

Weathering profiles and clay mineralogical developments, Bornholm, Denmark

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ABSTRACT

Saprock-saprolite associations were studied by field and laboratory methods (optical microscopy, X-ray powder diffraction, scanning electron microscopy, electron microprobe) in order to describe regolith development in the crystalline rocks of the Nygård kaolin pit (Bornholm, Denmark). The clay sequences and stages of porosity development are similar to those observed for reservoir rocks from the Utsira High (Riber, L., Dypvik, H., Sørli, R. and Ferrell, R. (2016) Clay minerals in deeply buried paleoregolith profiles, Norwegian North Sea. *Clays and Clay Minerals*, in press). The weathering of the parent granite began before the end of the Mesozoic. Two stages of syn- /pre-burial alteration, followed by diagenesis during burial, and then post-uplift weathering have been recognized. In stage I, plagioclase and some biotite (biotite-vermiculite-kaolinite) reacted to form elongate booklets of highly-ordered kaolinite or smaller, blocky pseudo-hexagonal crystals. Stage II represented more extreme weathering developed along local fracture systems. The higher potential for fluid flow in the fractures caused highly-ordered kaolinite to alter to halloysitic, poorly-ordered kaolinite. Plagioclase, biotite, and K-feldspar continued to interact with formation water and formed additional quantities of secondary clay minerals. As a consequence of inter-, intra-, and trans-granular cracks, the original rock fabric deteriorated and porosity increased. During later burial, diagenetic siderite crystals filled voids and chlorite formed at

the expense of kaolinite. After re-exposure, calcite precipitated in localized zones. Smectite formed on a broader scale wherever high ionic strength groundwaters were present. A mineralogical key to predicting where high porosity and permeability zones occur is the recognition of halloysitic, poorly-ordered kaolinite. Highly-ordered kaolinite is abundant, but it is ubiquitous. Siderite, chlorite and smectite adversely affect permeability.

1. INTRODUCTION

Recent petroleum discoveries in altered and fractured crystalline basement in the North Sea (Utsira High) has triggered new research to better understand how Mesozoic climate, Cenozoic uplift, and the evolution of fractures, influenced weathering of the crystalline regolith and porosity and permeability development in the region (Lundmark *et al.*, 2013; Riber *et al.*, 2015a, 2015b, in press).

Regolithic weathering of fresh granite/granodiorites generally produces three facies: coherent weathered rock, saprock, and saprolite (*e.g.* Nahon, 1991; Delvigne, 1998; Meunier, 2005; Velde and Meunier, 2008). The first two retain the structure and fabric of the parent rock. The proportion of secondary minerals and porosity increases from fresh-appearing rock to saprolite. Saprolite is a friable material containing altered and unaltered primary and secondary minerals. (*e.g.* Delvigne, 1998; Taylor and Eggleton, 2001; Wilson, 2004; Velde and Meunier, 2008). The secondary minerals may have formed in microenvironments along grain boundaries and fractures where the relative fluid to solid volume is low and the rate of exchange of chemical species is very slow (*e.g.* Korzhinskii, 1959; Meunier, 2005), or in enlarged fractures where the fluid is renewed more rapidly. In the latter situation, reaction products are greatly influenced by dissolution and precipitation reaction kinetics (*e.g.* Velde and Meunier, 2008) that are transport controlled. Protective surface layers (PSL) or unprotective surface layers (USL) may promote or retard the formation of secondary goethite,

gibbsite, or kaolinite depending on the quantities of available Fe and Al (Price *et al.*, 2005; Price *et al.*, 2013), producing changes on a 2 k.y. to 2 m.y. time scale (Schroeder *et al.*, 2001; Thiry, 2000; Price *et al.*, 2005).

Mineralogical, chemical, and microtextural variations in the altered regolith can be related to a variety of environments according to geomorphologic location, and history of the parent rocks (Sequeira Braga *et al.*, 1990; Gerrard, 1994). A detailed general sequence of mineral alteration may consequently be difficult to construct because of the parent rock variability and changes in the macroenvironment (Regüés *et al.*, 1995). In some areas there may also be differences due to superimposed weathering episodes (Dewandel *et al.*, 2006), removal of materials due to erosion (*e.g.* Lidmar-Bergström, 1997; Velde and Meunier, 2008), or diagenetic alteration during burial (Nesbitt and Young, 1989).

Alteration of the parent minerals often follows a standard sequence (from least to most stable): plagioclase feldspar, biotite, K-feldspar, and quartz, regardless of different weathering environments (*e.g.* Harris and Adams, 1966; Nesbitt and Young, 1989). Recent studies have revealed a variety of mineralogical alteration sequences and mechanisms based on various chemical weathering indexes (Price and Velbel, 2003; Négrel, 2006; Ceryan, 2008, 2015; Ceryan *et al.*, 2008; Sanjurjo-Sánchez and Vázquez, 2013), constraints revealed by geophysical surveys (Chandra *et al.*, 2010; Olona *et al.*, 2010; Holbrook *et al.*, 2014), dissolution rates of primary minerals (*e.g.* Velbel, 1984; Price *et al.*, 2013), and petrographic and mineralogical variations (Sequeira Braga *et al.*, 2002; Doval *et al.*, 2012; Weber *et al.*, 2012). Multiple mineralogical alteration sequences may be produced by distinct weathering events associated with burial, uplift, erosion, (O'Beirne-Ryan and Zentilli, 2003; Dewandel *et al.*, 2006), changing paleoclimatic conditions (Ahlberg *et al.*, 2003; Yang *et al.*, 2006), and the influence of fracture development (*e.g.* Eliasson, 1993). A more extensive use of multiple, closely spaced

samples, quantitative XRD, clay mineral crystallography, whole sample and individual mineral chemical analyses, and petrographic descriptions of texture and fabric at macroscopic and microscopic levels should provide the best opportunity to detect multiple stages of alteration.

Modern studies of saprolite alteration sequences are based on detecting changes in rock texture and fabric, and physical properties, in parent and reaction product mineralogy, and loss or gain of chemical constituents. Most studies are of limited applicability because they rely primarily on just one analytical method. Drill cores about 3 cm in diameter and other sampling techniques also only provide a limited sample of the large-scale and micro-scale heterogeneity produced by weathering.

The purpose of this investigation is to utilize detailed mineralogical determinations of mineral quantities and structure, single mineral measurements of chemical composition, and optical and other microscopic methods for characterization of rock texture and fabric to establish an integrated genetic sequence of Mesozoic weathering along the Fennoscandian Border Zone (Figure 1). Increased understanding of the processes, relative timing of development, and their variability will provide a more thorough understanding of regolith weathering. The results will provide a preliminary evaluation of secondary porosity evolution and timing due to mineral dissolution and precipitation.

The Nygård kaolin pit (Figure 1) provides an excellent opportunity to study and describe an alteration sequence in both vertical and horizontal directions which may serve as an analog for offshore reservoir studies and therefore provide valuable information about the weathering processes, and porosity of the Utsira High reservoir, North Sea. Based on drill core analyses, comparable Utsira High rocks are deeply weathered, well-developed granitic paleoregoliths formed under Mesozoic humid and tropical conditions (Riber *et al.*, 2015a, 2015b, in press). The basement rocks of southern Scandinavia were deeply weathered during Late Triassic to

Cretaceous times under humid to arid climates, and kaolin and smectite have been identified as the main weathering products in these areas (*e.g.* Lidmar-Bergström *et al.*, 1997; Ahlberg *et al.*, 2003; Olesen *et al.*, 2012). The Nygård kaolin pit weathering (Bornholm, Denmark) developed on comparable parent materials and within a horst blocks setting similar to that in the Utsira area, both along the Fennoscandian Border Zone (Bondam and Störr, 1988; Fredin *et al.*, 2013; Oberhardt, 2013; Riber *et al.*, 2015a) (Figure 1). The region experienced Mesozoic climate changes and Cenozoic uplift.

On Utsira High, reservoir properties were formed in deeply buried profiles by physical chemical alteration of granitic rocks. In one well, porosity and permeability were mainly created by intense dissolution of plagioclase, generally increasing upwards in the profile (Riber *et al.*, in press). Clay minerals formed from plagioclase dissolution changed upward from dominant R0 I-S and kaolinite in the altered coherent rock facies to kaolinite dominated in the saprock and saprolite facies. Increased porosity and clay formation were reflected in the reduced bulk density of the saprock and saprolite facies. In the saprolite, collapse of the rock fabric and clogging of fractures by clay are believed to have reduced permeability significantly (Riber *et al.*, in press). The Nygård kaolin pit samples obtained from more closely spaced sample sites should disclose more details of the general alteration sequence, and further the construction of a general model for the Utsira High and other regions in southern Scandinavia.

2. MATERIALS AND METHODS

2.1. Samples

The Nygård kaolin pit weathering profile is irregular in thickness, with maximum original regolith thicknesses of approximately 30 m (Bondam, 1967). The weathering sections are overlain by the Early Cretaceous, lacustrine Rabekke Formation, characterized by coarse to medium sized, poorly sorted sandstones with abundant organic

material and sideritic concretions (Gravesen *et al.*, 1982). The Nygård kaolin and associated smectite and halloysite developed from weathering of granites/granodiorites with fairly high Fe contents (Graff-Petersen and Bondam, 1963). Stable isotope characterization of Gilg *et al.* (2013) show Bornholm (Rønne) kaolinite to have a supergene origin, reflecting warm and humid weathering conditions comparable to most central European kaolins.

Twenty one samples were collected from two 3.1 m vertical sections (profiles B and D) approximately 3 m apart (Figures 1 and 2). Most of the samples were selected at closely spaced intervals, in order to acquire detailed information on the small scale (cm to m) lithological variations in materials ranging from saprock and friable saprolite to carbonate cemented concretions (Figures 2 and 3). Protolith composition was determined from one sample of fresh, homogeneous (Rønne Granite) from the nearby Klippeløkken quarry.

2.2. Petrographical and mineralogical analysis

Twenty two rock samples were impregnated in blue-dyed epoxy at Petrological Section Service (Petro-Sec) of Oslo, Norway, and by Salahalldin Akhavan (University of Oslo, Oslo, Norway). After curing, they were glued onto 2.5 cm x 4.5 cm glass slides and polished to a thickness of about 30 μm . Microfabric and qualitative chemical variability at the nm to μm scale within the carbon-coated polished sections were determined with back-scattered electron (BSE) and secondary electron (SEI) imaging of the sections in a JEOL JSM-6460LV microscope with standard Wolfram filament (15kV) and a LINKINCA Energy 300 energy dispersive spectrometer (EDS) from Oxford Instruments (Oxfordshire, UK). Element compositions were determined with a CAMECA SX100 electron microprobe, (CAMECA Instruments, Gennevilliers, France) fitted with five

wavelength dispersive spectrometers (WDS) and one EDS. Additional fabric and structural data were collected from freshly-fractured, gold-coated surfaces of bulk samples glued on brass stubs with SEI and BSE imaging.

Quantitative chemical analysis was achieved in the microprobe operating in WDS mode with an accelerating voltage of 15 kV, a beam current of 10 nA, and a focused electron beam. Points for analysis were selected with the help of BSE images and qualitative EDS results. The PAP matrix correction procedure (CAMECA software) was calibrated with standards (natural minerals and synthetic compounds): wollastonite (for Si and Ca), Al₂O₃, MgO, Fe metal, pyrophanite (Mn, Ti), Cr₂O₃, albite (Na) and orthoclase (K). Results for Si, Al, Ca, Fe, Mn, Cr, Mg, Na, K, and Ti were expressed as wt.%. In order to increase the accuracy and to decrease the influence of surrounding minerals, only homogenous-appearing single mineral grains larger than the 3 μm diameter electron beam were analyzed. In the electron microprobe (EMP) analyses, the percent standard deviation and mean weight % element were typically: 0.2 % and 21 wt.% for Si; 0.19 % and 20 wt.% for Al; and 0.02 % and 0.04 wt.% for K. Ca, Fe, Mn, Cr, Mg, Na, and Ti errors were similar to K, but varied with sample.

2.3. X-ray powder diffraction (XRD) analysis

A swing mill was applied to produce a coarse powder from whole rock samples. An aliquot was suspended in 50 ml of distilled water and disaggregated for about 10 min with an ultrasonic probe. Gravity settling of the slurry was used to separate < 2 μm clay-sized particles. Oriented clay mineral aggregates (<2μm) were prepared on glass slides by the Millipore transfer method (Moore and Reynolds, 1997). The mineralogical composition of the whole rock sample and the clay fraction (<2 μm) was determined by XRD at the University of Oslo on a Bruker D8 Advance (40kV and 40mA) Diffractometer

using a Lynxeye XE High-Resolution Energy-Dispersive 1D Detector (Bruker Corporation, Billerica, Massachusetts, USA), using $\text{CuK}\alpha$ radiation. XRD patterns were recorded after air-drying, ethylene glycol saturation, plus 350°C and 550°C heating for one hour. The data were collected from 2 to $65^\circ 2\theta$ for whole rock powders and air-dried oriented clay samples, and 2 to $35^\circ 2\theta$ for clay samples treated with ethylene glycol and after heating. Intensities were measured in 0.02° steps with a counting time of 0.3 s per step. Diffraction peaks were analyzed with Diffrac EVA software (Bruker Corporation, Billerica, Massachusetts, USA) and manually reviewed according to methods described by Moore and Reynolds (1997). The whole sample quantitative analysis of top loaded powders used Siroquant version 4.0 (Sietronics Pty Ltd, Canberra, Australia), a Rietveld fitting procedure, to determine the wt.% of all the identified minerals. The analysis followed the five-stage approach suggested by Hillier (2000), with an additional stage using six orientation cycles and a dampening factor of 0.4 . The misfit between each model and experimental pattern was lower than 5% . The results are quantitative representations (QR) of mineral weight percentages with an approximate precision of $10\text{-}15\%$ at the 10 wt.% level.

The peak height proportion (approximately equal to wt %) of minerals in the clay fraction was determined with intensity correction factors reported in Heath and Piasias (1979) and calculated for 7 \AA minerals with NEWMOD II (Reynolds and Reynolds, 2012). The results were repeatable at the 5% level.

2.4. 7 \AA diffraction peak analysis.

The peak width at half the maximum peak intensity (FWHM) and average d-values were obtained by decomposition of overlapping $\sim 7 \text{ \AA}$ peaks on EG (ethylene glycol saturated) clay mineral patterns with Topas version 4.2 software (Coelho, Brisbane,

Australia). Based on the individual 7 Å diffraction peaks, structural properties of several clay varieties were modelled and quantified using NEWMOD II. In the NEWMOD II simulation, the following parameters were crucial: octahedral sheet Fe content, interlayer complexes, *d*-value, crystal thickness (average number of primary layers forming a coherent scattering domain), and random and ordered stacking sequences (Table 1).

2.5. Structural formulas.

Kaolinite and vermiculite structural formula calculations (Bain and Smith, 1987) were based on the anion content of the ideal O₁₀(OH)₈ framework with 28 negative charges for 1:1 layers, and O₂₀(OH)₄ with 44 negative charges for 2:1 layers. Fe was assumed to be Fe³⁺ for kaolinite and Fe²⁺ for vermiculite. The presence of Ti in kaolinite was attributed to adsorbed impurity phases (e.g. rutile, anatase, or ilmenite) and Ti was not included in the calculation (Wilson, 2013). The element ratios in the structural formulas were assumed to be reasonable if tetrahedral Si did not exceed four or eight, and octahedral cation occupancy totals were close to four or six for the respective layer types. Atoms were assigned to structural positions by the recommended procedure (Bain and Smith, 1987).

3. RESULTS

3.1. Whole sample mineral content

Quartz, biotite, siderite, microcline, calcite, plagioclase, kaolin, chlorite, and hornblende were detected by whole sample XRD quantitative analysis (Table 2). The Quartz/Feldspar (Q/F; F=microcline + plagioclase) representing the abundance of a resistant mineral, Q, to those more susceptible to alteration, F, was also calculated to provide a general mineralogical indicator of weathering (Muhs, 1982; Dorransoro and Alonso, 1994; Bockheim *et al.*, 1996). The fresh granite (Sample Q-1) contains higher

quantities of hornblende and lower percentages of microcline compared to the least altered samples from weathered sections (Table 2). The mean wt.% and standard deviation of quartz were typical of the expected values in granite. The standard deviation of the K-feldspar, plagioclase, siderite, and other mean mineral abundances increased when alteration influences were more significant.

3.2. Clay minerals

Two varieties of kaolin (highly-ordered kaolinite and halloysitic, poorly-ordered kaolinite), chlorite, smectite, biotite, randomly mixed layered kaolinite-smectite (K-S), and vermiculite were detected in the clay fraction by XRD analyses. Highly-ordered kaolinite, the most abundant and widely distributed kaolin (Table 3), produced sharp peaks at around 7.16 Å and 3.58 Å that collapsed at 550°C (Brindley, 1980) and typically contained crystallites that were modeled to be 245-490 Å thick in the NEWMOD II simulations. Poorly-ordered, halloysitic kaolinite was identified by a broad peak with a d -value >7.2 to 7.3 Å and the presence of elongate tubes that appeared to have been produced by rolling up very small plates (Table 1). Smectite was identified by the expansion of the 14 Å peak in AD to around 17 Å after treatment with EG and its collapse to 10 Å after 350°C and 550°C treatment. Chlorite was mainly identified by a narrow 14 Å peak and its shift from 6.3 to 6.4° 2θ in the 550°C treated samples (Moore and Reynolds, 1997). Heating to 350°C for one hour collapsed vermiculite to 10 Å, but chlorite remained unchanged at 14 Å (Moore and Reynolds, 1997). After heat treatment at 350°C, a small reduction in the 14 Å peak intensity confirmed the presence of vermiculite (Figure 4). The mixed layered kaolinite-smectite producing an 8 Å peak on the EG pattern was modeled with NEWMOD II. Higher order diffraction peaks were too small to improve the reliability of these minor mineral identifications.

The quantitative representation of clay mineral abundances revealed a major difference in the composition of the clay fractions in the two profiles (Table 3). Highly-ordered kaolinite dominated the D profile. Chlorite was a minor phase in D, and mostly absent from B profile samples. Halloysitic, poorly-ordered kaolinitic was not detected in profile D. K-S was a minor representative of the clay fraction in some B profile samples.

3.3. Structural formulas

Vermicular (vermiform, not vermiculitic) kaolinite samples produced structural formulas with minimal deviation from the ideal for kaolinite, $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ (Table 4). In the sample derived from biotite the number of Si atoms in the tetrahedral sheet was slightly less and there was more Fe and Mg in the octahedral sheet than in the kaolinites derived from feldspars. Small charge deficiencies in the total tetrahedral and octahedral sheet charge that were not completely accounted for by interlayer K, Na, and Ca indicated that the layers had some exchange capacity. Pseudomorphic kaolinite and other morphological varieties of kaolinite produced structural formulas with $\text{Si}_{(\text{tet})}$ slightly greater than 4 and more complex octahedral and interlayer components than in the vermicular kaolinites. These differences suggest the presence of impurities, particularly Si, due to incomplete dissolution of the parent minerals, or the precipitation of other minerals. The mineral vermiculite was tentatively recognized by the atom ratio of $(\text{Mg}+\text{Fe}+\text{Al}+\text{Ca})/\text{Si}$ between 1.5 and 1.7 (Table 4) (Figure 7) (Deer *et al.*, 1992). The vermiculite exhibited a reduction in octahedral Fe, smaller numbers of interlayer cations, and limited changes in $\text{Si}_{(\text{tet})}$ when compared to a reference biotite from the quarry. Vermiculite was not detected by whole sample XRD quantitative analysis, indicating that only very small quantities of biotite had altered to vermiculite.

3.4. Petrography and microfabric

3.4.1. Profile D

Many of the samples from profile D (e.g. DR28-12, DR9-12) exhibited moderately well preserved textures inherited from the original granite (Figure 5). The average size of the interlocking, equidimensional mineral grains of quartz and K-feldspar making up the bulk of the rock was approximately 0.2 cm. Quartz was mostly transparent in transmitted light and K-feldspar was dark gray. The large light gray area (~1 cm in 2-dimensions) near the center of Figure 5 was secondary kaolinite infilling an original plagioclase phenocryst. Biotite associated with small dark grains of siderite or Fe-oxy-hydroxides were shades of dark gray with irregular outlines. Small areas with euhedral crystal outlines were kaolinite pseudomorphs after plagioclase. Grain boundaries and some cleavage planes were accentuated due to the presence of grain-coating kaolinite. Plagioclase was not detected in these thin sections (Figure 5). The approximate volume ratios of quartz and K-feldspar were proportional to the wt.% ratios reported in Table 2.

The most common weathering products of plagioclase are fine-grained massive, randomly oriented kaolinite, and larger vermicular kaolinite booklets (Figure 6). The massive, randomly oriented kaolinite consisted of individual crystals that were connected by high Si content bridges (Figure 6A). Some of the larger grains exhibited very distinct vermicular stacks made of euhedral pseudo-monoclinic minicrystals (Figure 6B). In the well-formed vermicular kaolinite, intergranular voids between individual flakes were well connected.

Exfoliated biotite flakes with inter-lamellar kaolinite were observed commonly in relatively early stages of weathering (Figure 7). Alteration was greatest at the edge of the biotite, but it often extended continuously across the entire grain. The plates within individual kaolinite crystals were frequently oriented perpendicular to the basal cleavage planes of the biotite. Clay minerals similar to vermiculite were occasionally encountered

in the altered zones between the cleavage planes. Euhedral apatite was also observed in close proximity to biotite grains (Figure 7).

A massive appearing kaolinite was associated with vermicular stacks of kaolinite having length to width ratios greater than 5:1 (the arrow of Figure 8A). Typical massive appearing kaolinite (Figures 8A, B) grains were blocky with average dimensions less than 5 μm . Individual subhedral crystals were closely packed and randomly oriented.

In general, the porosity is less poorly developed in profile D samples. Most pores formed as a result of the limited dissolution of plagioclase. The voids between vermicular, well-ordered kaolinite were well developed.

3.4.2. Profile B

More extensive and extreme alteration was evident in BR28-12 (Figure 9) and other samples from profile B. Plagioclase and biotite were almost completely dissolved or altered to secondary clay minerals (Table 2). K-feldspar alteration was more volumetrically abundant. Voids up to 0.5 cm in length were common. Fracture formation and alteration along the cracks significantly changed the original rock texture. Primary minerals previously in contact were separated from each other, creating disaggregation textures. Siderite later filled many fractures and voids, thus locally reducing porosity and permeability (Figure 9).

In BSE images, only a few residual biotite fragments were present, indicating nearly complete replacement by kaolinite. The prominent biotite cleavage planes were not detected, only the outlines of the original biotite grains were preserved. Two distinct types of kaolinite formed from biotite: a massive kaolinite; and a vermicular kaolinite growing along the residual biotite cleavage planes (Figure 10).

Sample BR5-12 contained sand-sized grains of K-feldspar coated with kaolinite. The coating penetrated the margins of the feldspars and filled cracks in slightly weathered K-

feldspar crystals. (Figure 11A). More extensive weathering, with the secondary minerals characterized by small vermicular or platy kaolinite aggregates, was recognized in some samples (BR28-12, Figure 11B). Remaining K-feldspar grains have been fractured and infilled by kaolinite, displaying well-developed porosity with good connectivity (Figure 11B).

The average size of blocky kaolinite aggregates in profile B was approximately 2 μm (Figure 12). Some kaolinite booklets were densely compacted with large numbers of stacked plates (Figure 12B). Some original “large” kaolinite booklets appeared etched, corroded, and now formed new and smaller ($<1\mu\text{m}$) kaolinite plates (3 in Figure 12B) produced by delamination and disintegration of original booklets. In addition, minor quantities of needle-shaped, small crystals were intimately associated with vermicular kaolinite booklets (1 in Figure 12A). The elongate forms could have been K-S materials, illite, or halloysite (Figure 12A). The Si and Al intensity ratios were about the same for kaolin needles (spectrum 2 and spectrum 3, Figure 13) and a flat kaolin region (spectrum 4, Figure 13). The absence of K, Mg, Na, and Ca, the elongate morphology, and the presence of d-values above 7.20 \AA supported the interpretation that the unknown tubular materials were halloysite. Larger crinkled flakes were smectite (Figure 13). Variably sized pits and cavities produced by etching were often the first signs of K-feldspar dissolution (Figure 14A). Rhombohedral siderite crystals and spherical rosettes of Mn-rich chlorite frequently grew from etch-pitted K-feldspar surfaces (Figure 14B).

In general, profile B represents well developed porosity with good connectivity. Most porosity occurs in the local fracture system with almost complete dissolution of plagioclase and biotite, and partial dissolution of K-feldspar. However, the precipitation of siderite significantly reduces porosity and permeability.

4. DISCUSSION

4.1. Recognition of different weathering stages

Weathering conditions and stages were established on the basis of the Q/F ratios and the quantities of well-ordered kaolinite. Although a high Q/F ratio is produced in more weathered intervals, Q/F ratios cannot be used alone as an empirical weathering index due to possible heterogeneity in the original mineralogical compositions (Mikesell *et al.*, 2004). Kaolinite and halloysite are the two kaolin polymorphs that are formed during subaerial weathering (Murray, 1988). Halloysite is thermodynamically less stable than kaolinite, and therefore the replacement of halloysite with the more stable kaolinite phase, through dissolution-precipitation processes, is expected with increasing degree of weathering (Jousein *et al.*, 2005; Inoue *et al.*, 2012). In nature, however, the opposite reaction, where halloysite forms from kaolinite, has also been observed (Robertson and Eggleton, 1991; Singh and Gilkes; 1992; Bobos *et al.*, 2001). Intensified weathering may induce high-defect structures and reduced particle size of previously formed well-ordered kaolinite (Keller, 1977; DeLuca and Slaughter, 1985; Hart *et al.*, 2002; Khawmee *et al.*, 2013). Bobos *et al.* (2001) demonstrated that the gradual formation of halloysite from well-ordered kaolinite in the weathering regime was expressed by decrease of structural order and increase of structural water content.

In the present study two distinct groups of weathering products were revealed by a crossplot of the Q/F ratios versus the proportions of highly-ordered kaolinite (Figure 15). The weight fraction of highly-ordered kaolinite from all profile D samples exceeded 0.8 and all but one had a Q/F ratio less than 0.6. In contrast, the fraction of highly-ordered kaolinite was always less than 0.6 and just one sample from profile B had a Q/F ratio below 0.6. Based on the Q/F ratios and the fraction of clay-sized, highly-ordered kaolinite, the weathering succession from Bornholm can be divided in two. Weathering stage I was

well developed in profile D, while profile B was dominated by weathering stage II (Figures 2 and 3). The greater loss of feldspar relative to quartz ($Q/F > 0.6$) as well as smaller fractions of highly-ordered kaolinite in profile B indicated that weathering had been more extensive in profile B compared to the samples from profile D.

4.2. Weathering stage I, pre-/syn-burial

The initial weathering of bedrock at Nygård kaolin pit was pre-Late Jurassic, during tropical and humid paleo-climatic conditions (Gravesen *et al.*, 1982; Lidmar-Bergström, 1983; Oberhardt, 2013). Alteration resulted in a several meter-thick saprock-saprolite association containing highly-ordered kaolinite booklets derived from plagioclase. Initially, there was no significant destruction of the parent rock structure or volume (Figure 5) (Millot and Bonifas, 1955; Taylor and Eggleton, 2001). Some higher porosity and permeability values, however, occurred as a result of the minor dissolution of plagioclase. The higher quantities of hornblende, which were only observed in fresh granite (Q-1) (Table 2), might suggest a somewhat different original mineral composition for granite from the Klippeløkken Quarry compared to the original fresh granite in the weathered profiles, or hornblende was more soluble and partially dissolved earlier in the regolith development. Kaolin precipitated in intragranular and grain-boundary fissures. Skeletal fragments of plagioclase grains were replaced and infilled by pseudomorphic kaolinite with considerable quantities of micro-impurities indicated by the departure of their structural formulas from the ideal one for kaolinite. Increased weathering resulted in dissolution of the kaolinite pseudomorphs and precipitation of smaller, vermicular, and more highly-ordered kaolinite. Their structural formulas were close to the ideal ones with only small amounts of Fe in the octahedral sheet (Table 4). The presence of highly-ordered kaolinite indicated that the weathering took place under more poorly drained

conditions, probably below the general groundwater table (Keller, 1977; Churchman *et al.*, 2010). The voids between kaolinite grains became highly connected, leading to a possible increase in permeability (Nahon, 1987, 1991). With limited vertical drainage and transport of water to the inter-particle voids in the deeper parts of the saprock-saprolite associations and possibly the coherent weathered rock zones, highly-ordered and chemically purer varieties of kaolinite formed.

Most of the biotite and hornblende weathered to kaolinite via vermiculite in less drained micro-environments (Ghabru *et al.*, 1987; Feldman *et al.*, 1991). Materials in these poorly-drained transitional microsites also could have been smectite. Under humid tropical climates, the biotite-vermiculite-kaolinite weathering sequence is commonly confined to the deeper parts of weathering sections (Tardy, 1971). Kaolinite formed from biotite under weathering stage I (sample 2, Table 4) exhibited low interlayer cation numbers, and high octahedral Fe and Mg abundances. Regolith alteration at Nygård kaolin pit was associated with intermittent stripping and renewed deep weathering, based on analogs from Mesozoic saprolites in Southern Sweden and Norway (Thomas, 1980; Olesen *et al.*, 2012) and the absence of soils beneath the Mesozoic sedimentary cover. The alteration was originally much more extensive, but intermittent erosion and denudation significantly reduced the volume of these highly weathered materials in the Nygård kaolin pit. Only the deeper parts of the original weathered zone were preserved. The saprolite and upper zone of saprock-saprolite associations were stripped and eroded before deposition of the overlying Rabekke Formation. This is in agreement with the deeply buried paleoregolith profiles observed at the Utsira High, where only the poorly drained, lower part of the paleoregolith profile was preserved (Riber *et al.*, in press). Low-to-moderate burial temperatures based on vitrinite reflectance values of 0.3-0.6% (Ahlberg,

1996; Ahlberg and Olsson, 2001) for nearby correlative Mesozoic paleoregolith profiles in southern Sweden established the near surface setting for stage I weathering.

In general, the weathering stage I is comparable to the middle to deeper parts of the weathering profiles in Utsira High. Both of them show less intense weathering environment and moderate dissolution of plagioclase into well-ordered kaolinite (Riber *et al.*, in press).

4.3. Weathering stage II, pre-/syn-burial

Weathering stage II was characterized by more extensive and extreme weathering than stage I. Earlier formed highly-ordered kaolinite of stage I was transformed to poorly-ordered kaolinite. Increasing amounts of plagioclase, biotite, and K-feldspar weathered to secondary clay minerals (Table 2). Alteration along intergranular and intragranular fissures and cracks significantly changed the parent rock textures. Primary minerals previously in contact were separated from each other, creating disaggregation textures with additional reactive surfaces in new microchemical environments. The distinguishing characteristic of stage II was the hydration of earlier formed kaolinite to halloysitic, poorly-ordered kaolinite.

4.4. Fractures and associated weathering environments in Stage II

Two local fracture zones were observed in the section at Nygård kaolin pit (Figure 2). They both intersected the entire B-profile, causing significant changes in the weathering environment and the resulting secondary minerals compared to profile D. The fractures promoted fluid flow and contributed to the generation of spheroidal weathering zones with less altered parent rock cores surrounded by secondary mineral zones. The

alteration zones near the center of the core exhibited weathering conditions similar to those acting on plagioclase and biotite during Stage I.

Accelerated weathering in the fractured zones was responsible for the major mineral differences observed in sections B and D. The effects of increased fluid flow with an inferred difference in composition led to the formation of halloysitic, poorly-ordered kaolinite, the key secondary mineral occurring in Stage II. The precipitation or transformation of this variety of kaolinite occurred in environments where fluids had a high ionic strength, favoring disorder and rapid crystal growth. Crystal defects favored hydration of kaolinite to form recognizable tubes of a halloysitic nature (Figure 12, 13) (Giese, 1988). The halloysitic material also could be formed in well-drained, wet, and severe weathering conditions (Keller, 1977; Churchman *et al.*, 2010). Stage II followed Stage I. The timing of the alteration was not always chronologically distinct as Stage I and Stage II processes may have been contemporaneous within adjacent regions. The meteoric water entered the rocks through fracture networks by gravity flow and capillary forces until the rock matrices were totally impregnated (Velde and Meunier, 2008).

In the Nygård kaolin pit, the dissolved chemicals in the fractures were essentially isolated in capillary-size pores or diluted by groundwater when the fractures enlarged through the dissolution of parent rocks. The increasing chemical dissolution of parent minerals weakened the mechanical resistance of the rock and the structure of the altered parent minerals until finally the primary mineral grains formed a skinny framework separated by well-connected voids (Figure 9) (Berner *et al.*, 1982).

Under such well-drained, extreme weathering conditions, biotite was completely altered to pseudomorphic kaolinite without any vermiculite intermediate stages (Rebertus *et al.*, 1986; Buol and Weed, 1991). Increased K-feldspar dissolution was triggered in the cracks at selective sites of weakness (Holdren and Speyer, 1985). Micro-shattering or

corrosion pitting (Figure 14) happened in the early stages of kaolinization of K-feldspar (Parham, 1969; Keller, 1978; Banfield and Eggleton, 1990) and indicated a weathering environment characterized by acidic solutions and/or non-equilibrium solutions (Berner and Holdren, 1977, 1979; Nesbitt *et al.*, 1991; Teng, 2004). Based on the microprobe results, early weathering products of K-feldspar contained high tetrahedral Si, high interlayer charges, along with high Fe and Mg in the octahedral sheet (Table 4) consistent with the presence of K-S or smectite (Eswaran and Bin, 1978; Banfield and Eggleton, 1990). The high Fe and Mg contents of stage II secondary minerals indicated that Fe and Mg most likely were imported and transported along fractures from other horizons or came from other unknown minerals (non-feldspar) in the same horizon.

Fracture growth alteration during stage II inevitably destroyed the original textures of previous saprock-saprolite associations, and a new weathering environment characterized by high rates of fluid exchange and non-equilibrium reactions between kaolinite and parent minerals were established. The well-ordered kaolinite booklets of stage I were converted into small, irregular halloysitic tubes, and poorly-ordered kaolinite flakes (Figure 12) under highly variable local geochemical conditions (Keller, 1977; Bobos *et al.*, 2001).

In general, weathering stage II could be considered as an analog for middle to upper parts of weathering profiles in Utsira High, where extensive weathering environment, etch-pitted K-feldspar, direct transformation of biotite to kaolinite, and disordered kaolinite have been observed (Riber *et al.*, in press). The comparable mineralogical and micromorphological alteration between Utsira High and Nygård kaolin pit may suggest the paleoregolith formations of these two areas were under similar weathering conditions. Compared to the weathering profiles in Utsira High, where the weathering sequences are only constrained in the vertical direction (Riber *et al.*, in press), this study shows the

degree of weathering also to be varied in the lateral directions. This is important, since the lateral resolution of subsurface exploration is limited by the width of the core, and in regolith weathering profiles the lateral variability in reservoir properties is less constrained compared to conventional sandstone reservoirs.

4.5. Post weathering -Diagenetic reactions

4.5.1. Siderite formation

Abundant siderite in profile B and the lower part of profile D (Figure 2, Table 2) was detected along fractures and in pore spaces. Calcite has commonly been reported to be the most abundant carbonate in saprock-saprolite associations, while siderite and ankerite are rare (James, 1954). As a consequence, the evaluation of the large quantities of siderite formed in this Fe-depleted, feldspar-rich saprock-saprolite associations was important. The siderite overgrowths on weathered K-feldspar particles (Figure 14) indicated a younger age of carbonate formation than the main weathering stages. This was consistent with comparable studies where siderite had been interpreted as a diagenetic phase (Dimroth and Chauvel, 1973; Klein, 1974; Klein and Fink, 1976; Floran and Papike, 1978). The Nygård kaolin pit siderite was formed after burial of the saprock-saprolite associations in fresh-water, lacustrine environments of the Lower Rabekke Formation (Lindgren *et al.*, 2008). Comparable results were also recorded for the Appalachian Plateau by Gardner *et al* (1981). In the Nygård kaolin pit site, the overlying coarse- to medium- sized, poorly sorted, ferruginous, and sideritic sediments of the Lower Rabekke Formation was a likely Fe²⁺ source (Gravesen *et al.*, 1982). During diagenesis, Fe²⁺ was transported through fractures into the underlying altered materials and precipitated on fracture walls and in pores. The siderite probably formed at pH values from 6.2 to 7.0 (Kazakov *et al.*, 1957; Klein and Bricker, 1977). Large amounts of siderite in profile B

reflect low sulphide contents, significantly lower bacterial sulphate reduction activities, and strongly reducing conditions, because siderite was only stable at extremely low dissolved sulphide activities (Berner, 1964).

4.5.2. Chlorite formation.

Rosettes of chlorite crystals occurred on the same substrates (etched K-feldspar) and in the same pores as siderite (Figure 14). This is comparable to the Utsira High paleoreolith profiles, where the diagenetic chlorite was also detected (Riber *et al.*, in press). In the present study, chlorite crystals likely precipitated from the same Fe and Mg rich solutions, which precipitated siderite. Chlorite was neither detected in most samples from profile B nor in the fresh Rønne Granite. XRD results established its presence in profile D. The presence of chlorite in the profile was less affected by large-scale fractures probably due to an increase in dissolved Si activity favoring the precipitation of chlorite over siderite. The alteration of biotite to chlorite has been more often associated with hydrothermal reactions at high temperature (Eggleton and Banfield, 1985). However, the stable H-O isotope compositions of kaolins from Nygård kaolin pit do not support hydrothermalism in this area (Gilg *et al.*, 2013). In addition, the potential role of biotite as a direct source of Fe and Mg should be downplayed because altered biotite occurred throughout the sections. The association of chlorite with siderite also suggested they were syngenetic (Figure 14 B), derived from an external source similar to the high-leaching environments (Sartori *et al.*, 1979; Tolpeshta *et al.*, 2010) represented by the Lower Rabekke Formation. Chlorite could also have formed at the expense of kaolinite during shallow burial, dependent on the Mg^{2+}/H^+ ratio in pore water (Nesbitt and Yong, 1989).

4.6. Re-exposure

Large amounts of calcite were detected in the upper part of profile D (sample DR19-12 to DR31-12) compared to the lower part (Table 2). The calcite cementation post-dated

siderite formation. It probably occurred when the section was uplifted and exposed to modern-day near surface groundwater or Cenozoic water tables (Nesbitt and Young, 1989). Late Cretaceous to Early Cenozoic tectonic inversion resulted in severe erosion of the Bornholm Mesozoic sediments (Gry, 1969; Gravesen *et al.*, 1982). As a result, the weathered materials were re-exposed to surface weathering and groundwater movements were reactivated. Calcite most likely precipitated at this very late phase of alteration. The absence of calcite in the upper part of profile B might be related to high degree of siderite cementation, which significantly reduced porosity and permeability.

Smectite precipitation was a late event in the alteration history. It was more pronounced in the regions of enhanced permeability associated with abundant fractures in profile B. High ionic strength solutions inherited from the Rabekke Formation were gradually diluted until saturation with respect to smectite took place. In some places these solutions were also responsible for dissolution of siderite. Re-opened fractures in profile B provided a pathway for the introduction of oxidizing Na-rich surface waters and smectite became the major secondary mineral to form in open pores and fractures.

5. CONCLUSIONS

XRD, SEM, and EMP analyses of multiple samples from the Nygård kaolin pit at Bornholm provide an improved and detailed appraisal of changes associated with weathering of the granitic regolith. Detailed clay mineral analyses revealed the presence of biotite (illite), smectite, chlorite, vermiculite, highly-ordered kaolinite, halloysitic poorly-ordered kaolinite, and a kaolinite-rich randomly oriented kaolinite-smectite. The two varieties of kaolin were distinguished by NEWMOD II modeling.

Plagioclase was the most easily weathered parent mineral, followed by biotite and microcline. No hornblende was detected in the samples, although it is present in

unweathered Rønne Granite. EMP data used to calculate structural formulas identified traces of impurities in the secondary kaolinite based on the departure of the calculated formulas from the ideal stoichiometry. Major differences in the state of weathering among samples from profiles B and D (about 3 m apart) was indicated with crossplots of the weight percentages of quartz to total feldspar versus the weight fraction of highly-ordered kaolinite. The relative greater loss of feldspar and smaller fractions of highly-ordered kaolinite, in profile B indicated that weathering was more pronounced than in profile D. Mineralogical discrimination of weathering stages at the macro-scale proved generally effective even when the sequence of crystallization at the micro-scale differed.

The paragenetic sequence of mineral dissolution and precipitation determined by micro-fabric analysis with the SEM was very useful for establishing the relative timing of weathering stages. Texture and fabric were particularly useful in recognizing that the earliest stage of kaolinite formation was pseudomorphous after plagioclase and that poorly-ordered kaolinite was derived from highly-ordered kaolinite. Crystal form and location in large pores established that siderite, chlorite, and smectite formed during a later diagenetic stage.

Stages of weathering

The initial stage of crystalline bedrock weathering at Nygård kaolin pit was pre-Late Jurassic during tropical and humid paleo-climatic conditions (Gravesen *et al.*, 1982; Lidmar-Bergström, 1983; Oberhardt, 2013). Four stages of weathering and alteration produced a thick kaolin-rich saprock-saprolite associations, where the weathering stage I and stage II are comparable to the middle to deeper parts and middle to upper parts of the weathering profiles in Utsira High (Riber *et al.*, in press), respectively.

1. Weathering stage I.

Large quantities of plagioclase as well as some biotite were transformed to highly-ordered kaolinite. The main secondary kaolinite (<2 μ m) formed highly-ordered, vermicular crystals. Small quantities of kaolinite formed from biotite through an intermediate vermiculite step. Initial reactions took place in narrow intergranular fissures and cracks. Some pseudomorphic precipitation occurred in plagioclase and biotite. The overall altered rock texture changed very little. The volume of reacting fluid was limited and groundwater flow rates were minimal.

2. Weathering stage II.

Stage II weathering follows stage I, but they may occur contemporaneously in different areas. The majority of plagioclase and biotite, and some fractions of the K-feldspar were affected by this most severe stage of alteration. Etch pits were detected on the majority of K-feldspar grains. Mixed-layer K-S and discrete kaolinite were produced. In this stage, some previously formed well-ordered kaolinite booklets were re-organized into smaller, poorly-ordered kaolinite booklets or flakes. Small amounts of halloysite (needle-shaped small crystals) formed from kaolinite in higher volumes of fluids. Reactions associated with stage II were confined to the fractured materials in profile B where more rapid exchange of fluids was indicated. Halloysitic poorly-ordered kaolinite produced during this stage is the best indicator of high permeability.

3. Diagenesis.

In Nygård kaolin pit early diagenesis was characterized by the formation of large amounts of siderite in fracture controlled regions (profile B). The overlying Lower Rabekke Formation being the most likely source of Fe²⁺. Chlorite grew at the expense of kaolinite at relatively low temperatures during periods of high Mg²⁺/H⁺ ratios, following the first siderite precipitation phase.

4. Re-exposure.

During later uplift and re-exposure of the section, the upper part of the existing weathering profile was located above or just within area of ground water saturation, and large amounts of calcite precipitated locally. Higher quantities of low ionic strength groundwater promoted the precipitation of smectite in the larger pores.

Compared to the weathering profiles in Utsira High, this study displays lateral degree of weathering. In addition, the recognition of a link between poorly-ordered kaolinite (halloysitic) abundance and the presence of large, interconnected pores (only estimated in SEM and optical microscopy) is also the main result of this study; the presence of halloysitic poorly-ordered kaolinite could therefore indicate proximity to a potential reservoir. The spatial distribution of rocks containing this association was limited primarily to zones affected by local fracture systems.

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Figure 1. A: Approximate location of Nygård kaolin pit on Bornholm Island, Denmark. The Fennoscandian Border Zone (modified after Liboriussen *et al.*, 1987) is marked by a red line (Insert), while Bornholm Island and the Utsira High are identified by stars. The Precambrian crystalline basement is marked by the grey colored area in the center of the figure. Down-faulted sedimentary basins on the south side of the island are shown in other colors (modified after Graversen, 2009). B: Location of sampling profiles on quarry wall (circle in A) (modified from Oberhardt, 2013).

Figure 2. Distribution of major lithologies in the Nygård kaolin pit quarry wall. White continuous lines mark the position of the profiles studied (modified after Oberhardt (2013)). The sideritic cementation parts were divided into two classes; one dominated by siderite (>50%) (sideritic cementations/saprock-saprolite associations), the other dominated by saprock (saprock-saprolite associations/sideritic cementations).

Figure 3. Location of samples and lithology from profile B (BR number) and profile D (DR number) in profiles B and D (modified after Oberhardt, 2013).

Figure 4. XRD patterns of sample DR9-12 with prominent 7 Å peaks after four treatments. From bottom to top: Air-dried (black), Ethylene glycol saturated (red), 350°C heated for 1 h (blue), and 550°C heated for 1 h (green).

Figure 5. Polished thin section of moderately weathered Rønne Granite, DR28-12. The dark blue represents epoxy filled pore-space, while the paler blue color contains secondary clay

minerals and epoxy. Bt: biotite, Qz: quartz, Kln: kaolinite, Kfs: K-feldspar.

Figure 6. Microtextural differences in kaolinite from samples DR28-12 (A) and DR9-12 (B), were revealed in BSE. Vermicular Kln: vermicular kaolinite, pseudomorphic Kln: pseudomorphic kaolinite.

Figure 7. BSE image of biotite alteration (kaolinization) in DR9-12. Bt: biotite, Ap: apatite, Kln: kaolinite, Vrm: vermiculite.

Figure 8. SEM images of kaolinite booklets in samples DR7-12 (A) and DR9-12(B). The arrow points to a kaolinite flake with a length to width ratio greater than 5:1.

Figure 9. Thin section photomicrograph of BR28-12. The dark blue represents epoxy filled pore-space, while the pale blue color contains epoxy with secondary clay minerals. Bt: biotite, Qz: quartz, Kln: kaolinite, Sd: siderite, and Kfs: K-feldspar.

Figure 10. BSE image of biotite kaolinization in BR28-12. Vermicular Kln: vermicular kaolinite, massive Kln: Massive kaolinite, and Bt: biotite.

Figure 11. BSE images of K-feldspar kaolinization in BR5-12(A) and BR28-12(B)). Kln: kaolinite, Kfs: K-feldspar.

Figure 12. Microtexture and fabric of kaolinite (BR28-12(A, B) and BR23-12(C)). 1: needle-shaped small crystals, 2: disordered kaolinite booklets, 3: etched kaolinite booklets.

Figure 13. Elongate kaolin minerals. The similar Si and Al intensity ratios of kaolin needles (spectrum 2 & spectrum 3) with a “flat region” (spectrum 4) of typical kaolinite, as well as the absence of K, Mg, Na, and Ca suggest the needles are halloysite.

Figure 14. Etched K-feldspar (A), siderite, and chlorite (B) attached to etched K-feldspar.
etched Kfs: etched Kfs, Sd: siderite, Chl: chlorite.

Figure 15. Crossplot of quartz/feldspar –ratio (Q/F) versus the fraction of highly-ordered kaolinite based on XRD analyses.

Table 1. Parameters used in NEWMOD II simulations.

Minerals	d-value (Å)	Number of unit layers	Crystal thickness	Others
chlorite (trioctahedral)	7.08Å	24	336Å	1.5 Fe in the 2:1 octahedral sheet, 1.5 Fe in the interlayer octahedral sheet
highly-ordered kaolinite,	7.13 Å to 7.16 Å	35 to 70	245-490 Å	
poorly-ordered halloysitic kaolinite,	7.21 Å to 7.33 Å	10 to 12	70-84 Å	
kaolinite-smectite, randomly interstratified (K-S)	>8 Å	3	72 Å	90% kaolinite 10% smectite, 1 Fe in 2:1 octahedral sheet, random stacking sequences

Table 2. Mineral composition (wt.%) of whole rock samples from profiles B and D.

Sample	Distance	Quartz	Biotite	Siderite	Microcline	Calcite	Plagioclase	Kaolin	Chlorite	Hornblende	Q/F
BR1-12	10	25.9	2.7	11.2	40.5	-*	2.6	16.7	-*	-*	0.6
BR2-12	20	24.6	3.9	7	49.8	-*	-*	14.6	-*	-*	0.49
BR4-12	40	27.4	4.5	1.9	41.9	-*	3.8	15.1	4.9	-*	0.6
BR5-12	50	21.9	1.8	30.9	34.3	-*	-*	10.8	-*	-*	0.64
BR7-12	70	21.7	1.5	35.4	30.9	-*	-*	10.5	-*	-*	0.7
BR13-12	130	18.3	1.2	42.9	25.3	-*	-*	12.3	-*	-*	0.72
BR16-12	160	17.2	1.2	51.6	19.3	-*	-*	10.5	-*	-*	0.89
BR19-12	190	21.7	0.5	49.2	18.8	-*	1.2	8.4	-*	-*	1.09
BR21-12	215	16.5	1.2	59	17	-*	-*	6.2	-*	-*	0.97
BR23-12	235	24.2	1.4	24.1	31.3	-*	0.9	18.1	-*	-*	0.75
BR28-12	300	15.7	1	56.7	18.5	-*	-*	8	-*	-*	0.85
DR3-12	30	22.6	1.3	21.3	38.6	-*	4.1	12.1	-*	-*	0.53
DR7-12	70	26.1	0.9	14.3	37.4	-*	9.5	10.3	1.3	-*	0.56
DR9-12	90	22.3	4.4	12.7	38.4	5	5.2	11.8	-*	-*	0.51
DR10-12	100	21.5	3.1	13	36.1	7.9	3	12.3	3.2	-*	0.55
DR13-12	130	30.5	2.5	12.2	30.3	7.1	4.9	9.3	3.1	-*	0.87
DR19-12	190	21.7	4.2	-*	36.4	20.8	3.6	13	-*	-*	0.54
DR20-12	200	20.5	4	-*	42.9	16.2	3.5	12.5	-*	-*	0.44
DR24-12	240	25.3	3.7	0.9	42	-*	5.9	14.5	7.6	-*	0.53
DR28-12	280	22.2	3.3	-*	37.4	18.2	7.4	11.4	-*	-*	0.5
DR31-12	300	20.6	4.8	-*	40.5	15.5	4.7	13	0.7	-*	0.46
Mean+s.d.		22.3±3.7	2.5±1.4	21.2±19.9	33.7±9.0	4.4±6.9	2.9±2.7	12.0±2.79	1.0±2.0	0.0±0.0	0.65±0.18
Q-1		16	4	-*	26	-*	38	-*	-*	14	0.25

Distance in cm from the base of the B or D profile; -*, not detected, lower than 0.5wt.%;

s.d.: Standard deviation; Q=quartz; F=microcline+plagioclase ; Q-1 : fresh granite from Klippeløkken quarry.

Table 3. Weight fraction of minerals in clay-sized material

Sample	Smectite	Biotite	Highly-ordered Kaolinite	Halloysitic, poorly- ordered kaolinite	Chlorite	K-S
BR1-12	0.20	0.03	0.35	0.35	-*	0.06
BR2-12	0.23	0.03	0.46	0.27	-*	0.0
BR4-12	0.02	0.04	0.58	0.18	0.19	0.0
BR5-12	0.14	0.03	0.47	0.36	-*	0.0
BR7-12	0.20	0.02	0.37	0.33	-*	0.09
BR13-12	0.27	0.01	0.53	0.14	-*	0.04
BR16-12	0.05	0.01	0.63	0.31	-*	0.0
BR19-12	0.17	0.01	0.49	0.25	-*	0.07
BR21-12	0.07	0.01	0.50	0.38	-*	0.05
BR23-12	0.21	0.0	0.44	0.23	-*	0.12
BR28-12	0.15	0.02	0.40	0.43	-*	0.0
DR3-12	0.03	0.05	0.84	0.0	0.08	0.0
DR7-12	0.01	0.06	0.86	0.0	0.07	0.0
DR9-12	0.01	0.03	0.90	0.0	0.06	0.0
DR10-12	0.03	0.04	0.86	0.0	0.06	0.0
DR13-12	0.02	0.04	0.88	0.0	0.07	0.0
DR19-12	0.02	0.02	0.88	0.0	0.08	0.0
DR20-12	0.04	0.01	0.91	0.0	-*	0.0
DR24-12	0.02	0.02	0.84	0.0	0.11	0.0
DR28-12	0.05	0.01	0.93	0.0	-*	0.0
DR31-12	0.07	0.01	0.93	0.0	-*	0.0

*, not detected.

Table 4. Structural formulas of selected secondary minerals.

Sample	Fabric	Parent Mineral	Formula	
BR28-12	3	Vermicular kaolinite	Biotite	$(K_{0.06}Ca_{0.01})(Al_{3.66}Fe^{3+}_{0.26}Mg_{0.08})(Si_{3.97}Al_{0.03})O_{10}(OH)_8$
DR9-12	6	Vermicular kaolinite	Plagioclase	$(K_{0.02}Ca_{0.01})(Al_{3.96}Fe^{3+}_{0.02})Si_{4.01}O_{10}(OH)_8$
BR4-12	8	Vermicular kaolinite	K-feldspar	$(K_{0.03}Ca_{0.01})(Al_{3.9}Fe^{3+}_{0.06}Mg_{0.01})Si_{4.01}O_{10}(OH)_8$
BR28-12	4	Massive kaolinite	Biotite	$(K_{0.02}Ca_{0.01})(Al_{3.57}Fe^{3+}_{0.21}Cr_{0.01}Mg_{0.07})Si_{4.11}O_{10}(OH)_8$
DR9-12	2	kaolinite	Biotite	$(K_{0.01}Ca_{0.01})(Al_{3.39}Fe^{3+}_{0.52}Mg_{0.23})(Si_{3.82}Al_{0.18})O_{10}(OH)_8$
DR28-12	5	Pseudomorphic kaolinite	Plagioclase	$(K_{0.02}Na_{0.01}Ca_{0.03})(Al_{3.59}Fe^{3+}_{0.2}Mg_{0.03})Si_{4.12}O_{10}(OH)_8$
BR1-12	7	Pseudomorphic kaolinite	K-feldspar	$(K_{0.28}Na_{0.01}Ca_{0.07})(Al_{2.99}Fe^{3+}_{0.36}Cr_{0.01}Mg_{0.08})Si_{4.33}O_{10}(OH)_8$
DR9-12	1	vermiculite	Biotite	$K_{0.01}(Al_{2.45}Fe^{2+}_{2.15}Cr_{0.01}Mn_{0.03}Mg_{1.42})(Si_{5.41}Al_{2.59})O_{20}(OH)_4$
Reference		Biotite	fresh	$(K_{1.78}Na_{0.03}Ca_{0.02})(Ti_{0.75}Fe^{2+}_{3.4}Mn_{0.02}Mg_{1.68}Cr_{0.01})(Al_{2.29}Si_{5.52})O_{20}(OH)_4$