mineral mapping (AQM)

Automated quantitative mineral mapping (AQM) of sample 103R was performed at GEUS on a ZEISS Sigma 300VP Field Emission Scanning Electron Microscope (SEM) using the ZEISS Mineralogic software platform. The analysis was carried out under low vacuum (VP) conditions with an acceleration voltage of 15 kV, a 120 μ m² aperture, a beam current of ca. 80 μ A, and with 0.15 s dwell time. For further details about the AQM and the setup in ZEISS Mineralogic see Keulen et al (2020). An area of approximately 9x8 mm covering the location of the Ar/Ar dating spot site was selected for the analysis to characterize the bulk mineralogy of the sample and to screen for U/Pb dateable mineral phases. To increase resolution and to detect smaller grains, a step size between EDS analysis points of 5 µm was chosen. The AQM mineralogic results is presented in area% and not wt% as this would require more precise measurements of the phase chemistry.

2.c. U/Pb dating

U/Pb geochronology on apatite was carried out by laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) at GEUS. The U/Pb dating were performed in-situ on the same polished rock chip of sample 103R as for the Ar/Ar dating. Based on the AQM screening analysis, apatite mineral grains of preferably > 20 um in size were selected for the LA-ICPMS dating. The location of each apatite mineral grain as identified by the AQM and BSE images were transferred to the LA-ICPMS instrument by using a linear transformation matrix from the two coordinated frames, using six reference points, and thereby matching the position between the three (AQM + BSE images and LA-ICPMS instrument). A NWR 213 frequency-quintupled solid state Nd:YAG laser system from Elemental Scientific Lasers (ESL) mounted with a standard TV2 ablation cell was coupled to an ELEMENT 2 double-focusing single-collector magnetic sector-field ICPMS from Thermo-Fisher Scientific. The mass spectrometer is equipped with a new jet interface pump system, a detector amplifier, and employed Ni jet-type sampler and standard H-type skimmer cones. Operating conditions and data acquisition parameters are listed in Appendix 1. Prior to loading, the chip section and standards were carefully cleaned with ethanol to remove possible surface contamination. To ensure stable laser output energy, the laser was heated prior to operation, providing a stable laser power and flat ablation craters. The mass spectrometer was run for at least one hour before analysis to stabilize the background signal. The ablated material was swept by the helium carrier gas and mixed with argon gas ca. 0.5 m before entering the mass spectrometer. The ICP-MS was optimized for dry plasma conditions through continuous linear ablation of the GJ-1 zircon standard. The signal-to-noise ratios for the heavy mass range of interest (i.e. 202Hg to 238U), emphasizing on 238U and 206Pb, were maximized, while simultaneously opting for the lowest element-oxide production level by minimizing the UO2/U ratio. To minimize instrumental drift, a standard-sample-standard analysis protocol was followed, bracketing 7-8 samples by 4 standard measurements for each bracket. Standard analyses and results were validated by analyses of the natural apatite standards McClure (Schoene and Bowring 2006) and Durango (Chew et al. 2011), and the Plešovice (Slama et al. 2008) and GJ-1 (Jackson et al. 2004) zircon standards. All standards demonstrated an averaged

age accuracy within 3% deviation (2σ) from reference values, and internal uncertainties of < 2-3% (2σ). Data processing was performed off-line using the software Iolite v. 2.5 (Paton et al. 2010, 2011) with the VizualAge data reduction scheme (Petrus & Kamber 2012). Data were corrected for background, session drift and down-hole isotopic fractionation by using GJ-1 as the primary reference material. Data was acquired from single spot analysis using a laser spot size of for the analyses of 25 μ m. A laser fluence of ca. 3 J/cm² and a pulse rate of 5 Hz was applied. Acquisition sequence included 30 s background measurement, then laser ablation on for 40 s, and finally washout for 40 s. Factory-supplied software was used for the acquisition of the transient data, obtained through automated running mode of pre-set analytical locations.

Apatite usually require common Pb correction. However, for apatites with a high proportion of common Pb, assumption that the common Pb ratio is invariant will mean that any error in the isotope ratios assigned to common Pb will result in a consistent bias, rather than a random, of the calculated 206Pb/238U and 207Pb/206Pb radiogenic ratios (Ludwig, 1998). Thus, using a ''SemiTotal–Pb/U isochron'' approach (Tera and Wasserburg, 1972), the background- and session-drift corrected ratios can be plotted on the Tera-Wasserburg concordia diagram without correction for common Pb. If (and only if) the true 206Pb/238U and 207Pb/206Pb radiogenic isotope ratios represent comparable dates, the non-common Pb corrected data will be dispersed along a line whose lower intercept with the concordia curve defines the age of the episode responsible for this line (Ludwig, 1998). This is the case for the apatite grains herein, and thus the lower intercept age reported here for the apatites is not corrected for common Pb, assuming that this intercept age denotes the U/Pb isotopic age of a specific geological event recorded by the apatite mineral grains. Diagrams and statistical information were produced through the software IsoplotR (Vermeesch 2018).

2.d. 40Ar/39Ar dating

For 40Ar/39Ar age determination whole-rock mini-cores and biotite crystal separates were loaded into pits in aluminum irradiation disks. Each unknown was surrounded the neutron flux monitor Fish Canyon sanidine (FCs) with an assigned age of 28.201 (Kuiper et al., 2008).

The irradiation disks were then wrapped in aluminum foil and encapsulated in a heat-sealed quartz glass tube. The samples were irradiated in the cadmium-lined in-core (CLICIT) facility at the Oregon State University TRIGA reactor for 9 hours. Argon isotopic analyses of the gas released by laser step-heating of the whole-rock mini-cores and biotite separates (Supplementary data) were made on a fully automated, high-resolution Nu Instruments Noblesse multi-collector noble-gas mass spectrometer (Nu Instruments) at the Natural History Museum of Denmark, using previously documented instrumentation and procedures (Storey et al., 2007, Rivera et al., 2011). The data are reported relative to the astronomically calibrated 40 Ar/ 39 Ar age of 28.201 Ma for the Fish Canyon sanidine monitor mineral (Kuiper et al., 2008)).

3. Results

3.a. Petrography of the core samples

Representative optical microscopy images of thin section for the samples 103R, 104R, 108R and 110R are shown on Figure 3. As described by Vallier et al (1998), the mineral assemblages of all 4 samples are characteristic of the greenschist metamorphic facies, and the description given by Vallier et al (1998) is generally in accordance with our observations herein. The major mineral phases identified are chlorite that is omnipresent, white mica occurring exclusively as sericite, altered plagioclase feldspar (to chlorite, quartz, secondary feldspar, epidote and sericite), actinolite (from altered amphibole or pyroxene?), quartz, and epidote, with subordinate biotite, leucoxene, and Ti-oxides (most probably brookite or anatase). In addition, colorless, subhedral apatite (< 1 modal%) was identified in sample 103R, which is also the rock sample that contains 0.51 wt% P_2O_5 . (Vallier et al, 1998). As described by Vallier et al (1998) recrystallization and metamorphic alteration has destroyed the original mineralogy and most original features. However, pseudomorphs after plagioclase feldspar laths in what resembles ophitic texture is observed in the samples 103R, 108R and 110R (Fig. 3A, C and D). In sample 103R and 108R, the laths are as large as 1 mm in length, and whereas in 108R the habitus of the laths are well defined (Fig. 3C), they appear more

subhedral in sample 103R, in particular when occurring adjacent to the micro-crystalline "pseudomorph" domains that most probably has replaced glass matrix (Fig. 3A). This indicates a volcanic origin for especially the sample 103R (laths and glass) and

Thin-layered bedding dominated by quartz and subordinate feldspar and chlorite was observed in sample 104R and 110R (Fig. 3B, D). Small veins composed of primarily quartz with subordinate albite, chlorite and anhedral epidote was recognized in sample 103R only. Most epidote, though, appears in irregular, separate enclaves together with leucoxene and quartz. Titanite was not identified in any of the samples. Brown, pleochroic biotite occurs as a minor component (varies from <<1 % to a few modal%) in all four samples. In samples 104R and 108R occurrences of small, spherical structures of up to 200 µm in size and composed of a core of chlorite+quartz and with a rim of mainly feldspar with bluish 2. order interferences colors are observed. These structures were in Vallier et al (1998) interpretated as the original presence of radiolarians, thus being sedimentary structures. However, the resemblance to gas vesicles and thus micro-amygdules cannot be rules out.

3.b. Automated quantitative mineral mapping

The sample 103R is dominated by two main mineral phases, viz. chlorite/clinochlore and a phase characterized as "weathered amphibole", which corresponds to actinolite + various alteration overprints. Together, these phases cover ca. 88% of the sample area of sample 103R (Fig. 4). Quartz and Ti-oxides (most probably brookite, anatase, or leucoxene) cover ca. 2 area%, and all other phases <0.5 area% each. Apatite makes up circa 0.4 area% of the sample, and in general vary in mineral grain size according to the location of the apatites in the irregularly developed bedding that can be identified from the AQM image.

3.c. Apatite U/Pb dating

Uncertainty ellipses of the 25 individual spot analyses displayed in the Tera-Wasserburg Concordia (Fig. 5) are in 2σ level (Table 1). As the aim was to estimate a date for the deposition of the meta-volcaniclastic rocks, analytical procedures were optimized for single analysis of these small apatite grains. The unanchored lower intercept date of 905 +/- 21 Ma is

reasonably well constrained with a MSWD = 1.6 due to a large spread in the radiogenic to common-Pb ratios, thus represent a robust age.

3.d. 40Ar/39Ar dating

Laser step-heating 40 Ar/ 39 Ar experiments were carried out on chloritized and rare, \sim 1-2 mm detrital biotite crystals found in core intervals 104R: 65-100 cm, 108R: 44-91 cm and 110R: 22-80 cm. Biotite crystals large enough for ⁴⁰Ar/³⁹Ar dating were not found in the uppermost of the 4 samples examined in this study (103R: 80-115 cm). In addition to the biotite analyses, 40 Ar/ 39 Ar experiments were also carried on \sim 2 mm diameter whole-rock mini-cores of all four samples obtained using a Dremmel rotary tool. Argon isotopic abundances, including the apparent ages of the individual steps and J-values, are given in Table 2 while step-heating plots are presented in Appendix 1.

Biotite

Depending on the gas yield, the laser step-heating $40Ar/39Ar$ experiments on single grain biotite were carried out in 2-3 steps, with the final step resulting in melting and complete outgassing of the grain. All the experiments gave Paleoproterozoic ages, with the youngest ages being typically associated with the first, low-power, laser step suggesting minor loss of radiogenic argon $(^{40}Ar^*)$ due to alteration. Of the ten single grain experiments carried out, 5 yielded 2-step concordant ages and these are shown in Figure 2. These less isotopically disturbed grains indicate biotite crystallization/resetting semi-quantitative ages of around 1950 to 1850 Ma. The relatively small yield of 40Ar and low precision for these biotite analyses is indicative that they have suffered K loss by chloritization.

Whole-rock mini-cores

Detailed 40Ar/39Ar laser step heating experiments on 4 whole-rock mini-cores were carried out in order to investigate the provenance of the bulk meta-sediment as well as the age of the possible volcaniclastic unit represented by103R: 80-115 cm.

At lower laser power settings, the whole-rock mini-cores from 104R: 65-100 cm and 110R: 22-80 cm both yielded a staircase shaped pattern consistent with low temperature loss of 40Ar. Increasing laser power gave Paleoproterozic ages but failed accepted statistical tests

for an age plateau. Nonetheless, the range of ages yielded by these higher temperature steps is similar to the single crystal biotite 40 Ar/ 39 Ar data and suggests a single provenance for the bulk sediment for these samples.

In contrast to the stair-case shaped age spectra of the mini-cores from 104R: 65-100 cm and 110R: 22-80, the laser step-heating gas release patterns for the 2 mini-cores of the topmost, possible volcaniclastic, sample (917A-103R-85-115) yielded distinctive "U" shaped age profiles with minimum (Neoproterozoic) values for intermediate laser power steps (Fig. 6A). Both are also notable for having much higher Ca/K ratios when compared to data from the other mini-cores (Appendix 1) consistent with the presence of a compositionally distinct volcaniclastic component. The second of the two mini-cores analyzed from this sample produced a robust age plateau of 840 \pm 50 Ma (MSWD = 0.64, p = 0.74) comprising 8 individual heating steps and 60% of the total 39 Ar released. These 8 steps yield an isochron age of 820 \pm 40 Ma with a ⁴⁰Ar/³⁶Ar intercept of 410 \pm 150 (Fig. 6B) which is within uncertainty of the atmospheric value of 298.56 (Lee et al., 2006). The isochron provides a minimum (Neoproterozoic) age for this potential meta-tuff layer in the upper part of Hole 917A.

4. Discussion and conclusion

The whole-rock mini-cores and chloritized biotite single crystal ${}^{40}Ar/{}^{39}Ar$ ages give semiquantitative Paleoproterozoic ages from the lower samples and a robust Neoproterozoic isochron age from the top ones (Fig. 2). Here we explore whether the much younger age of 820 ± 40 Ma given by the mini-core from 103R-85-115 is the result of a partial reset due to the contact metamorphism of an overlying olivine-phyric basalt flow that were emplaced at ca. 1180 °C in subaerial conditions. In the Kangerlussuaq Basin, which is suggested to be the analogue for Core 917A (Larsen et al., 1994; Vallier et al., 1998), the only contact metamorphism documented is restricted to narrow zones close to the base of the lava flows, and the diagenetic processes in the entire sedimentary basin were enhanced by deep burial due to the thick pile of basalts of the Blosseville Group (Larsen et al. 2016). Other evidences that exclude the overprint of the Paleogene magmatism are: (1) the absence of thermal effects in the quartz-rich sandstone including unaltered micas that was recovered between the basalts and the meta-volcaniclastic rocks; (2) the chlorite geothermometer (Vallier et al., 1998) yielding average temperatures of 296°C for the top interval 103R, 300°C for interval 104R and 356°C for interval 108R at the bottom, thus showing no increase of temperature toward the contact with basaltic rocks (Fig. 2); (3) the distribution and chemistry of zeolites and clay minerals in the basalts from Core 917A (Demant et al. 1998) established that the mineralogical assemblages indicate a temperature of the metamorphism below 170°C and the zeolites formed during hydrothermal processes as late post-emplacement event affecting the whole volcanic pile (Fig. 2); (4) apatite fission tracks from interlava sediments of Leg 152 from Sites 914 and 915 (Clift et al. 1996) located on the continental shelf, and Site 918 that lies on oceanic crust of the Irminger Basin (Fig. 1) established that the central ages are significantly older (ca. 231 Ma to 150 Ma) than sample depositional ages (42 to 22 Ma). This implies that the samples did not experience significant post-depositional annealing (i.e. $T > 110^{\circ}$ C), and thus the temperature in the clastic rocks intercalated with the Paleogene basalts were never above 60°C, in agreement with the zeolites zonation.

For the abovementioned reasons we believe that the thermal heating irradiating from the Paleogene magmatism is quite unlikely and thus can be excluded. The greenschist facies metamorphism should then be older and not Cretaceous as it was assumed before. The same conclusion is valid for the supposed Cretaceous age of the meta-volcaniclastic rocks off-shore SE-Greenland that is now shown to be Neoproterozoic bracketed between 905 Ma and 820 Ma. The slightly younger whole-rock ⁴⁰Ar/³⁹Ar tuff age is consistent with low-temperature greenschist alteration of volcanic glass and secondary mineral growth (e.g. Verati and Jordan, 2014) presumably as a result of sedimentary burial in an extensional regime. The burial temperature was not sufficiently high, however, to significantly reset detrital and partly chloritized biotite from deeper in the sequence as these consistently give, all be it semiquantitatively, Paleoproterozoic ages of around 1.9 to 1.8 Ga. All samples show that they were mainly composed of plagioclase feldspar grains, now replaced by albite and/or chlorite while other beds consist of irregular rock fragments now replaced by albite, chlorite, and

quartz. These beds may have been lithic tuffs, consisting originally of plagioclase, volcanic glass, and volcanic rock fragments and ovoid quartz/albite masses in some thin sections, flattened parallel to bedding, may be replaced by vesicular volcanic glass, as also indicated by Vallier et al. (1998).

The absence of tectonic fabric together with the low-grade metamorphism could indicate that the thermal alteration is probably due to sedimentary burial during extensional tectonics as also suggested by Vallier et al. (1998) at 820±40 Ma, establishing the minimum age for the volcaniclastic succession.

The 905±21 Ma U/Pb age obtained from apatites in the tuff layer of core 917A allows possible correlations with Neoproterozoic successions across the North Atlantic and even though the data are limited only to this sample, this could potentially be equivalent to the Torridon Group succession in the Hebridean Foreland of the Scottish Caledonides (Fig. 7). Turnbull et al. (1996) obtained Rb-Sr data from analyses of whole-rock shale samples for the Diabaig Formation (994 \pm 48 Ma) and for the Applecross Formation (977 \pm 32 Ma) and interpreted as the time of albitization and clay conversion. These dates, which agree well with palaeomagnetic estimates, are interpreted as the time of early diagenesis which is probably within error of the time of deposition of the Torridon Group (Turnbull et al., 1996). Volcanic rocks of Torridonian age are rare in Scotland and volcanic deposits known from eastern Laurentia have a slight older age between 1300-1100 Ma (Batchelor 2011). The discovery of a crystal tuff in the Stoer Group (Batchelor and Prave 2010) established the earliest example so far of tholeiitic volcanic activity within the Torridonian of Scotland around 1187±35 Ma (Kinnaird et al., 2007). The calc-alkaline nature of the meta-volcaniclastic rocks in core 917A (Vallier et al., 1998) and the 905±21 Ma age of the tuff layer could indicate a correlative connection between the sedimentary basin offshore South-East Greenland and the 915±18 Ma magmatism associated with the Renlandian event (Leslie and Nutman 2003) of the Valhalla Orogeny (Cawood et al., 2010) or the volcanism/metamorphism in the West Highland domain of the Scottish Caledonides (Fig. 7). In any case the new data presented in this paper show for the

first time the evidence for a Neoproterozoic sedimentary basin offshore South-East Greenland extending the foreland basins of the Scottish Caledonides to the conjugate margin also giving new insights for the interpretation of sedimentary basins below Tertiary basalts offshore Ammassalik and Rockall Plateau.

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Declaration of Interest

The authors have no conflict of interest.

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Figure captions

Figure 1. South-East Greenland and Rockall conjugate margins (with shaded relief bathymetry/topography as background) and distribution of the North Atlantic Igneous Province (modified after Hopper et al. 2014). The location of the ODP Leg-152 sites is also provided. **Figure 2**. Condensed log summary for Site 917, bottom part of the Hole 917A (modified after Larsen et al., 1994). Zeolite zonation typical of very low-grade corresponds to temperatures less than 170°C (Demant et al. 1998). The temperature of equilibration of chlorite in the metasedimentary rocks of Hole 917A (after Vallier et al. 1998) increases downhole. 40Ar/39Ar age of the basalts (*) after Storey et al. 2007. Biotite ⁴⁰Ar/³⁹Ar concordant ages of the metavolcaniclastic rocks and U/Pb apatite age this study.

Figure 3. Optical microscopy images of the thin sections investigated in this study. (A) PPL of sample 103R showing pseudo-intersertal texture with subhedral pseudomorph laths after plagioclase in a microcrystalline matrix replacing most likely the original glass matrix. Further, the typical appearance of cross-cutting quartz veins and of apatite mineral grains. (B) XPL of sample 104R showing recrystallized original bedding with thin layers of mostly quartz interbedded with layers composed of predominantly chlorite, actinolite, sericite white mica, feldspar and leucoxene. (C) PPL of sample 108R with relatively large, anhedral pseudomorph laths after plagioclase feldspar in a metamorphic matrix composed of chlorite, actinolite, recrystallized feldspar, sericite white mica and leucoxene. (D) PPL of sample 110R showing the original bedding with a thin layer of mostly quartz as well as chlorite and feldspar surrounded by layers composed predominantly of chlorite, actinolite, sericite white mica, plagioclase feldspar pseudomorph laths, leucoxene, biotite and epidote.

Figure 4. Scanning Electron Microprobe mineral map. (A) Back scattered electron (BSE) map; (B) AQM mineral map with detailed inset.

Figure 5. Unanchored Tera-Wasserburg Concordia diagram for the apatite grains measured in this study. The regression line and corresponding uncertainty have been determined using model 2 of the IsoplotR as described in Vermeesch (2018).

Figure 6. 40Ar/39Ar step-heating (A) and isochron (B) plots for a mini-core from sample 103R-85-115 from ODP hole 152-917A. See text for further details.

Figure 7. Neoproterozoic paleogeographic reconstruction of Laurentia and Baltica (modified after Cawood et al., 2010; Spencer et al. 2019) showing the position of the meta-volcaniclastic rocks of site 917A compared to the Torridon Group in the Hebridean Foreland of the Scottish Caledonides that were depocenters for sediments derived from the Grenville and Valhalla orogens.

Tables

Table 1. U/Pb dating results.

Table 2. ⁴⁰Ar/³⁹Ar biotite and whole-rock mini-core laser step heating data.

Appendices

Appendix 1. Operating conditions for LA-ICPMS analysis.

Appendix 2. 40Ar/39Ar step-heating plots for biotite single crystals and mini-cores.

Fig. 2

 \langle Fig. 6 \rangle

Fig. 7

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Tab. 1.

Tab. 2

NOTES:
Samples were irradiated for 9 hours. Sanidine from the Fish Canyon Tuff was used as the neutron fluence monitor with a reference age of 28.201
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Ma (Kupe et al., 2008).

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Nucleogenic production mios:

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(${}^{68}\text{Ar}^{68}\text{Ar}^{3}\text{$

Tab. 2.

5.2 U-Th/Pb age dating of rock samples from SE Greenland

The U-Th/Pb dating of rock samples from South-East Greenland confirmed the presence of tectono-thermal events in the Archaean and Palaeoproterozoic time as known from the literature and characteristic for the North Atlantic craton and for the Nagssugtoqidian orogen. The data show also the presence of early Mesoproterozoic age events overlapping the timing of the Ammassalik batholith and, finally the presence of Caledonian ages in samples from the Batbjerg area (Fig. 1) at Lat 68ºN as summarized in Figure 2 and the following table.

Figure 2. Summary of age distribution of samples analysed in the project.

 $\frac{1}{100}$

 $\frac{1}{2.4}$ $\frac{1}{2.6}$

