The evolution of the mineralogical and petrophysical properties of a weathered limestone in southern Belgium

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ABSTRACT. The weathering of limestone results in the partial dissolution of calcium carbonate and leaves a soft porous material called alterite. The properties of the weathered rock differ significantly from those of its parent due to the changes in composition and the removal of soluble materials. The resulting increase in porosity modifies the hydrological properties of the rock such as its permeability, hydraulic conductivity, and reservoir capacity. The loss of material also weakens the structure of the rock and decreases its mechanical resistance. This study quantifies the progressive changes in the mineralogical, petrographic and mechanical properties that occur during the weathering of the Carboniferous Petit Granit, a limestone found around Soignies in southern Belgium. The rock samples, representing various stages of weathering, were collected within the same stratum and analysed in terms of their porosity, permeability, density, carbonate content, and mechanical resistance. The mineralogical and petrophysical changes were documented through X-ray diffraction and thin sections analysis. It is clearly seen that weathering exerts a great influence on the rock properties: the widespread increase in porosity is associated with a decrease in density, a large increase in permeability, and a fall in the mechanical strength to zero. We show how these properties change with the intensity of the weathering.

KEYWORDS: Carboniferous limestone, CaCO₃, dissolution, characterisation, Belgium.

1. Introduction

It is well known that acidified water flowing through calcareous geomaterials causes progressive weathering by dissolution. The weathering of limestone, also called ghost-rock karstification (Quinif, 2010; Quinif et al., 2014), occurs in two simultaneous stages: (i) the most soluble phases of the rock are dissolved while the less soluble phases remain in place; (ii) the dissolved species are evacuated by the flow of water. The resulting material is called alterite, “a weathering product with slight or no change in rock volume and remnant rock structure”, as defined by Delvigne (1998). The weathering process induces significant changes in the composition and properties of the geomaterial. These changes may have important implications since limestone has many industrial applications such as in the production of aggregate, ornamental stone, lime, and chemicals. In addition, stability problems for civil engineering may arise from the deterioration of the mechanical properties of the bedrock due to such weathering. The increase in the hydraulic transmissivity of the rock mass allows contamination to spread faster and further and thereby increases the vulnerability of aquifers to chemical pollution while the high porosity of the weathered areas increases the capacity of the reservoir. In order to better comprehend these phenomena it is important to understand the changes to the material properties that occur as a result of the weathering.

There have been a number of studies that have investigated the influence of weathering processes on both plutonic (e.g. Begonha & Sequeira, 2002; Ceryan et al., 2008; Delvigne, 1998; Gupta & Seshagiri Rao, 2000; Irfan & Dearman, 1978; Lan et al., 2003; Lumb, 1982-83; Ruxton & Berry, 1967; Sequeira Braga et al., 2002) and volcanic magmatic rocks (Bozkurtoğlu et al., 2006; Moon & Jayawardane, 2004; Orhan et al., 2006). Fischer et al. (2009), Gardner & Walsh (1996), Jayawardena & Izawa (1994), Marques et al. (2010), Pellegrino & Prestinini (2007), and Price & Velbel (2003) have carried out similar studies in metamorphic rocks while Chigira (1990), Chigira & Sone (1991), Chigira & Oyama (2000), and Islam et al. (2002) have investigated the effects of the weathering on non-calcareous sedimentary rocks. Hawkins et al. (1988), Qi et al. (2009), and Tugrul & Zarif (2000) have presented a comprehensive characterisation of calcareous alterite weathering profiles while Kaufmann et al. (1999), Havron et al. (2007) and Dubois et al. (2011) have focused their research at the microscopic scale.

The limestone bedrock of southern Belgium represents one of the most important aquifers in the country and it is also quarried extensively for aggregate and ornamental stone. This limestone is commonly associated with karstification and weathering (C.W.E.P.S.S., 2005; Kaufmann, 2000; Quinif & Quinif, 2002; Quinif et al., 1993; Quinif et al., 1997; Quinif et al., 2006; Vergari, 1998; Vergari & Quinif, 1997) although few studies have yet to quantitatively investigate the material properties of the alterite that results from the weathering process. The purpose of this paper is to present a detailed analysis of one specific section of weathered crinoidal limestone (“Petit Granit”) from the Upper Tournaisian of Soignies (Belgium).
2. Geological setting

This paper focuses on the Petit Granit, also known as the “Belgian Bluestone”, a highly fossiliferous limestone that predominately comprises crinoids and other organisms such as corals, bryozoans, and brachiopods (Doremus & Hennebert, 1995 a, b). The CaCO₃ content of the limestone reaches 95 % and it is very compact with a very low bulk porosity and dark blue-grey colour. It is mainly extracted in the area around Soignies in southern Belgium due to its aesthetic and durable qualities which gives it a high market value. This formation dates from the Upper Tournaisian of the Lower Carboniferous and it is part of the geological unit Soignies Member (Fig. 1).

In this area the Paleozoic strata form a monoclinal structure oriented North 100° and dipping 12° to the South. This unit is affected by intensive fracturing that follows three main directions: N60°E, N120°E, and N100°E. The associated joints are often affected by the weathering phenomena. Individual beds are from 0.7 to 2 meters thick and the total thickness of the unit is about 30 meters within the studied area. It is unconformably overlain by Cenozoic overburden.

3. Methodology

3.1. Sampling

A well-exposed section of weathering was selected in a quarry from the area around Soignies (Fig. 2A). The limestone in this section is weathered for about 50 cm either side of a near vertical fracture and it appears that the weathering intensity gradually lessens away from the fracture. The macroscopic description of the weathered rocks follows the standard terminology of Price (2009) (Tab. 1) with five symmetrical zones recognised on the basis of this classification (Fig. 2B): Grade I is represented by unweathered rock; Grade II is represented by a darker coherent rock in which the darker shade is imparted by the presence of water; Grade III is represented by a weaker but coherent rock in which there has been a substantial reduction in its mechanical strength; Grade V is represented by a friable dark grey material, also called alterite, in which the structure of the rock is preserved although it is completely decomposed; Grade VI is represented by a black alterite found around the initial fracture in which the weathered III rock (texture less compact); V: completely weathered rock (loose material = alterite); VI: residual soil (black alterite).

Some of the samples were vacuum-impregnated for thin-sectioning. The petrographic analyses were undertaken using both optical and cathodoluminescence (CL) microscopy with a CITL Mk5 CL stage operated at 15 kV and 500 μA beam voltage and current, respectively. CL was used because carbonate minerals are often brightly luminescent in yellow-brown (calcite) and yellow-red (dolomite) under electron excitation, which enables them to be identified in polished thin-sections (e.g. Barbin and Schoerer, 1997 and references therein).

3.2. Analysed parameters and measuring procedures

Weathering description | Grade | Rock material description
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Fresh | I | No visible changes of weathering.
Slightly weathered | II | Slight changes in color; slight weakening.
Moderately weathered | III | Changes in color; considerable weakened but cannot be broken by hand.
Highly weathered | IV | Considerable weakened; larges pieces can be broken by hand.
Completely weathered | V | Considerably weakened; disintegrate in water; original texture apparent.
Residual soil | VI | Soil derived by in-situ weathering but having lost retaining original texture and fabric.

Table 1. The standard terminology for the description of rock weathering (from Price, 2009)

Thirteen samples were taken sequentially from the same stratigraphic horizon across this weathered feature. They were selected from both sides of the centre so as to characterise the broad variations in weathering intensity (Fig. 3). Three different sampling methods were used according to the stiffness of the material. The competent rocks were sampled using a diamond core bit mounted on a portable drill. It was more difficult to sample the loose and soft alterite because care had to be taken not to disturb the material structure. For the main analyses (chemical and mineralogical composition, density, and porosity) the soft alterites were sampled by manually inserting plastic pipes with a diameter of 25 mm and a length of 50 mm and, therefore, another sampling technique was developed to fulfil these requirements. This consisted of recovering the material in a metallic pipe with a diameter of 25 mm and this was then placed directly into the permeameter.

Figure 2. A. The weathered zone (= ghost-rock feature) in the Petit Granit selected for sampling. B. Sketch of the weathered zone: samples were taken in stratigraphic continuity and are identified by their distance in cm from the centre (zone VI). The five parts were defined according to the standard terminology for the description of weathered rocks - I: fresh rock; II: slightly weathered rock (dark shade); III: moderately weathered rock (texture less compact); V: completely weathered rock (loose material = alterite); VI: residual soil (black alterite).
The semi-quantitative mineralogical analyses on powdered bulk samples were conducted by X-ray diffraction (XRD) using a Bruker-Siemens diffractometer equipped with a graphite rear monochromator, which eliminates iron fluorescence at the expense of signal intensity (operating conditions: 40 kV – 30 mA). The oriented aggregates were prepared according to Holtzapffel (1985) and X-rayed to identify the clay mineral assemblage. Three separate oriented aggregates were prepared for each sample and these were subjected to different treatments: drying in air (“normal”), 2 hours heating at 490°C (“heated”), and a minimum of 2 hours in ethylene glycol (“glycolated”). The purpose of these treatments is to enable the clays to be detected more easily by changing the interplanar spacing.

The rock composition was determined by measuring the calcium carbonate content using a Dietrich-Frünhling calcimeter (Lama et al., 2005). This analysis mixes a known quantity of crushed rock with hydrochloric acid in order to measure the volume of CO₂ produced, which in turn indicates the amount of CaCO₃ present in the rock.

Standard petrophysical analyses were undertaken to measure apparent density and porosity using a volumeter and a helium pycnometer (Webb, 2001). The permeability was studied using a gas permeameter (Klinkenberg, 1941; Long et al., 1988; Lydon, 1993) with nitrogen injected at an imposed pressure and the flow rate through the sample measured. The permeability of the material was then computed using Darcy’s law for gases (Eq. [1]) (Scheidegger, 1974):

\[
k_g = \frac{S \cdot F}{\mu \cdot L \cdot dP}
\]

Where \( k_g \): permeability; \( \mu \): viscosity of the gas; \( S \): section of the sample; \( L \): length of the sample; \( F \): flow rate; and \( dP = (P_{Injection} - P_{atm})/(2 \cdot P_{atm}) \) to take into account the compressibility of the gas (\( P_{Injection} \): injected pressure and \( P_{atm} \): atmospheric pressure). The use of a gas rather than water to measure permeability reduces the risk of damaging friable materials such as highly weathered rock during fluid injection. In addition the gas permeameter is easier to handle than the water permeameter and the test is very fast especially as the sample must not have been previously saturated with water. However, due to the phenomenon of gas slippage, the measured values are different to those that would be obtained from measuring the water. This method gives a relative permeability between the various samples.

The mechanical strength of the samples was obtained during instrumented core drilling with the force applied to core the rock.
determined from a fixed penetration rate (100µm/r) and imposed rotation speed (250 rpm). This method of analysing the strength of the material has been adapted directly from principles developed for testing the strength of rock fragments by micro-drilling (Dagrain et al., 2010). For the micro-drilling tests have shown that the drilling strength correlates strongly with the uniaxial compressive strength for natural materials and that the force measured during the core drilling test can then be considered to represent the compressive strength of the rock.

4. Evolution of the properties of the alterite with the weathering

4.1. Petrography of the alterite

Thin sections (Fig. 4A) in fresh (Grade I) and weathered (Grades III and V) samples of Petit Granit reveal a crinoidal packstone following the classification of Dunham (1962). The fresh rock (PG130) is mainly composed of closely packed crinoids and other bioclasts while there are no significant differences between the fresh and weathered samples until the weathering is most intense (i.e. in zone V). In sample PG08, for example, there is a clear increase in the porosity indicating that the smallest calcite grains have been dissolved and this has left the larger grains in a loose or poorly-cemented structure.

The total XRD spectra for three representative samples of weathered Petit Granit. This presents a semi-quantitative analysis of the composition of the crystallised part of the rock - zone I: mainly calcite (~ 97 %) with some quartz (~ 2 %) and dolomite (~ 1 %); zones II to V: mainly calcite (~ 98 %) with quartz (~ 2 %) and traces of dolomite and gypsum; zone VI: comparatively less calcite (~ 75 %) compared to the insoluble materials of quartz (~ 19 %), dolomite (~ 2 %), pyrite (~ 3 %), gypsum (~ 0.5 %) and clays (~ 0.5 %).

Most of the limestone matrix in fresh rock (e.g. PG130) exhibits a dull brownish luminescence under CL (Fig. 4B) while crinoids display a dark CL with scattered red-luminescing speckles, which are micrometer-size dolomite rhombs resulting from diagenetic stabilisation of the magnesian calcite produced by echinoderms (Blake et al., 1984). Diagenetic dolomite, which often displays growth zoning, also occurs as larger rhombs in the matrix of the rock and many of these dolomite rhombs exhibit bright yellow-luminescing patches that are preferentially clustered along their outer rim. This calcite results from the partial dedolomitisation of the dolomite, which is a common ‘late diagenetic’ process induced by fluids with a low Mg/Ca ratio, such as meteoric water (Ayora et al., 1998). In moderately weathered rock (e.g. PG21), CL analysis reveals that all the dolomite was dedolomitised except for the micrometric dolomite inclusions in crinoids and it appears that the sparite formed an efficient barrier that protected the dolomite inclusions against the dedolomitising fluids. However, in highly weathered rock (PG08), dedolomitisation started to affect the inclusions along cracks that are, to a greater or lesser extent, influenced by cleavage planes (Fig. 4). It has been found that cracked crinoids are very common in the alterite (about 90 %) and this poses questions regarding the origin of these cracks: (i) tectonic stresses could have cracked the crinoids during or after the formation of the initial fracture within the rock; (ii) the cracks may have originated from compaction due to loss of the bearing capacity of the alterite; (iii) given that calcite has higher density than dolomite, volumetric expansion during dedolomitisation could have developed internal stress in crinoids which lead to their subsequent cracking. Irrespective of the origin of the cracks, the fracture-controlled dedolomitisation of crinoids demonstrates the importance of permeability during dedolomitisation and for weathering in general at the microscopic scale. It also appears that fine-grained apatite crystals, dark organic matter, and pyrite are more abundant in the alterite but as yet there is insufficient data that can be used to assess their origins and their relationship with the weathering processes.

The powder X-ray diffraction (Fig. 5) has highlighted a three-stage evolution in the crystallized composition of the alterite. The fresh rock (zone I) is composed of more than 97 % calcite, the remainder being quartz and dolomite. From the slightly (zone II) to the completely (zone V) weathered rock there is a strong decrease in dolomite and this disappears almost completely as a result of dedolomitisation while the ratio of calcite to quartz remains unchanged. The residual soil (zone VI) shows a large change in the rock composition. As a result of the dissolution of calcite, the concentration of insoluble components increases, with calcite representing 75 % of the crystalline phase and the concentration of quartz increasing almost tenfold (~ 18 %) while the accessory crystallised minerals are pyrite, dolomite, gypsum, and clays. Although dedolomitisation is greatest in the alterite, the dolomite that is still detected in XRD is associated with micro-inclusions in calcite. Gypsum, which quickly forms as the alterite is exposed to the atmosphere, is derived from the oxidation of pyrite and subsequent reaction of the resulting sulphuric acid with calcite.

XRD analysis of oriented aggregates (Fig. 6) enabled the different clay minerals to be determined. The fresh to moderately weathered rock (zones I to III) contains only well-crystallised illite peaking at 10Å. Smeectite is observed in the more weathered samples (e.g. in zone V). This is a swelling clay, which peaks at ca. 12 Å in natural preparation, around 17 Å when glycolated, and at 10 Å after heating. Kaolinite is found at 7.15 Å in the residual soil (zone VI) whose structure collapses when heated, which indicates it is a poorly crystallised kaolinite most probably formed by low-T weathering and not from diagenetic dickite, which is a common accessory mineral in many Palaeozoic rocks in Belgium including the Carboniferous limestones. However, it is not clear whether or not the neoformation of kaolinite is linked to the same processes that caused weathering of the Petit Granit, as it may instead relate to the downward infiltration of the Lower Cretaceous (Wealdian) sediments, which were observed previously in other sections within the quarry and contain palaeosol-derived kaolinite (Quinif et al., 2006).
4.2. Petrophysical and mechanical properties of the alterite

As detailed in Section 2.3, different analyses were undertaken in order to quantify the CaCO$_3$ content and to determine the petrophysical and mechanical properties of the rock. The obtained results are summarised in Table 2 and have been drawn into graphs on Figure 7. It has been found that the measured properties of the competent host rock demonstrate that the Petit Granit is a compact limestone (density of about 2.65 g/cm$^3$ and porosity of less than 2 %), very pure (CaCO$_3$ mass content of 98 %), with a high mechanical resistance (resistance force to drilling of more than 1000N). The Petit Granit has a rather homogeneous composition as shown by the low standard deviations measured on the sample of fresh rock. It is clear that weathering has a large influence on all of these properties.

The rock density (Fig. 7A) decreases regularly with the weathering down to 0.7 g/cm$^3$ in the residual soil, almost four times less than the initial density. The calcium carbonate mass content (Fig. 7B) continues to be stable for low levels of weathering, drops to about 90 % for moderate levels of weathering, then decreases dramatically to about 40 % of the total mass of the sample in the residual soil. From mass content of m$_{CaCO_3}$ and the density (d) of the samples, the volume content of v$_{CaCO_3}$ is easily computed using Equation [2]:

$$v_{CaCO_3} = \frac{m_{CaCO_3}}{d}$$

CaCO$_3$ (v$_{CaCO_3}$) is easily computed using Equation [2]:

with d$_{CaCO_3}$ = 2.71 g/cm$^3$ the density of the calcite. The development of the volume content is plotted on Fig. 7C. Initially the calcium carbonate represents 95 % of the rock volume but this figure decreases steadily with weathering until it drops dramatically in the residual soil to only 10 %.

The total porosity increases steadily from the fresh rock to the residual soil where the porosity attains up to 65 % (Fig. 7D). Paradoxically, this increase in porosity is not visible on the thin section of zone III (Fig. 4), from low to intermediate weathering, which suggests that the increase in porosity is due to micro-porosity. The weathering changes the rock from an impermeable limestone to a material equivalent of coarse gravel. The nitrogen permeability (Fig. 7E) also increases with weathering. The permeability of the fresh rock is lower than the sensitivity of the equipment, so it is less than 0.57mD. This increases exponentially to reach more than 17 D in the completed weathered rock (Grade V). However, the permeability decreases again in the residual soil, to 2 D, a trend that may be explained by the presence of greater
quantities of clay and organic matter in zone VI. The resistance of the Petit Granit to drilling (Fig. 7F) shows a slight increase at the boundary between the fresh and weathered zone (PG49). It is not possible to accurately determine if this is due to weathering or the heterogeneity of the rock in this transition zone as there are insufficient measurements. However, the standard deviation of the strength of the fresh rock is about 3% but increases in sample PG49 to 6% and it is, therefore, likely that this is due to the weathering. Indeed, the materials dissolved during weathering are carried away by the flow and may precipitate elsewhere within the system, especially if the physico-chemical conditions change abruptly as happens at the boundary between the fresh and weathered rock. This slight increase is followed by a very sudden drop in the resistance to reach only 16 N at the contact between hard rock and loose alterite. The test could not be performed in the alterite because its resistance is below the measuring range of the equipment and it was, therefore, considered equal to zero.

4.3. The relationships between porosity and the other alterite properties

The petrophysical and mechanical properties have been plotted against porosity in order to assess the changes in each property against one indicative of the weathering intensity. The best fit curves were constructed using the least squares curve fit method. It is clear that a linear increase in porosity (Φ) caused by the dissolution of CaCO₃ induces a linear decrease in density (d) and volume content of CaCO₃ (V_{CaCO₃}). The points from zones I to V correlate strongly and the regression lines fit well: \( d = 2.68 - 2.52 \cdot \Phi \) (Fig. 8A) and \( V_{CaCO₃} = 0.97 - 1.05 \cdot \Phi \) (Fig. 8B) but the measured values are lower than those predicted by the regression lines in zone VI, which is interpreted to result from compaction due to the weathering. The nitrogen permeability (k) increases exponentially with porosity: \( k = 0.57 \cdot \exp(48 \cdot \Phi^{1.58}) \) (Fig. 8C) with the exception of the final point taken from the residual soil (zone VI). It is clear that the curve fitted by the least squares method is influenced strongly by outliers and these skew the whole curve. To reduce the influence of these outliers another best fit curve was calculated using a robust method. Finally, the strength (R) of the rock decreases rapidly and linearly with porosity: \( R = 1046 - 3374 \cdot \Phi \) (Fig. 8D).

5. Limitations and discussions

The permeability of the loose alterite is difficult to measure following the sampling method used in this study as the material has to be recovered in a metallic pipe with a diameter of 25 cm.
mm and placed directly into the permeameter. In order to avoid leakage between the sample site and the apparatus, a confining pressure is applied to the sample. However, with this type of sample, it is only possible to apply the confining pressure to the metal tube. This has a beneficial effect but may also have a negative effect on the measure: as the sample is very soft, the metal tube prevents the sample from becoming crushed under the confining pressure but the seal between the tube and the sample is no longer guaranteed. It is, therefore, imperative to take some precautions so as to prevent leakage flows when measuring the permeability. The test must be conducted soon after sampling and without drying the sample in order to avoid shrinkage of the material and the creation of cracks within it.

Through XRD analysis, major changes in composition of clay samples were revealed during weathering and especially the appearance of kaolinite in the heart of the alterite. It will be necessary to determine its origin and its influence on the decrease in permeability observed in zone V. Moreover, the Petit Granit is a fossiliferous rock naturally rich in organic matter, and the proportion of organic matter becomes more important in the alterite. It would be interesting to study its specific content and its origin to determine whether the organic matter was simply concentrated during the weathering or if external inputs should be considered.

Finally, it would be beneficial to develop a method that could be used to measure the mechanical properties of the rock across the whole weathering profile, even in those places where the material is soft and has a very low resistance. One possible method is the micro-drilling. However, the design of the drill bit must be adapted to allow a good chip evacuation even in the case of more plastic materials such as the alterite. Finally, as this test is very local, it is necessary to repeat the measure a sufficient number of times to take into account the heterogeneity of the material.

6. Conclusions

The Carboniferous limestone aquifer in southern Belgium is the main source of drinking water in this region. It is affected by weathering phenomena in many areas and this has created interconnected zones with modified rock properties at the centimetre to decimetre scale. This weathering network influences the flow of water and its retention capacity while also making the material and the creation of cracks within it. This weathering network influences the flow of water and its retention capacity while also making the material and the creation of cracks within it. This weathering network influences the flow of water and its retention capacity while also making the material and the creation of cracks within it.

Further work will provide a more detailed understanding of the changes in rock composition and in its crystallographic structure.

7. Acknowledgments

The authors would like to thank Les Carrières de la Pierre Bleue Belge for granting access to their quarries and for providing the materials used in this study. Finally, we express our thanks to the reviewers Matt Rowberry and Laurent Bruxelles for the helpful comments and corrections which greatly improve the present manuscript.

8. References


Fischer, C., Schmidt, C., Bauer, A., Gaupp, R. & Heide, K., 2008. Implications of dedolomitisation and the neoformation of clays, reported here for the first time, are comparatively minor and not thought to impact greatly upon the rock properties.