**Pedogenic carbonate nodules as soil time archives:
challenges and investigations related to OSL dating**

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Abstract

Pedogenic carbonate nodules have been observed in the Far North region of Cameroon. They have been interpreted as Vertisol relic components inherited from the African Humid Period (AHP), however their processes of formation remain poorly constrained. Here we explore the possibility of targeting the minerals trapped within such nodules, which represent a residual soil fraction, to date the deposition time of the soil parent material using optically stimulated luminescence (OSL). As the trapped minerals have a complex history, related to pedogenesis and sedimentary processes since their deposition, it was necessary to identify a suitable mineral population. To achieve this, a nodule collected at the surface was investigated in order to compare the OSL signals from feldspar minerals from within its external and internal parts. The resultant luminescence data were then compared with minerals trapped in a buried nodule, with the scatter in OSL signals between the different populations indicating potential partial bleaching of grains and/or pedoturbation processes. Our results show that the minerals from the internal part of the nodule are appropriate for OSL dating. Furthermore, the environmental dose rate has changed through time following carbonate precipitation and the radionuclide decay series may be in disequilibrium. Because of its solubility, the ^{238}U -series is particularly affected, and when a complete absence of ^{234}U daughters is assumed, our calculations show a maximum and significant decrease of 20% in the environmental dose rate compared to secular equilibrium. Finally, changing the time of carbonate nodule precipitation results in a maximum OSL age range of 12 ka (from 15 to 27 ka) for the deposition of the soil parent material. Despite this relatively high uncertainty, these ages suggest that the deposition occurred before the AHP. Consequently, if their formation time is well constrained from independent methods, the pedogenic carbonate nodules can be exploited as valuable time archives, providing temporal information on soil parent material deposition and thus a maximum age for the onset of pedogenesis.

Key-words: Partial bleaching; U-series disequilibrium; Environmental dose rate; African Humid Period; Northern Cameroon

1. Introduction

Pedogenic carbonates comprise CaCO_3 accumulations in soil horizons (Lal and Kimble, 2000; Tanner, 2010), which can have various morphologies such as nodular, laminar, tubular, and also different strengths (e.g. Durand et al., 2007). They are widespread and their geochemical properties (e.g. stable carbon and oxygen isotopic composition) can be used as proxies for reconstructing palaeo-climatic conditions (e.g. Dworkin et al., 2005; Retallack, 2005; Yang et al., 2014), palaeo-elevations (Quade et al., 1989; Quade et al., 2007) and also for assessing palaeo-vegetation (Cerling, 1984; Ding and Yang, 2000). The occurrence of pedogenic carbonate is generally observed in soils where there is enough water to provide ions in solution (e.g. Ca^{2+}) and, at the same time, where the moisture regime can be sufficiently xeric (i.e. dry) to reach calcite supersaturation and lead to secondary carbonate precipitation and accumulation (Deocampo, 2010; Gocke et al., 2012; Zamanian et al., 2016). Consequently, pedogenic carbonates are characteristic soil features of arid to sub-humid climatic conditions or where soil moisture conditions alternate strongly (Cerling, 1984; Gocke et al., 2012). Pedogenic carbonates also comprise an important part of the global soil carbon budget (around 30-40% of the global soil carbon inventory is soil inorganic carbon; Eswaran et al., 2000), and, in addition to understanding the processes of their formation, it is also important to constrain the time scale of carbonate precipitation. Numerical dating is possible with methods such as U/Th dating (e.g. Durand et al., 2007; Violette et al., 2010) and radiocarbon dating (e.g. Williams and Polach, 1971; Achyuthan et al., 2010). Furthermore, pedogenic carbonates may also contain a substantial non-carbonate fraction and we show here that this fraction can give important temporal constraints for sedimentary processes and soil formation.

In the Far North Region of Cameroon (Fig. 1A), pedogenic carbonate nodules formed in clay-rich soils have been investigated in granitic watersheds belonging to the Chad Basin. These soils are highly eroded and degraded (Fig. 1B), and have been interpreted as Vertisol relics (Diaz et al., 2016) likely inherited from the African Humid Period (AHP), which lasted from c. 15 ka to c. 5 ka (deMenocal et al., 2000). Consequently, the carbonate nodules may be important continental palaeo-environmental archives for this region (Alonso-Zarza and Tanner, 2010), where major precipitation variations occurred in relation to the northern migration of the monsoon

front (deMenocal et al., 2000; deMenocal and Tierney, 2012; Shanahan et al., 2015). The aim of this study is to explore the potential of the carbonate nodules as time archives using the mineral fraction trapped within them. The nodules are pedogenic in origin (Diaz et al., 2016), i.e. were formed *in situ* in the host soil, meaning that primary minerals trapped within them represent a residual soil fraction (Fig. 1C). Singhvi et al. (1996) previously explored this trapped mineral fraction in carbonate nodules using thermoluminescence (TL) dating, to assess the age of carbonate precipitation. Here we aim to use this trapped mineral fraction for dating the deposition time of the soil parent material, i.e. the sediment from which Vertisols and then carbonate nodules formed, through the measurement of optically stimulated luminescence (OSL). The trapped minerals have a complex post-deposition history linked to pedogenesis (i.e. Vertisol genesis) and subsequent geomorphological processes (i.e. erosion; Diaz et al., 2016). This needs to be carefully addressed for accurate interpretation of the luminescence measurements and OSL age calculations.

Luminescence dating is a useful method for establishing absolute Quaternary chronologies in continental sedimentary sequences. It is widely used to determine the time that has elapsed since buried sediments were last exposed to sunlight. During burial, trapped electrons accumulate in the minerals in response to environmental radiation (α -, β -particles and γ -rays) emitted by the decay of radiogenic elements present in the host sediment and by cosmic rays. These electrons recombine when the minerals are exposed to light or heat, resulting in the emission of light (luminescence), and can thus be used to date the deposition time of the sediment (Aitken, 1998). In luminescence dating, an age (ka) is derived from:

$$Age = \frac{D_e}{\dot{D}} \quad (1)$$

where, D_e is the equivalent dose (Gy) and relates to the natural dose received by the mineral, and $\dot{D}$ is the environmental dose rate ($Gy\ ka^{-1}$).

Successful OSL dating of trapped minerals within pedogenic carbonate nodule requires two main challenges to be addressed. First, the D_e value of the sample needs to be carefully determined, as some nodules were brought at the surface

following erosion processes and were thus exposed to light. Consequently, there is a risk that the OSL signal of the trapped minerals has been partially reset, which would result in an underestimation of the sediment depositional age. Moreover, the investigated soils are Vertisol relics. Vertisols are clay-rich, smectitic-rich soils and are affected by swelling-shrinking processes due to soil moisture changes (Wilding, 2004; Southard et al., 2011). These processes induce vertical crack structures leading to the input of surficial soil material in deeper horizons (Food and Agriculture Organization, 2014). Consequently, these pedoturbation processes can potentially cause a mixing between younger and older sedimentary grains. Both partial bleaching, due to erosion, and sediment mixing, due to pedoturbation, are expected to induce some variability in the D_e distribution (Bateman et al., 2003). The second challenge is to accurately characterize the environmental dose rate ($\dot{D}$). Carbonate accumulation must have led to chemical changes in the soil environment. The concentration of radionuclides surrounding the trapped minerals has thus changed since carbonate precipitation, affecting the $\dot{D}$ (Aitken, 1998). Environmental radiation is mainly emitted following the decay of the uranium (U) and thorium (Th) series and the simple decay of potassium (K) and rubidium (Rb), as well as an additional cosmic dose component. In luminescence dating, the decay series are generally assumed to be in secular equilibrium, implying that the dose rate is constant through time (Olley et al., 1996; Aitken, 1998). However, in the case of carbonate nodules, it is likely that disequilibrium has occurred due to the precipitation of carbonate (Ferronsky and Polyakov, 2012). Finally, as relic soils have been subsequently eroded, the contribution from cosmic rays may have also changed through time, which should also be assessed.

To summarize, two main questions are investigated in this study: (1) is there a suitable population of trapped minerals within the pedogenic carbonate nodules for luminescence dating, and (2) can the $\dot{D}$ changes through time and potential disequilibrium effects be adequately accounted for? Overcoming both challenges would enable the minerals trapped within the carbonate nodules to be used to date the deposition time of the soil parent material. This would also set a maximum age for the onset of pedogenesis, constraining the carbonate nodule genesis that related to the formation and evolution of the Vertisols. As such, pedogenic carbonate

nodules can be used as sedimentary archives in a multi-proxy approach using not only the carbonate fraction but also the silicate fraction, which is the objective of this study.

2. Material and Methods

2.1 General settings and sample preparation

The pedogenic carbonate nodules were collected from soils located in the Diamare piedmont (Far North region of Cameroon) where they form mima-like mounds in eroded areas (Fig. 1B; Diaz et al., 2016). This specific soil morphology was recently attributed to pedogenesis and later erosion processes. The mounds were defined as Vertisol relics, i.e. degraded Vertisols, and the precipitation of carbonate nodules is related to Vertisol genesis (Diaz et al., 2016). In the present-day, non-degraded Vertisols occur downstream in piedmont waterlogged areas (Brabant and Gavaud, 1985). This suggests that Vertisols were more extensive under past wetter climatic conditions, where humid areas were widespread (Diaz et al., 2016). Due to changes in the position of the monsoon front during the Quaternary, such expansion must have occurred during the AHP (Lézine et al., 2011; Armitage et al., 2015), as precipitation is strongly linked to the position of the monsoon front (Fig. 1A). The assessment of the time of soil parent material deposition is thus crucial for constraining the onset of Vertisol genesis and confirming their possible inheritance from the AHP.

For logistical reasons, soil samples were not collected under light-safe conditions and thus cannot be directly used for luminescence dating. Consequently, we propose to explore an alternative approach by using the trapped mineral fraction within the carbonate nodules to assess the time of soil parent material deposition. In the mima-like mound settings, the carbonate nodules are found both as a cover at the surface and within the soil matrix (Fig. 1B). Thin sections show that a significant fraction of the carbonate nodules comprises a residual soil component (Fig. 1C). X-ray diffraction measurements also confirm this observation, with averages ($n = 5$) of $57 \pm 8\%$ calcite (CaCO_3) and of $43 \pm 8\%$ other minerals (e.g. quartz, feldspars, phyllosilicates, oxides). These non-carbonate minerals have been shown to represent the surrounding host sediment mineralogy (Diaz et al., 2016). However, in such settings, this trapped mineral fraction has experienced a complex history from

grain deposition to sampling for OSL analysis. Several steps can describe the trapped mineral history (Fig. 2). First, the mineral grains are deposited and buried to constitute a sediment sequence (step I). From this sediment deposit, soils (e.g. Vertisols) have then developed during step II. Vertisol genesis induced favourable conditions for secondary carbonate accumulation (Wieder and Yaalon, 1974; Ahmad, 1983) with pedogenic carbonate nodule precipitation that trapped a host soil fraction (step III). Note that there are unknown time gaps between steps I and II, and between steps II and III. Finally, erosion affected the Vertisols leading to the present-day mima-like mound Vertisol relics with some nodules brought to the surface (step IV). As already stated, this complex history has direct implications for the equivalent dose data and for the dose rate assessment.

To investigate the possibility of using trapped minerals for OSL dating despite the complex setting, two carbonate nodules were selected. One nodule was collected at the surface (NO1, diameter ($\emptyset$) = 10 cm) and a second nodule was collected at 100 cm depth in a mima-like mound (NO2, $\emptyset$ = 4 cm). Due to its surficial position, sample NO1 was exposed to light for an unknown duration. To assess the influence of sunlight exposure on the luminescence signal, the outer most layer of sample NO1 (NO1_{Ext}, 2-3 cm thick) was removed under red light conditions using a diamond saw and isolated from the central part (NO1_{Int}). The luminescence properties of grains from both NO1 subsamples and the buried sample NO2 were then compared. A non-light-safe mineral population should exhibit partial bleaching, following sample exposure to sunlight after carbonate precipitation, and thus a scatter in the equivalent dose (D_e) distribution should be expected. Consequently, a scatter in the equivalent dose distributions could be induced by pedoturbation processes (Bateman et al., 2003), affecting NO1_{Ext}, NO1_{Int}, and NO2, while we expect sunlight exposure to preferentially affect NO1_{Ext}.

The nodules were treated with HCl (35%) to remove carbonates and with H₂O₂ (20 vols) to remove any organic material. Samples were then sieved to isolate the 90-180 μ m fraction, which was selected for further analysis because of the abundance of grains in this range. The minerals were then separated by density using sodium polytungstate to isolate quartz (2.7-2.62 g cm⁻³), plagioclase (2.62-2.58 g cm⁻³) and K-feldspar (<2.58 g cm⁻³). A low abundance of quartz led us to the use the K-feldspar

fraction, which was not etched (Duller, 1992). Each sample preparation step was performed under subdued red light conditions.

2.2 Luminescence measurements

Luminescence measurements were performed using a Risø TL/OSL-DA-20 reader (dose rate $\approx 0.1 \text{ Gy s}^{-1}$) at the Institute of Earth Surface Dynamics (University of Lausanne). To assess the D_e , a single-aliquot regenerative post-IR IRSL protocol was used to access a high temperature signal from feldspars, which is in theory less affected by anomalous fading (Thomsen et al. 2008; Buylaert et al., 2009). A pre-heat of 250°C for 60 seconds was followed by an IR stimulation at 50°C for 100 seconds (IR₅₀) and a post-IR IRSL stimulation at 225°C for 100 seconds (pIRIR₂₂₅). This pIRIR₂₂₅ protocol was chosen instead of the pIRIR₂₉₀ protocol to limit high potential residual doses from partial resetting and thus age overestimations (Thiel et al., 2011, Roberts, 2012). The measured responses of the aliquot to a regenerative dose (L_x) and to a test dose (T_x) were integrated over 3 seconds, and the background signals were integrated over the last 10 seconds of stimulation. Measurements were done using small aliquots (SA, $\varnothing = 1 \text{ mm}$, 100-150 grains measured per aliquot), mounted on stainless steel discs, and single grain measurements were done using aluminium discs (hole diameter $\varnothing = 300 \text{ }\mu\text{m}$, 10-20 grains per hole). Due to a high number of grains in the single grain disks, we refer to these as pseudo-single grain (PSG) measurements. However, SA and PSG comparison still allow us to further investigate the possibility of partial bleaching through reducing the number of analysed grains by one order of magnitude (Duller, 2008). The measurement protocol was validated using a dose-recovery test (Murray and Wintle, 2003) and PSG measurements ($n = 3 \text{ discs} \approx 120 \text{ measurements}$), whereby samples were exposed for 4 hours to direct sunlight in Lausanne prior to measurement. Samples were given a dose approximately equal to the equivalent dose ($\sim 30 \text{ Gy}$) and dose recovery ratios were calculated following subtraction of measured residuals ($n = 3 \text{ discs} \approx 120 \text{ measurements}$).

Although the post-IR IRSL protocol reduces the effects of anomalous fading, a fading test was done for both samples ($n = 3 \text{ SA discs}$) following Huntley and Lamothe (2001). Previously measured aliquots were given a dose approximately equal to the equivalent dose ($\sim 30 \text{ Gy}$) and measured following increasing delays ($n =$

4) between 100 and 800 minutes. The resulting g-values (%/decade) were calculated following Auclair et al. (2003) and were normalised to 2 days (Huntley and Lamothe, 2001).

Finally, the D_e values were determined using Analyst v.4.31.7 (Duller, 2015) according to the following acceptance criteria: recycling ratios within 5 and 10% of unity for SA and PSG measurements respectively, maximum test dose and palaeodose error <10%, and maximum recuperation <10% of the natural luminescence signal. The D_e values of the samples were calculated using the central age model (CAM; Galbraith et al., 1999) and are cited at 1σ uncertainty. The sample residual doses and the dose recovery test D_e values are reported with standard error (SE) and 1σ uncertainties, respectively.

2.3 Environmental dose rate assessment

The external dose rate ($\dot{D}_{ext}$ in Gy ka⁻¹) is defined as:

$$\dot{D}_{ext} = \dot{D}_{\alpha} + \dot{D}_{\beta} + \dot{D}_{\gamma} + \dot{D}_{cos} \quad (2)$$

where, $\dot{D}_{\alpha}$, $\dot{D}_{\beta}$ and $\dot{D}_{\gamma}$ are the energy emitted by α -, β -particles and γ -rays, respectively, and $\dot{D}_{cos}$ is the cosmic ray dose rate. As K-feldspars are used in this study, it is also necessary to consider the contribution of the internal dose rate ($\dot{D}_{int}$) resulting from the internal K decay. The combination of the external and internal doses gives the environmental dose rate ($\dot{D}$). The soil and nodule U (ppm), Th (ppm), K (%) and Rb (ppm) compositions were assessed by X-Ray fluorescence at the Institute of Earth Sciences (University of Lausanne) and by ICP-MS at Actlabs (Activation Laboratories, Ancaster). The internal K-content (%) was measured on individual feldspar grains (n = 187) with a JEOL 8200 Superprobe at the Institute of Earth Sciences (University of Lausanne). The calculations of $\dot{D}_{int}$ and $\dot{D}_{cos}$ were done with the online dose rate calculator DRAC v1.1 (Durcan et al., 2015). The beta grain size attenuation factors of Guérin et al. (2012) and alpha grain size attenuation factors of Bell (1980) were used. The cosmic ray dose rate contribution was assessed using the protocol outlined by Prescott and Hutton (1994) corrected for the geomagnetic latitude (11.789°N; F = 0.39, J = 0.55 and H = 4.35), and taking into account the cosmic-ray attenuation with depth (0 and 100 cm for nodules NO1 and

NO₂, respectively). We used the water content attenuation factors of 1.5 (α), 1.25 (β) and 1.14 (γ) following Zimmerman (1971) and Aitken and Zie (1990).

2.3.1 External dose rate changes through time

Due to carbonate precipitation, the chemical environment surrounding the minerals varied since the time of deposition (t_0), resulting in external dose rate ($\dot{D}_{ext}$) changes (Fig. 2). During the time period T_1 , environmental radiation is solely derived from the radionuclides within the soil matrix and the cosmic dose rate ($\dot{D}_{ext1}$). However, following carbonate precipitation (i.e. during the time period T_2), the α - and β -contributions are derived from radionuclides composing the carbonate nodule, whilst the γ -dose is derived from both the surrounding soil and the carbonate nodule (Aitken 1985). As nodule diameters are 10 cm (NO1) and 4 cm (NO2), the nodules cannot be seen as an infinite matrix, and γ -rays emitted by the host sediment have to be considered. The γ -dose contribution thus needs to be scaled by the nodule size. To summarize, the carbonate nodule formation results in a different external dose rate ($\dot{D}_{ext2}$). However, beyond this simple time frame, there are some potential complexities that still need to be investigated:

- a. During the time period T_1 , pedogenesis begins followed by potential carbonate accumulation, leading to a different soil chemical environment (step II). How does this affect the $\dot{D}_{ext1}$ assessment?
- b. When the minerals become trapped in a nodule (step III), the nodule growth rate is unknown. The nodule size has most likely increased incrementally through time with different precipitation events, resulting in an uncertainty on the scaled γ -dose. This may also influence the β -dose, but only at the early onset of precipitation when the carbonate size was <3 mm (Aitken, 1985); we thus assume this effect to be negligible. Concerning the γ -dose, can the nodule growth rate affect the $\dot{D}_{ext2}$ assessment?
- c. Has the cosmic ray contribution changed through time, due to late-stage erosion (step IV), which would then affect the $\dot{D}_{ext2}$?

These different points need to be addressed in the assessment of the environmental dose rate changes, and will be individually discussed in the next sections.

2.3.2 Decay chain disequilibrium

In typical silt/sand alluvium, the U and Th decay chains can contribute up to approximately 50% of the external dose rate $\dot{D}_{ext}$ (Olley et al., 1996). In most luminescence dating applications, the decay chains are assumed to be in secular equilibrium with $\dot{D}_{ext}$ constant over Quaternary timescales (Armitage, 2015). However, because some radionuclides are mobile, in surficial sediments the ^{238}U decay chain is likely to be in disequilibrium (e.g. Osmond and Cowart, 1983; Short et al., 1989, Olley et al., 1996), and this disequilibrium is very common in environments where carbonates are present or where weathering processes occur (e.g. Guibert et al., 2009; Zander et al., 2013). Therefore, in the context of pedogenic carbonate nodules, the disequilibrium is linked to the incorporation of U within carbonate during nodule precipitation. In oxic environments, U exists mainly as uranyl species (UO_2^{2+}) and in waters it can form uranyl carbonates ($\text{UO}_2(\text{CO}_3)_2^{-2}$) (Chabaux et al., 2008). The disequilibrium of U is mainly caused by the α -recoil of ^{238}U in minerals, inducing the ejection of ^{234}Th at the mineral boundaries. This radionuclide will decay rapidly to ^{234}U , and due to high U solubility it will be leached in pore fluids (DePaolo et al., 2006; Dosseto et al., 2008). Another process is the preferential release of ^{234}U from crystal lattices that are damaged by α -recoil (e.g. Andersen et al., 2009). Consequently, natural surficial waters are generally enriched in ^{234}U compared to ^{238}U .

As secondary carbonate precipitates from a supersaturated soil solution, the U incorporated in the secondary mineral has similar disequilibrium; because U is a heavy element, further fractionation can be assumed to be negligible. In most natural river waters the ($^{234}\text{U}/^{238}\text{U}$) activity ratio is close to unity when chemical weathering processes are dominant (Chabaux et al., 2003), higher than unity (up to 4) when physical erosion processes are dominant (e.g. Vigier et al., 2001; Andersen et al., 2009) or when groundwaters are contributing to surficial waters (Andersen et al., 2009; Chkir et al., 2009), and lower than unity if there is no renewal of sediment and thus a strong depletion in ^{234}U (Israleson et al., 1997; Riotte and Chabaux, 1999). In this study, low material availability prevented high-resolution gamma spectrometry to directly determine the degree of U-series disequilibrium. Consequently, following the literature summarized above, different ($^{234}\text{U}/^{238}\text{U}$) activity ratios between 0.5 and 3 have been investigated. Moreover, in order to illustrate the effect of the most extreme

disequilibrium scenario on the environmental dose rate, we have assumed that all the daughter radioisotopes of ^{234}U are absent following carbonate precipitation.

As a carbonate nodule precipitates within a soil, U is also derived from minerals within the residual soil fraction trapped in the nodule. This fraction of U is assumed to be in secular equilibrium, unlike the U included as $\text{UO}_2(\text{CO}_3)_2^{-2}$. In contrast to U, as chemical processes, such as ion leaching and secondary mineral formation, have no or very little effect on Th, this radionuclide should not accumulate in secondary minerals as a soluble phase (Ferronsky and Polyakov, 2012). A comparison of the granite, the soil and the carbonate nodule chemistry (Table 1), shows that Th is four to five times more abundant than U in the granite and soil, whereas the Th and U contents are approximately equal in the carbonate nodule. Uranium is thus in excess in the carbonate nodules, which is a consequence of U inclusion as $\text{UO}_2(\text{CO}_3)_2^{-2}$ during carbonate precipitation; whereas all Th within the carbonate nodule is a component of the trapped residual soil fraction. Consequently, considering the Th/U ratios of the soil $\left(\frac{\text{Th}}{\text{U}}\right)_{so}$ and nodule $\left(\frac{\text{Th}}{\text{U}}\right)_{no}$ given in Table 1, it is possible to distinguish the proportion of U derived from the residual soil fraction (f_{so}) included in the nodule, as follows:

$$\left(\frac{\text{Th}}{\text{U}}\right)_{no} = \left[\left(\frac{\text{Th}}{\text{U}}\right)_{so} * f_{so}\right] + \left[\left(\frac{\text{Th}}{\text{U}}\right)_w * f_w\right] \quad (3)$$

where f_{so} is the U fraction of the residual soil fraction trapped within the nodule, and f_w is the U fraction composed in water as $\text{UO}_2(\text{CO}_3)_2^{-2}$, and,

$$f_{so} + f_w = 1 \quad (4)$$

$$\left(\frac{\text{Th}}{\text{U}}\right)_w = 0 \quad (5)$$

so,

$$f_{so} = \frac{\left(\frac{\text{Th}}{\text{U}}\right)_{no}}{\left(\frac{\text{Th}}{\text{U}}\right)_{so}} \quad (6)$$

The sum of the two fractions represents the total U in the nodule (Equ. 4) and as all Th within the nodule is derived from the trapped residual soil fraction, the second term of Equation 3 is equal to zero (Equ. 5). The fraction of U included in the nodule

as a soil detrital fraction, and thus assumed to be in secular equilibrium, can thus be calculated according to Equation 6.

For the nodule samples and hypothesizing that the carbonate precipitation event is the main factor affecting disequilibrium, we can assume that only the ^{238}U -series is in disequilibrium. Concerning the ^{235}U -series, it comprises only 0.07% of total natural U. Its contribution to the total U dose rate is relatively small: c. 4% (α -decay), ~2% (β -decay) and ~1% (γ -decay) (Guérin et al., 2011). Consequently, we assumed this decay chain to be in secular equilibrium, while a potential disequilibrium (if present) would be negligible relative to the total U dose rate. Finally, as all Th is derived from the trapped residual soil fraction, i.e. not to the carbonate precipitation event, the ^{232}Th -series is also assumed to be in secular equilibrium.

2.3.3 Proposed burial scenarios

To assess the effect of disequilibrium from carbonate precipitation on the $\dot{D}$ (Gy ka^{-1}) and thus on the resulting OSL ages, two end-member scenarios have been considered (Fig. 2): (1) the surrounding environment of the minerals has changed through time but radionuclides have remained in secular equilibrium during both time periods T_1 and T_2 ; and (2) the surrounding environment of the minerals has changed through time, and, in addition, carbonate precipitation induced disequilibrium of the ^{238}U -series during time period T_2 . The relationships between the measured equivalent doses, the dose rates, and the time periods are as follow:

$$D_e = D_{e,so} + D_{e,no} = T_1 * \dot{D}_{so} + T_2 * \dot{D}_{no} \quad (7)$$

and,

$$\dot{D}_{so} = \dot{D}_{int} + \dot{D}_{ext1} \quad (8.1)$$

$$\dot{D}_{no} = \dot{D}_{int} + \dot{D}_{ext2} \quad (8.2)$$

where, D_e (Gy) is the equivalent dose, $D_{e,so}$ (Gy) is the dose received during the time period time T_1 which thus results from $\dot{D}_{so}$; and $D_{e,no}$ (Gy) is the equivalent dose received during the time period T_2 which thus results from $\dot{D}_{no}$. The internal dose rate ($\dot{D}_{int}$) does not change through time whereas the external dose rate is different during time T_1 ($\dot{D}_{ext1}$) and time T_2 ($\dot{D}_{ext2}$) as explained above. During T_1 , the soil environment also varied through time as carbonate progressively accumulated. In the

present-day soil, the proportion of carbonate nodules is 7% maximum. To assess this potential influence on the dose rate, the external dose rate for $\dot{D}_{so}$ was also calculated as mixture of a 7% $\dot{D}_{ext2}$ and 93% $\dot{D}_{ext1}$. Moreover, during time T_2 , the cosmic ray contribution varied following late-stage erosion (step IV). As the intensity and the timing of the erosion event are unknown, a mean $\dot{D}_{cos}$ was calculated assuming erosional removal of 30 cm of soil during approximately 30% of the total time period, i.e $T_1 + T_2$ (see section 3.2). Finally, the nodule growth rate during time T_2 remains unconstrained. As the nodule size is expected to increase incrementally through time, this would result in an uncertainty on the scaled γ -dose ($\dot{D}_\gamma$), which was calculated with varying nodule diameters from 0.5 to 10 cm.

2.4 Calculations

2.4.1 External dose rate

To assess the relative contributions of the different decay series to the external dose rate ($\dot{D}_{ext}$, Gy ka⁻¹), the method outlined by Stokes et al. (2003) and later applied by Armitage (2015) was used. It is possible to calculate the external dose rate for both time periods T_1 and T_2 (i.e. $\dot{D}_{ext1}$ and $\dot{D}_{ext2}$, respectively), either assuming secular equilibrium (scenario 1) or taking into account various degrees of ²³⁸U-series disequilibrium during T_2 (²³⁴U/²³⁸U ratios from 0.5 to 3, scenario 2). The resulting environmental dose rates calculated for scenarios 1 and 2 will then be compared to highlight the potential effect of disequilibrium on calculated environmental dose rates and OSL ages.

In the following section, each step leading to the calculation of the α , β and γ -event contributions to the $\dot{D}_{ext}$ are detailed. For the simple decay of K and Rb, the β and γ -dose contributions are calculated according to the conversion factors reported by Guérin et al. (2011). However, for the ²³⁸U-series, the radioisotope specific activity (k) needs to be calculated for each radiation event in order to account for potential disequilibrium.

The following calculations must be done for the α -, β - and γ -decays of each radioisotope. Here we detail a representative example for the α -decay contribution (k_α) of a radioisotope x ($k_{x\alpha}$):

$$k_{x\alpha} = (\sum_{parent}^{n\ daughters} E_{x\alpha}) * a * b * c_{\alpha} \quad (9)$$

where, $E_{x\alpha}$ is the decay energy (MeV/Bq s⁻¹) of a radioisotope x and for an α -decay (Table A.1), a is the number of seconds per ka, b is the number of joules (J) per MeV and c_{α} is the grain size attenuation factor for α -radiation (e.g. Bell, 1980). The k factor is thus expressed in J/Bq ka⁻¹. As U comprises two decay chains with different abundances in nature (99.29% for ²³⁸U and 0.07% for ²³⁵U), the k factors for each decay event (α , β and γ) must be adjusted by their relative abundance. The k factor for a given decay chain varies with the number of daughter radioisotopes that are considered, i.e. for a decay chain in secular equilibrium, all daughters will be considered in $E_{x\alpha}$ (i.e. the total energy of all α -particles for a given parent, listed in Table A.1).

As a result, the attenuated radiation (Gy ka⁻¹) for an α -decay event of an element X is calculated as follows:

$$X_{\alpha} = [X] * A_x * k_{x\alpha} \quad (10)$$

where, $[X]$ is the element concentration in ppm (or in % for K), A_x is the isotopic activity of the radioisotope x in Bq/kg ppm (i.e. the number of decays occurring in a given time for a specific number of atoms), and $k_{x\alpha}$ is the specific activity of radioisotope x for an α -decay event (Equ. 9).

Both ²³⁸U and ²³⁵U radionuclides have to be added and scaled by their respective activities (A) and k factors for a given U content $[U]$ (Equ. 11). Finally, for α -decay events, it is necessary to take into account the effectiveness of the α -particles (Aitken, 1985; Aitken, 1998) and thus to multiply the outcome of Equation 8 by the a -value (a_{val}). Balescu and Lamothe (1993) measured the alpha efficiency of 150-250 μ m K-feldspar grains for their samples, estimating an a_{val} of 0.11 $\pm$ 0.03, which we use in this study. The final equation to assess the energy of the U α -decay event (Gy ka⁻¹) is:

$$U_{\alpha} = ((A_{238U} * k_{238U\alpha} * [U]) + (A_{235U} * k_{235U\alpha} * [U])) * a_{val} \quad (11)$$

This calculation is valid for U series in secular equilibrium. However, for scenario 2 the ^{238}U -series is in disequilibrium; we can assume that all daughter radioisotopes below ^{234}U are absent, and that ^{234}U may be in excess or in deficit. Consequently, only the parent radioisotopes are considered in the calculation of E_x (Equ. 9), and $[U]$ is scaled by its ($^{\text{daughter}}X/^{\text{parent}}X$) activity ratio μ , which represents the excess or lack of $^{\text{daughter}}X$ compared to $^{\text{parent}}X$. Consequently, the U α -decay dose rate, where ^{234}U is in disequilibrium with ^{238}U , is:

$$U_{\alpha} = ((A_{238\text{U}} * k_{238\text{U}\alpha} * [U]) + (A_{234\text{U}} * k_{234\text{U}\alpha} * [U] * \mu) + (A_{235\text{U}} * k_{235\text{U}\alpha} * [U])) * a_{val} \quad (12)$$

Furthermore even in scenario 2, not all U within the nodule can be considered to be in disequilibrium because some is derived from the residual soil fraction (Equ. 6). Consequently, the U_{α} dose rate needs to be calculated for both equilibrium and disequilibrium, and the U concentrations $[U]$ must be multiplied by the relative proportions calculated in Equation 6.

After the calculation of the contribution for each element, the same decay events' contribution must be added together and corrected for water attenuation using the appropriate factor (here for $\alpha = 1.49$; Aitken and Xie, 1990). The following equation shows an example for the total α -dose rate contribution ($\dot{D}_{\alpha}$):

$$\dot{D}_{\alpha} = \frac{U_{\alpha} + Th_{\alpha}}{(1 + 1.49 * \frac{WF}{100})} \quad (13)$$

where, U_{α} and Th_{α} are the attenuated doses calculated in Equations 11 or 12, depending on the scenario (1 or 2), and WF is the water content (%) of the sample (estimated here to be $10 \pm 2\%$).

Finally, the γ -dose rate ($\dot{D}_{\gamma}$) needs to be scaled during the time period T_2 . Because the nodule diameter is <30 cm, a nodule cannot be considered as an infinite matrix (Fig. 2). The final $\dot{D}_{\gamma}$ then accounts for the self-dose from the nodule and a contribution from the host sediment (Aitken, 1985):

$$\dot{D}_{\gamma} = \frac{p}{100} \dot{D}_{\gamma}^i + (1 - \frac{p}{100}) \dot{D}_{\gamma}^{ex} \quad (14)$$

where, the self-dose p (%) is calculated by multiplying the diameter of the nodule (cm) by its density (2.7 g cm^{-3} , as estimated for the nodules ($n = 5$)), $\dot{D}_\gamma^i$ is the gamma dose emitted by the decay of radionuclides present in the carbonate nodule, and $\dot{D}_\gamma^{ex}$ is the gamma dose emitted by the decay of radionuclides present in the soil.

2.4.2 OSL ages

The OSL age (ka) of trapped minerals, reflecting the deposition time of the soil parent material (t_0), can be calculated as follows:

$$t_0 = T_1 + T_2 = \frac{D_{e,so}}{\dot{D}_{so}} + \frac{D_{e,no}}{\dot{D}_{no}} \quad (15)$$

so,

$$t_0 = \left(\frac{D_{e,so}}{\dot{D}_{so}} \right) + T_2 \quad (16)$$

The length of T_2 , or the age of carbonate nodule formation, is thus important to assess. The objective here is to evaluate the effect of different T_2 durations on the OSL age (t_0) for both scenarios. As specified in section 2.1, the pedogenic carbonate nodules are expected to form in Vertisols inherited from the AHP from c. 15 to 5 ka BP; deMenocal et al., 2000). Moreover, it is not excluded that carbonate is still precipitating in the present-day, as the soil chemical conditions are still favourable (Diaz et al., 2016). Consequently, the two end-members, represented by the minimum and maximum deposition ages, are:

$$t_{min} = \frac{D_e}{\dot{D}_{so}} \quad (17)$$

$$t_{max} = \frac{D_e}{\dot{D}_{no}} \quad (18)$$

where, t_{min} considers that the carbonate nodule never precipitated, i.e $T_2 = 0$, and t_{max} considers that the carbonate nodule always existed, i.e $T_2 = t_0$. The true sediment age should lie between these two unlikely end-members, i.e. some residence time in the soil followed by a second phase trapped in the nodule (Equ. 15 and 16).

For the disequilibrium scenario, the OSL ages are first calculated with a ($^{234}\text{U}/^{238}\text{U}$) activity ratio of 1.31, assuming that the ^{234}U daughters are absent. This ratio value is used following the $^{234}\text{U}/^{238}\text{U}$ ratios measured for Holocene pedogenic carbonate nodules from a similar environment in India (Violette et al., 2010). Different activity ratio values are also tested in subsequent calculations in order to more specifically determine this effect on the OSL ages.

3. Results

3.1 Luminescence results

A summary of the luminescence results is given in Table 2 for nodules NO1 and NO2. The SA overdispersion values (OD) for subsample NO1_{Ext} are much higher than for subsample NO1_{Int} for both the IR₅₀ ($19.4\pm0.6\%$ and $8.6\pm0.3\%$, respectively) and pIRIR₂₂₅ ($8.4\pm0.3\%$ and $1.1\pm0.8\%$, respectively) signals. PSG measurements have higher OD values than SA measurements, but follow the same trends. The IR₅₀/pIRIR₂₂₅ ratios, which represent the relationship between the doses derived by the IR₅₀ and the pIRIR₂₂₅ signals, are 0.50 and 0.41 for PSG and SA respectively for NO1_{Ext}. For NO1_{Int}, they are 0.74 and 0.64, while for NO2 they are 0.66 and 0.60. This ratio is expected to be less than unity as the IR₅₀ signal is more affected by anomalous fading (Thomson et al., 2008). This is supported by the measured $g_{2\text{days}}$ values ($n=3$), which are $4.5\pm0.9\%$ /decade (NO1) and $5.0\pm0.7\%$ /decade (NO2) for the IR₅₀ signals, and $1.7\pm0.6\%$ /decade (NO1) and $1.9\pm0.6\%$ /decade (NO2) for the pIRIR₂₂₅ signals. Moreover, the pIRIR₂₂₅ signal has been shown to bleach more slowly than the IR₅₀ signal (Buylaert et al., 2012), supported for these samples by the residual doses measured after sunlight bleaching (~ 4 Gy for the IR₅₀ signal and ~ 8 Gy for the pIRIR₂₂₅ signal, Table 3). The dose recovery ratios (measured dose - residual dose/given dose) measured using PSG for both samples show acceptable deviations from unity within 10% (Table 3). The OD values for the PSG dose recovery test range between 10 and 24% (Table 3).

The D_e values determined using the PSG and SA measurement approaches are within uncertainties for all samples, and only the NO1_{Ext} IR₅₀ signal has a ratio beyond 10% of unity, i.e. 1.3 (Table 2 and Fig. 3). The kernel density estimate (KDE) plots illustrate the SA D_e distribution for NO1_{Ext} and NO1_{Int}, with both IR₅₀ (Fig. 4A)

and pIRIR₂₂₅ (Fig. 4B) signals. The difference between the two sample D_e values is smallest for the pIRIR₂₂₅ signal.

3.2 Dose rate assessment

Electron microprobe micro-analysis on individual grains indicated that the <2.58 g cm⁻³ mineral extract comprises 30% K-poor plagioclases (Oligoclase, K-content <5%) and 70% K-rich feldspars (Orthoclase), resulting in a mean K-content of 12.65±0.10% (±1σ) for the K-rich feldspar fraction. Assuming the K-rich feldspars contribute mostly to the measured signal, the calculated $\dot{D}_{int}$ is 0.45±0.09 Gy ka⁻¹ for both NO1 and NO2. The $\dot{D}_{cos}$ may have varied during T_2 following late-stage erosion (Step IV, Fig. 2). The extent of erosion is unknown but if we assume a total erosion of 30 cm, $\dot{D}_{cos}$ changes from ~0.21 Gy ka⁻¹ (before erosion) to ~0.29 Gy ka⁻¹ (after erosion) for NO1, and from ~0.17 to 0.18 Gy ka⁻¹ for NO2. The other unconstrained parameter is the proportion of time affected by the change in the $\dot{D}_{cos}$, i.e. when the erosion event occurred. As proposed by Diaz et al. (2016), this event occurred after nodule formation and could therefore have been initiated towards the end of the African Humid Period. The proportion of time affected by the change in $\dot{D}_{cos}$ should then be ~30%. Consequently, $\dot{D}_{cos}$ values of 0.25±0.03 Gy ka⁻¹ and 0.17±0.02 Gy ka⁻¹ are obtained for NO1 and NO2, respectively, for the whole time period, i.e. $T_1 + T_2$.

The external dose rates in the nodule ($\dot{D}_{ext2}$) were calculated for both scenarios. Continuing with the example of α -decay as developed in sections 2.4, the energy values for an α -decay ($E_{x\alpha}$) of the ²³⁸U-series in equilibrium is 42.87 MeV/Bq s⁻¹, whereas in disequilibrium, $E_{x\alpha}$ is reduced to 4.19 MeV/Bq s⁻¹ (Table A.2). The resultant $k_{238U\alpha}$ factors (Equ. 6) are thus 0.036 and 0.003, for the equilibrium and the disequilibrium scenario, respectively. This represents a one order of magnitude reduction in $\dot{D}_{U\alpha}$ (Table A.3). All the attenuated radiation values, for each element and radiation type, in the soil and nodule and for both scenarios, are given in the supplementary material (Table A.3).

Following Equations 3-6 and geochemical measurements (Table 1), the calculation of the U fraction included in the carbonate nodule as a soil detrital fraction, and thus assumed to be in secular equilibrium, is 0.24 (i.e. 24%). This

implies that 76% U was included as $\text{UO}_2(\text{CO}_3)_2^{-2}$ and can thus be assumed to be in disequilibrium. The resulting external dose rate during the time period T_1 ($\dot{D}_{ext1}$, i.e. from the soil and cosmic ray dose during step I), is $5.36 \pm 0.34 \text{ Gy ka}^{-1}$ and $5.28 \pm 0.34 \text{ Gy ka}^{-1}$ for NO1 and NO2 respectively. The external dose rate during the time period T_2 ($\dot{D}_{ext2}$, i.e. from the nodule and the soil), is $3.67 \pm 0.34 \text{ Gy ka}^{-1}$ and $3.79 \pm 0.34 \text{ Gy ka}^{-1}$ for NO1 and NO2, respectively, when assuming secular equilibrium (scenario 1). If disequilibrium is accounted for (scenario 2), the $\dot{D}_{ext2}$ is $3.00 \pm 0.34 \text{ Gy ka}^{-1}$ and $3.18 \pm 0.34 \text{ Gy ka}^{-1}$ for NO1 and NO2, respectively (Table 3).

The total environmental dose rate, i.e. taking into account the $\dot{D}_{int}$, for the time period T_1 ($\dot{D}_{so}$) is thus $5.81 \pm 0.34 \text{ Gy ka}^{-1}$ (NO1) and $5.73 \pm 0.34 \text{ Gy ka}^{-1}$ (NO2). For the time period T_2 ($\dot{D}_{no}$), when assuming secular equilibrium, it is $3.92 \pm 0.34 \text{ Gy ka}^{-1}$ (NO1) and $3.96 \pm 0.34 \text{ Gy ka}^{-1}$ (NO2), while it is reduced to $3.25 \pm 0.34 \text{ Gy ka}^{-1}$ (NO1) and $3.35 \pm 0.34 \text{ Gy ka}^{-1}$ (NO2) if disequilibrium is accounted for (Table 4).

The effect of different nodule diameters on the dose rate shows an increase of $\sim 0.3 \text{ Gy}$ between nodule diameters of 0.5 and 10 cm, which represent a maximum error of c. 8%. Moreover, different ($^{234}\text{U}/^{238}\text{U}$) activity ratio values, ranging from 0.5 to 3 assuming that ^{234}U daughters are absent, were explored in the calculation of $\dot{D}_{ext2}$. Resulting dose rates range from 3.04 to 3.10 Gy ka^{-1} inducing a maximum change of 0.06 Gy ka^{-1} ($\sim 2\%$). Finally, the potential accumulation of carbonate during T_1 induced a maximum change of 0.2 Gy ka^{-1} ($\sim 8\%$) if we consider a concentration of 7% carbonate nodules in the soil according to the present-day observations. Regarding the lack of real quantitative constrains of these factors and the negligible effect on the calculated dose rates, we did not consider them in the age calculations.

3.3 OSL ages

Figure 5 illustrates the anomalous fading corrected and uncorrected ages for NO1. It shows the ages calculated for the secular equilibrium scenario (scenario 1) and between the end-members (Equ. 16-17-18). According to the $g_{2\text{days}}$ values (%-dec), the correction is more important for the IR_{50} ages than the pIRIR_{225} ages (Fig. 5A, 5B). The corrected IR_{50} ages are in good agreement, i.e. on the 1:1 line, with the uncorrected pIRIR_{225} ages (Fig. 5C). Greater deviation between values is observed

when comparing the corrected IR_{50} ages with the corrected $pIRIR_{225}$ ages (Fig. 5D). Even if the residual doses are subtracted from the $pIRIR_{225}$ D_e value and the IR_{50} D_e value, the corrected $pIRIR_{225}$ ages are ~25% greater than the corrected IR_{50} ages. The agreement between IR_{50} ages and $pIRIR_{225}$ ages is good when $pIRIR_{225}$ ages are uncorrected by anomalous fading.

Figure 6 illustrates the equilibrium and disequilibrium OSL ages for samples NO1 and NO2, calculated with time period T_2 ranging from 0 to 15 ka. The represented ages are the uncorrected $pIRIR_{225}$ ages. The OSL age (t_0) ranges from 15 ka to 22 ka. The difference between the equilibrium and disequilibrium OSL ages is <5% if the carbonate nodule precipitation age is <7 ka, and between 5 and 10% if the nodule precipitation age is 7 to 15 ka. This is represented by the deviation from the 1:1 line, which increases with the carbonate nodule age. The OSL ages shown in Figure 6 were calculated with a ($^{234}U/^{238}U$) activity ratio of 1.31 for scenario 2. However, if the effect of different ($^{234}U/^{238}U$) activity ratios (0.5 to 3), as a function of different T_2 durations, is added (Fig. 6, inset), this increases the difference between equilibrium and disequilibrium OSL ages by only 1%.

Figure 7 shows the resulting OSL ages of sample NO1 and NO2 calculated as a function of the carbonate nodule age. The black bold line and grey bold line represent the disequilibrium and the secular equilibrium scenarios, respectively. The minimum OSL ages (white stars) are obtained for a carbonate nodule age of 0 ka, i.e. the carbonate nodule never precipitated (=no disequilibrium effect on the dose rate), and are 15.2 ka (NO1) and 15.8 ka (NO2). However, when the carbonate nodule precipitates, the $\dot{D}_{ext}$ will differ according to the different scenarios. This results in two different age-accumulation rates (Figure 7), which deviate from one another with time, i.e. with increasing the carbonate nodule age. The slope of the lines assuming decay chain equilibrium for nodules NO1 and NO2 (~0.3) is lower than the disequilibrium lines (~0.4), which is a consequence of the greater $\dot{D}$. The maximum OSL ages (black stars) are c. 23 ka for scenario 1 and c. 27 ka for scenario 2, with a maximum deviation of 18%. These maximum ages imply that the OSL age is equal to the carbonate age (i.e. the carbonate nodule already existed at the deposition time). The grey area in Figure 7 represents the African Humid Period (AHP, c. 5 ka to c. 15

ka); if we consider that the carbonate nodule formed during the AHP (Fig. 7, white arrow), giving plausible OSL age ranges between c. 16 to 22 ka.

4. Discussion

4.1 Suitable mineral population

In this study, we investigated the potential issue of partial bleaching using PSG instead of strict SG. The number of grains is ~10-20 but chemical measurements of the $<2.58 \text{ g cm}^{-3}$ fraction showed that 70% of the grains were K-rich feldspars and 30% K-poor feldspars. Consequently, as K-rich feldspars are brighter, the number of responding grains is ~7-14 for each PSG measurement. Except for the IR_{50} signal of NO1_{Ext} , the OD values are $<30\%$. For PSG measurements, the high OD in the D_e values can be attributed to intrinsic factors, such as measurement uncertainties, thermal transfer, variable rates of fading and extrinsic factors, such as partial bleaching, post-depositional processes and potentially variable micro-dosimetry (e.g. Duller, 2008; Lamothe et al., 2012; Reimann et al., 2012; Mayya et al., 2006). As the grains might have been mixed by pedoturbation after deposition, and as the carbonate nodules were exposed to light after precipitation, scatter in the equivalent dose (D_e) distributions relating to partial bleaching, is anticipated.

Overdispersion from the dose recovery experiment should enable scatter caused by intrinsic factors only, to be characterised (Reimann et al., 2012), and for single-grain feldspar the OD values measured in other studies range from 6 to 22% (Neudorf et al., 2012; Reimann et al., 2012; Trauerstein et al., 2014; Smedley et al., 2015). The OD values of the dose recovery experiments for NO1 and NO2 (PSG) range between 10 and 24% (Table 3); which is significantly greater than the measured instrument reproducibility ($<10\%$ for PSG measurements). This could be explained by variability in rates of anomalous fading between grains from the same sample (Lamothe et al., 2012), or variations in the rate of signal bleaching (Buylaert et al., 2012; Smedley et al., 2015). When the OD values recorded for the natural measurements are contrasted with those from the dose-recovery measurements, it is apparent that most signals and samples contain some scatter attributed to extrinsic factors. Heterogeneous carbonate accumulations could result in micro-dosimetric variations that partly explain this apparent excess in dispersion. This would be true during step I (Fig. 2), however during step II, thin section analyses (Fig. 1) indicate a

near-homogeneous distribution of detrital minerals in the nodules. NO1_{Ext} has the greatest OD and had the greatest degree of sunlight exposure (nodule surface, sampled from the surface of a mima-like mound), which suggests that partial bleaching may be a key cause of the overdispersion that we observe. This interpretation is supported by the IR₅₀/pIRIR₂₂₅ ratio, which is significantly smaller (~0.2) for NO1_{Ext} (0.50) compared to NO1_{Int} (0.74), indicative of greater reset of the fast-bleaching IR₅₀ signal (e.g. Thiel et al., 2011; Buylaert et al., 2012). Furthermore pedoturbation processes, which are characteristic of Vertisols, may also have induced some of the observed scatter (Bateman et al., 2003). The OD value of NO2 is $29.9 \pm 0.2\%$ for the IR₅₀ signal, but the NO2 IR₅₀/pIRIR₂₂₅ ratio is similar to NO1_{Int} (0.66 and 0.74, respectively), suggesting that the luminescence signals have not been partially reset. Nevertheless, the OD values for both NO1_{Int} and NO2 assessed by PSG measurements suggest that any partial bleaching is not significant (i.e OD values are $\leq 30\%$) and the minerals from the internal part of the nodule are considered suitable for luminescence dating.

Contrasting the PSG and SA measurements indicates that although some SA D_e values are higher than the PSG D_e values, they are within errors and the difference between both approaches is $\leq 10\%$ (Fig. 3). The difference is greater ($>10\%$) for the IR₅₀ signal of NO1_{Ext}, emphasizing that post-deposition bleaching affects the exterior of surficial nodule NO1 and that the IR₅₀ signal bleaches most rapidly. Consequently, as PSG measurements are time consuming and technically challenging (Duller, 2008; Trauerstein et al., 2014), and as they do not significantly change the D_e values determined for these samples, it is suggested that the SA approach is both sufficient and appropriate.

Finally, comparing the SA measurements for NO1_{Ext} and NO1_{Int} (Fig. 4), the difference in D_e values between the internal and external parts is significant for both the IR₅₀ and pIRIR₂₂₅ signals, but is greatest for the IR₅₀ signal. This may be explained by the slower bleaching of the pIRIR₂₂₅ signal in comparison to the IR₅₀ signal (Buylaert et al., 2012), as also evidenced by our residual measurements (Table 3). Differences between the IR₅₀ and pIRIR₂₂₅ D_e values are explained by anomalous fading (Thomson et al., 2008; Buylaert et al., 2012). Fading corrections were done using the luminescence package (v.0.3.4) in RStudio (Kreutzer et al.,

2012) following Huntley and Lamothe (2001). According to Figure 5, the IR_{50} and $pIRIR_{225}$ ages are in good agreement when $pIRIR_{225}$ ages are uncorrected for anomalous fading (Fig. 5C). However, when $pIRIR_{225}$ ages are corrected for anomalous fading, they overestimate the age compared to corrected IR_{50} ages (Fig. 5D). Subtraction of the residual measured following 4 h of sunlight exposure in Lausanne cannot reduce the fading-corrected $pIRIR_{225}$ age overestimation, relative to the fading corrected IR_{50} ages. The g_{2days} values measured for the $pIRIR_{225}$ signal are close to 1.5%/decade within error, measuring such low fading rates accurately is difficult. Therefore, fading correction may not necessarily give more accurate ages (Wallinga et al., 2007; Roberts, 2012). Moreover, the residual dose was measured after sunlight exposure in Lausanne, which may be considerably different from the natural depositional environment in Cameroon. Finally, as discussed previously, our results suggest that the $pIRIR_{225}$ signals of $NO1_{int}$ and $NO2$ were not affected by partial bleaching. Consequently, regarding (i) the challenge of accurately constraining low rates of anomalous fading, (ii) the lack of an appropriate residual dose analogue, and (iii) the good agreement between fading-corrected IR_{50} ages and uncorrected $pIRIR_{225}$ ages, the latter are regarded as being the most representative of the true age (Fig. 5C).

4.2 Effect of carbonate nodule formation on the environmental dose rate

The carbonate nodule formation event induced two different effects: (1) a change in the radionuclide concentration, and (2) as assumed in this study, a disequilibrium in the ^{238}U -series. Consequently, the $\dot{D}$ is 50% lower during T_2 than during T_1 , as the respective radionuclide concentrations also reduced. Moreover, if the ^{238}U -series is considered to be in disequilibrium (scenario 2) during T_2 , the $\dot{D}$ is reduced by a further $19 \pm 3\%$ ($\sim 0.7 \text{ Gy ka}^{-1}$) than when secular equilibrium is assumed (scenario 1). This is a maximum estimate because we assume that all ^{234}U daughters are absent. However, this difference is significant and two times more important than the uncertainties induced by different ($^{234}U/^{238}U$) activity ratios or different carbonate nodule diameters, which exert maximum changes of 2% (0.07 Gy ka^{-1} between $^{234}U/^{238}U$ activity ratios of 0.5 and 3) and $8 \pm 1\%$ (0.3 Gy ka^{-1} between diameters of 0.5 and 10 cm), respectively. Finally, the progressive accumulation of carbonates during T_1 could induce a change in the infinite matrix dose rate. Calculating the dose rate assuming a maximum probable carbonate accumulation of 7% (as presently

observed in the soil), results in maximum change of $\dot{D}$ during T_1 of 3% (0.2 Gy ka^{-1}). Consequently, all combined, the maximum total uncertainty, without the disequilibrium effect, on the environmental dose rate may be $\sim 10\%$ ($\sim 0.5 \text{ Gy ka}^{-1}$).

4.3 Soil parent material deposition age

The significance of the disequilibrium effect depends directly on the age of the carbonate nodule, i.e. the duration of time period T_2 . Thus whilst the environmental dose rate ($\dot{D}$) may change considerably, the effect on the OSL age may be relatively limited. The uncertainty induced by the disequilibrium is $<10\%$ for nodule ages ranging from 0 to 15 ka. As $\dot{D}_{no}$ is lower than $\dot{D}_{so}$, when the $\dot{D}_{no}$ contribution increases, i.e. T_2 increases, the OSL age becomes older (Fig. 6). This is also apparent within the disequilibrium scenario. The effect of different ($^{234}\text{U}/^{238}\text{U}$) activity ratios (0.5 to 3) on the OSL age (Fig. 6), as a function of different T_2 durations, is even less significant ($\sim 1\%$) than the absence of ^{234}U daughters ($<10\%$). If some ^{234}U daughters were present, the difference between the equilibrium and disequilibrium OSL ages would be smaller. Furthermore, regarding Figure 7, it is possible to state that both minimum (c. 15 ka) and maximum (c. 23 or 27 ka) OSL ages are improbable: $T_2 = 0$ is impossible as the nodule exists, and $T_2 = t_0$ is unlikely as the carbonate nodule formed within the host soil. It is thus certain that the deposition event preceded carbonate accumulation (i.e. $T_2 < t_0$). The time of mineral deposition (t_0) should thus range between these two end-members (Fig. 7). Finally, the nodule growth rate is unknown but this effect on the final age would induce a maximum uncertainty of 5% ($\sim 2 \text{ ka}$). However, this is for t_{max} , if we look at OSL calculated ages between the expected T_2 range, the error would be less than 2% on the OSL age ($<1 \text{ ka}$), which is considered negligible as it is within errors.

Consequently, the maximum difference between the two scenarios is $15.5 \pm 1.5\%$ on average for both samples (Fig. 7). As the carbonate nodules are expected to form during the AHP (Fig. 7; grey area), the uncertainty induced by disequilibrium should be less than 10%. Nevertheless, even in this range, the most probable OSL age ranges are 17-20 ka and 17-22 ka for the equilibrium and the disequilibrium scenarios, respectively. The OSL age uncertainty is thus still $\sim 20\%$, which is significant. Consequently, it is crucial to independently assess the duration of T_2 to

calculate accurate OSL ages. The uncertainty attributed to the carbonate nodule age is higher than the uncertainty attributed to the disequilibrium. Finally, the uncertainties related to other parameters, such as the nodule growth rate, the degree of disequilibrium or the progressive accumulation of carbonate during T_1 , are even lower than the disequilibrium. Since these parameters have a negligible influence on the paleoenvironmental interpretation, they are not considered further.

4.4 Mineral fractions within pedogenic carbonate nodule as time archives

The minerals trapped in the pedogenic carbonate nodules can be used to assess the age of the soil parent material deposition. Despite the amount of uncertainty induced by the carbonate nodule age and the associated disequilibrium, calculated OSL ages show that the deposition of the soil parent material may have occurred before the AHP, i.e. before 15 ka. Such ages would suggest that the soil parent material was deposited during a drier period, termed the Bossoumian (Hervieu, 1970). This information is important and confirms the hypothesis that the soils may have been initiated during the AHP (Diaz et al., 2016) following the Bossoumian and thus the deposition of the soil parent material. However, to strengthen this statement the deposition ages need to be calculated more accurately, and in order to achieve this, the carbonate nodule precipitation ages must be determined independently with other methods (i.e. U/Th or radiocarbon dating). Nevertheless, pedogenic carbonate nodules are important time archives and can be used to get temporal information on the soil parent material deposition constraining the onset of pedogenesis, to which carbonate precipitation is related.

5. Conclusions

Carbonate nodules in soil relics can be used as time archives. As they are pedogenic in origin, the minerals trapped within them are representative of the soil parent material. Luminescence dating of these minerals can provide information on the deposition time of the sediments from which the soils developed. In this study, pedoturbation and post-deposition partial bleaching can affect the OSL signal of the minerals. We show that the minerals from the internal part of a nodule have low overdispersion values using either pseudo-single grain or small aliquot measurements, which suggests that this mineral population is unaffected by partial bleaching and/or pedogenic processes and is thus suitable for OSL dating. Moreover,

the carbonate precipitated from surficial waters and, in this context, the ^{238}U -series is likely to be in disequilibrium. We found that only 76% of U could be considered in disequilibrium, the other 24% being derived from the trapped residual soil fraction and thus assumed to be in secular equilibrium. Considering this context, the worst-case disequilibrium scenario is when all ^{234}U daughters are absent, which results in a decrease of the environmental dose rate by $19\pm 3\%$ ($\sim 0.7 \text{ Gy ka}^{-1}$), irrespective of the ($^{238}\text{U}/^{234}\text{U}$) activity ratio value included in the calculations (from 0.5 to 3). However, the effect of disequilibrium on the final OSL age is shown to be strongly dependent on the carbonate nodule precipitation age. As the carbonate nodules are expected to have precipitated during the AHP, the maximum uncertainty on the OSL ages should be c. 20% and the maximum error induced by the disequilibrium should be $<10\%$. To conclude, the assessment of the carbonate nodule age is important for OSL age calculations, when using minerals trapped within carbonate nodules. It is advisable to combine independent methods to assess the time of carbonate formation. However, this alternative dating approach is useful when fieldwork/logistical issues prevent the possibility of collecting soil or sediment samples for OSL dating. Moreover, our proposed method is promising and has the potential to constrain soil formation and associated pedogenic processes inducing secondary carbonate precipitation. Beyond being geochemical proxies, pedogenic carbonate nodules are thus also valuable sedimentary time archives.

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Table and Figure captions

Table 1: Thorium and Uranium composition (XRF and ICP-MS) of the granite bedrock, soil and carbonate (CaCO_3) nodule. n is the number of measurements.

Table 2: Comparison of pseudo-single grain (PSG) and small aliquot (SA) measurements for samples NO1_{Ext}, NO1_{Int} and NO2. The D_e values were calculated according to the central age model (CAM; Galbraith et al., 1999) with uncertainties expressed at $\pm 1\sigma$. The $\text{IR}_{50}/\text{pIRIR}_{225}$ ratio illustrates the difference between investigated signals. The PSG/SA ratio compares the two measurement approaches. n is the number of aliquots/grains measured.

Table 3: Residuals and dose recovery test results from pseudo-single grain (PSG) measurements. The residual D_e values were calculated according to the central age model (CAM; Galbraith et al., 1999) represented with uncertainties expressed at $\pm \text{SE}$ (standard error). The dose recovery ratio is calculated as the recovered dose - mean residual ($D_{e-\text{res}}$) divided by the given dose (D_{eg}) and are expressed at $\pm 1\sigma$.

Table 4: Internal ($\dot{D}_{\text{int}}$), cosmic ($\dot{D}_{\text{cos}}$) and environmental dose rates ($\dot{D}$) for NO1 and NO2, for the equilibrium (1) and disequilibrium (2) scenarios.

Figure 1: General setting and samples. A) Location of investigated samples along the Sudano-Sahelian belt in the Chad Basin (Far North region of Cameroon, red square). Dashed lines represent the present-day average latitudinal position of the ITCZ in August (I) and January (II) (Nicholson, 2009), which regulates wet and dry season occurrences during the year. B) Clay-rich soils forming mima-like mounds and covered by large amounts of carbonate nodules (up to 11 kg m^{-2}). Insets show nodules found within the soil and representative nodules. C) Thin section of a pedogenic carbonate nodule in polarized light (left) and cross-polarized light (right). The calcite precipitated around soil components, such as primary minerals (e.g. quartz, feldspars), secondary minerals (clays, oxides) and organic matter.

Figure 2: Schematic illustration of proposed scenarios for environmental dose rate changes through time. After deposition (t_0), K-feldspars are buried in the sediment (step I), from which the soil will form during period of time T_1 (step II). The luminescence signal ($D_{e,so}$) results from the environmental dose rate ($\dot{D}_{so}$), to which the decay of radionuclides (U, Th, K, Rb) composing the sediment contributes. After carbonate nodule precipitation (step III), the K-feldspars are trapped, and the luminescence signal ($D_{e,no}$) results from the environmental dose rate during time T_2 ($\dot{D}_{no}$), to which the decay of radionuclides composing the nodule and the sediment contribute (γ -dose rate is scaled). Finally, erosion brought some nodules (e.g. NO1) to the surface leading to their exposure to sunlight (step IV). Radionuclides are assumed to be in secular equilibrium during both T_1 and T_2 in scenario 1 (white). Some radionuclides are likely to be in disequilibrium since T_2 in scenario 2 (grey).

Figure 3: Comparison of the pseudo single grain (PSG) measurements with small aliquot (SA) measurements for sample NO1_{Int} (black), NO1_{Ext} (white) and NO2 (grey), showing both IR_{50} (square) and pIRIR_{225} (diamond) signals. Dashed lines show the

deviation percentage (5 and 10%) from the 1:1 line (bold). Uncertainties are shown at one standard deviation ($\pm 1\sigma$).

Figure 4: Kernel Density Estimate (KDE) plots. Comparison of the SA equivalent dose ($n=24$) for the external part of nodule NO1 (NO1_{Ext}) with its internal part (NO1_{Int}), for both IR₅₀ (A) and pIRIR₂₂₅ (B) signals. The equivalent doses for both signals are significantly different between NO1_{Ext} and NO1_{Int}. This difference is greater for the IR₅₀ signal than the pIRIR₂₂₅ signal.

Figure 5: Ages calculated for NO1, using different carbonate nodule ages (grey scale) and assuming secular equilibrium (scenario 1). A) Uncorrected IR₅₀ age versus fading corrected IR₅₀ age, B) Uncorrected pIRIR₂₂₅ age versus fading corrected pIRIR₂₂₅ age; the g-values are given in the boxes. C) Fading corrected IR₅₀ age versus uncorrected pIRIR₂₂₅ age, D) Corrected IR₅₀ age versus corrected pIRIR₂₂₅ age.

Figure 6: Effect of nodule precipitation on calculated OSL ages. OSL ages were calculated for NO1_{Int} (diamond) and NO2 (square) considering either an equilibrium or disequilibrium scenario. An activity ratio ($^{234}\text{U}/^{238}\text{U}$) of 1.31 was taken in the calculations. The difference between both scenarios increases with the carbonate nodule age (i.e. the duration of T_2). The inset shows the effect of changing the ($^{234}\text{U}/^{238}\text{U}$) activity ratio from 0.5 to 3 on OSL ages as a function of carbonate nodule age and duration of time T_2 . Calculations were done taking the most extreme scenario, i.e. assuming that all ^{234}U daughters were lacking. The error is <10% irrespective of the ($^{234}\text{U}/^{238}\text{U}$) activity ratio if the nodule age is 15 ka. The error associated with different ($^{234}\text{U}/^{238}\text{U}$) activity ratios (ranging from 0.5 to 3, grey area) increases with the carbonate nodule age but is negligible compared to the effect of the absence of ^{234}U daughters. If these were present, the disequilibrium scenario would get closer to secular equilibrium.

Figure 7: OSL ages for NO1 (left) and NO2 (right) as a function of the carbonate nodule formation age. The bold black line represents the equilibrium scenario (1) and the bold grey line represents the disequilibrium scenario (2). The end-members calculated assuming that the nodule has always existed (maximum OSL age, black stars) and late, instantaneous nodule precipitation until a nodule age of 0 ka, i.e. carbonate nodule never existed (minimum OSL age, white stars), calculated with Equations 17 and 18. The plausible OSL ages should thus range between these two end-members. As carbonate nodules are expected to form during the African Humid Period (grey area), the most plausible OSL age should range between 16 to 22 ka (white arrows).

Table A.1: Energies (MeV/Bq s⁻¹) emitted by alpha, beta and gamma events for the ^{238}U -series, ^{235}U -series and ^{232}Th -series (Guérin et al., 2011). The total of the energies are used in the calculations if the series are assumed to be in secular equilibrium. Otherwise, if daughter products are absent, their energies are removed from the total energy calculation and their loss accounted for in calculation of the k factor (Equ. 6).

1210 Table A.2: Energies E_x (MeV/Bq s⁻¹) and calculated k_x factors for decay chains of the
1211 element x, either considering equilibrium (black) or disequilibrium (i.e. assuming loss
1212 of daughters; grey) scenarios.

1213
1214 Table A.3: Attenuated dose rates for each component and scenario. The
1215 effectiveness of α -radiation is corrected using an a-value of 0.11 ± 0.03 according to
1216 Balescu and Lamothe (1993). The water content is estimated to be $10 \pm 2\%$. A
1217 (²³⁴U/²³⁸U) activity ratio of 1.31 is used (Violette et al., 2010) for the disequilibrium
1218 scenario.

1219
1220 Table A.4: Luminescence data for nodules NO1 and NO2 and calculated OSL ages
1221 for the two scenarios (1 = equilibrium and 2 = disequilibrium) for different T_2 durations
1222 (ka). The maximum carbonate nodule age ($T_2 = \text{Max}$) is equal to the OSL age
1223 depending on the scenario. An activity ratio (²³⁴U/²³⁸U) of 1.31 was chosen according
1224 to the study of Violette et al. (2010). pIRIR₂₂₅ ages are not corrected for fading.
1225

1226 **Table 1**

	n	K (%)	Rb (ppm)	Th (ppm)	U (ppm)	Ratio Th/U
Granite	1	5.0 ±0.07	215.8±1	12.0±2	3.4±1	4/1
Soil	35	2.7±0.03	126.6±1.2	20.1±0.3	4.3±0.1	5/1
CaCO ₃ nodule	12	0.7±0.03	36.1±0.9	6.1±0.1	5.4±0.2	6/5

1227
1228
1229
1230 **Table 2**

	Signal	Single grain (PSG)				Small aliquot (SA)				PSG/SA
		n	D_e (Gy)	$\frac{IR_{50}}{pIRIR_{225}}$	OD (%)	n	D_e (Gy)	$\frac{IR_{50}}{pIRIR_{225}}$	OD (%)	
NO1 _{Ext}	IR ₅₀	63	33.9±15.2	0.50	38.1±0.4	24	25.5±6.3	0.40	19.4±0.6	1.3
	pIRIR ₂₂₅	25	67.3±11.8		15.0±0.5	24	63.1±7.0		8.4±0.3	1.1
NO1 _{Int}	IR ₅₀	125	57.3±13.3	0.74	22.8±0.1	24	56.4±6.9	0.64	8.6±0.3	1.0
	pIRIR ₂₂₅	54	77.8±10.4		11.3±0.2	24	88.3±5.2		1.1±0.8	0.9
NO2	IR ₅₀	148	52.2±15.6	0.66	29.9±0.2	24	53.6±4.0	0.60	5.1±0.3	1.0
	pIRIR ₂₂₅	24	78.9±16.8		23.1±0.7	24	90.5±5.5		2.2±0.5	0.9

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	Signal	Residual dose		Recovery Test		
		n	$D_e \pm SE$ (Gy)	n	$D_{e-res}/D_{eg} \pm 1\sigma$	OD (%)
NO1 _{Ext}	IR ₅₀	98	3±0.3	48	1.03±0.30	22±0.4
	pIRIR ₂₂₅	59	8±0.6	22	1.13±0.25	10±0.6
NO1 _{Int}	IR ₅₀	106	4±0.4	149	1.03±0.23	16±0.1
	pIRIR ₂₂₅	75	8±1.0	81	0.97±0.58	24±0.2
NO2	IR ₅₀	194	3±0.2	211	0.93±0.14	10±0.1
	pIRIR ₂₂₅	168	6±0.3	96	0.94±0.19	14±0.1

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	$\dot{D}_{int}$ Gy ka ⁻¹	$\dot{D}_{ext1}$ Gy ka ⁻¹	$\dot{D}_{so}$ Gy ka ⁻¹	Scenario 1		Scenario 2	
				$\dot{D}_{ext2}$ Gy ka ⁻¹	$\dot{D}_{no}$ Gy ka ⁻¹	$\dot{D}_{ext2}$ Gy ka ⁻¹	$\dot{D}_{no}$ Gy ka ⁻¹
NO1	0.45±0.09	5.36±0.34	5.81±0.34	3.67±0.34	3.92±0.34	3.00±0.34	3.25±0.34
NO2		5.28±0.34	5.73±0.34	3.79±0.34	3.96±0.34	3.18±0.34	3.35±0.34

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