The origin of carbonates in termite mounds of the Lubumbashi area, D.R. Congo


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A B S T R A C T

The origin of carbonate accumulations in termite mounds is a controversial issue. This study is an attempt to elucidate the processes of carbonate precipitation in Macrotermes mounds built on Ferralsols in Upper Katanga, D.R. Congo, whereby a differentiation between pedogenic and inherited carbonates is considered. Carbonate features were investigated for a 9 m deep termite-mound profile, and for an 18 m wide cross-section through a termite mound and the adjacent soil, using field and laboratory techniques. Field evidence for a pedogenic origin includes morphological type (soft powdery materials, nodules, and coatings on ped surfaces) and distribution patterns of the carbonates. Thin-section studies reveal that the carbonates occur predominantly as impregnative orthic nodules and less commonly as coatings, both clearly pedogenic; calcareous pellets are interpreted as locally reworked pedogenic carbonates. X-ray diffraction (XRD), scanning electron microscopy/energy dispersive X-ray spectrometry (SEM–EDS) and stable isotope ($\delta^{13}C$) analyses show that all isolated carbonate features consist of high-Mg calcite ($4.9\text{--}12.3\text{ mol}\% MgCO}_3$) with $6.1\text{--}12.3 \text{ mol}\% MgCO}_3$ signatures ranging from $\delta^{13}C$ values of $-13.2\text{ to } -11.5\text{ mol}\%$. Weddelite ($CaC_2O_4 \cdot 2H_2O$) is identified in a thin-section and by XRD analysis, and appears to be locally transformed into calcite. The stable isotope composition of carbon suggests that calcite precipitated in equilibrium with soil CO2 generated during decomposition of soil organic matter, and locally most likely during oxidation of oxalate. This study proves that carbonates which accumulated in Macrotermes mounds are pedogenic precipitates, whose deposition is partly related to microbial decay of organic matter, subsequently redistributed to some extent by abiotic dissolution–reprecipitation and termite activity.

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1. Introduction

The miombo ecosystem of Upper Katanga (D.R. Congo) houses large termite communities which are dominated by fungus-growing species. They build massive fortress-style nests (ca. 8 m in height; ca. 15 m in width) which are scattered through the landscape with a density of 3 to 5/ha. The wood- and litter-feeding termite Macrotermes falciger (Isoptera, Macrotermitinae) is the main occupant of primary active termitearia and is the original builder of these dome-shaped mounds (Aloni, 1975; Coffinet, 1976; Malaisse, 1974; Sys, 1957). Fungus-growing termites have a primary function in tropical ecosystems. Through their building and feeding activities, fungus-growing termites deeply modify their immediate environment by increasing the concentration of fine particles and organic matter in the mound soil (Jouquet et al., 2007). Soil materials that were processed by termites are often enriched in mineral nutrients (e.g. ammonium, nitrate), exchangeable basic cations, and available phosphorus, and they have a more alkaline pH (Brauman et al., 2000; Brossard et al., 2007; López-Hernández et al., 2006; Mujinya et al., 2010). An increase in calcium content, compared to the surrounding soil, is noted in nearly all chemical analyses of termite mounds. In some cases, mounds of Macrotermes species especially Macrotermes spp.) contain CaCO3 concretions (Hesse, 1955; Lee and Wood, 1971a; Milne, 1947; Sijm, 1964; Watson, 1962, 1975). Several theories have been suggested to explain CaCO3 accumulation in termite mounds. Milne (1947) hypothesized that the CaCO3 accumulated in the termite mound either by upward movement of Ca$^{2+}$ and HCO$_3^-$ charged groundwater or from organic matter brought into the mound by termites. Hesse (1955) and Weir (1973) attributed CaCO3 accumulation in Macrotermes mounds to capillary rise of Ca$^{2+}$ and HCO$_3^-$ charged groundwater, followed by evaporation of water from the raised mound surface, resulting in the accumulation of carbonates within the mound. Watson (1969) investigated the hypothesis of upward movement of groundwater using a radioactive tracer and concluded that the Ca of carbonates in the
termite mound could not have been derived from the groundwater unless the mound is several thousand years old. He attributed the high base status of termite mounds compared to adjacent soils to differential leaching, with termite mounds being less leached than the surrounding soil. However, this model does not consider the manner in which base cations enter the mounds. Trapnell et al. (1976) and Watson (1975, 1976) postulated that the increased Ca content in the Macrotermes mounds of Zambian woodland must have been derived from ingested plant tissue, including wood with known high Ca content. This hypothesis was supported by the research of Lee and Wood (1971b). More recently, Liu et al. (2007) attributed the CaCO$_3$ accumulation in the aboveground termite galleries of semiarid ecosystems to the upward transport of CaCO$_3$ particles by termites. Overall, the processes that lead to CaCO$_3$ accumulation in Macrotermes mounds are still not fully understood.

Carbonates in soils are either pedogenic (authigenic) or inherited (Monger, 2002; West et al., 1988). Pedogenic carbonates are the product of biotic and/or abiotic processes. Biotic processes include direct precipitation by organisms as well as precipitation that is indirectly related to CO$_2$ input by microbial or root respiration. Abiotic processes are those whereby precipitation of carbonates results exclusively from temperature, moisture and pCO$_2$ changes unrelated to biological activity (Kraimer et al., 2005; Monger, 2002).

Stable isotope analysis is a powerful tool for distinguishing pedogenic and inherited carbonates (Nordt et al., 1996). Carbon isotope ratios in pedogenic carbonate are controlled by the stable isotope compositions ($\delta^{13}C$) of CO$_2$ in the soil. If soil carbonates precipitate in equilibrium with biologically produced CO$_2$, isotopic relationships between organic matter and pedogenic carbonates will be observed (Nordt et al., 1996). For soils formed on calcareous parent materials, it has been difficult to differentiate pedogenic from lithogenic carbonates (Monger, 2002). Field and microscopic analyses may assist in resolving of some of these pedological complexities (Nordt et al., 1996).

The purpose of this study is to identify the origin of carbonates accumulated within Macrotermes mounds of Upper Katanga, using field and laboratory techniques. Field investigations include the description of morphological features and distribution patterns. Laboratory studies involve thin section analysis, scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray spectrometry (EDS) and carbon stable isotope analyses.

2. Materials and methods

2.1. Environmental setting

The study was conducted in the northern part of the Lubumbashi region (Upper Katanga, D.R. Congo), located between about 11° 34′–11° 37′ S latitude and 27° 28′–27° 30′ E longitude. The miombo woodland is generally regarded as secondary, largely developing after destruction of the dry evergreen forest (Fanshawe, 1971). A typical characteristic of miombo is the presence of large, sparsely distributed (3 to 5 ha$^{-1}$) termite mounds, reaching 8 m in height and 15 m in width, and covering about 4.3 to 7.8% of the miombo (Aloni, 1975; Malaisse, 1974; Sys, 1957). The climate of Lubumbashi is characterized by one rainy season (November to March) and one dry season (May to September), and two transition months (October and April). July and August are always dry. The mean annual rainfall is 1270 mm and the rainy season lasts 118 days on average. The mean annual temperature is about 20 °C (Malaisse, 1974).

2.2. Termite mounds selection procedure

The selection of termite mounds for this study was dictated by the nature of the parent material. Two representative termite mounds on two different substrates, both with ferrallitic properties of the overlying soil, were selected (Table 1). The soil at Site 1, derived from Kakontwe limestone (dolomitic rock), is red (5.YR 5/5), clayey or sandy clayey, and well drained. The soil at Site 2, derived from shale, is strong brown to yellowish brown (7.5YR 5/3 to 10YR 5/4), with a silty loam texture and moderately well drained (Sys and Schmitz, 1959). The soil at Site 1 is classified as Red Latosol and the soil at Site 2 as Yellow Latosol in the INEC system (Sys and Schmitz, 1959), both corresponding to Ferralsol in the WRB system (Ngongo et al., 2009).

2.3. Mound and soil sampling

At Site 1, a profile of ± 9 m height/depth and ± 1.5 m width, extending from the top of the mound down through the different epigeal parts (outer crust, inner section and central hive) into the mound foot (Figure 1, Table 2) has been dug by hand through a large termite mound (5.7 m height and 16.7 m width). At Site 2 (Figure 2), a cross-section of a termite mound (± 5 m height, ± 3 m depth, ± 18 m width), extending laterally to the adjacent soil (± 3 m depth, ± 9 m width), was prepared. A 1 × 1 m sampling grid was established over the cross-section. Bulk soil samples for physico-chemical analyses were taken for all mound-profile parts at Site 1. At Site 2, all grid compartments were sampled for the same purpose, whereby each bulk sample consists of material collected over the entire 1 m$^2$ surface area of the grid cell. Undisturbed samples for (sub) microscopic study were collected for the same units at Site 1 (Figure 1) and in the successive grid compartments along the central column of the mound cross-section at Site 2 (Figure 2, Table 2). Carbonate nodules were separately sampled at Site 2 for mineralogical and (sub) microscopic analyses. The field morphological description of carbonate forms and associated pedofeatures at both sites were made according to the FAO guidelines (FAO, 2006). At Site 2, this was limited to the central column of the mound cross-section.

2.4. Laboratory procedures

Most analyses were performed on air-dried fine earth (±2 mm). The sand fraction (~63 μm) was separated by wet sieving after destruction of organic matter ($\text{H}_2\text{O}_2$ treatment) and carbonates (acetic acid buffer); the fine fraction (~63 μm) was analyzed for particle size distribution using the pipette method (ISO, 11277, 2006). The soil pH was measured potentiometrically in a 1:2.5 (W/V) suspension, in water. The CaCO$_3$ contents were gas volumetrically determined according to ISO 10693 (ISO, 10693, 2006).

The stable isotope composition ($^{13}C/^{12}C$) of soil organic carbon (SOC) occurrences was determined in duplicate using an elemental analyzer (ANCA-SL, PDZ-Europa) coupled to an isotope ratio mass spectrometer (SerCon 20-20) after a pre-treatment with 1 N HCl to remove carbonate.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>General information on selected termite mounds and sites, and classification of the pedons.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Site 1</td>
</tr>
<tr>
<td>Coordinates</td>
<td>S 11° 36′ 1.1″</td>
</tr>
<tr>
<td>E 027° 29′ 7″</td>
<td>E 027° 28′ 35.9″</td>
</tr>
<tr>
<td>Parent rocks</td>
<td>Kakontwe dolomite</td>
</tr>
<tr>
<td>INEAC</td>
<td>Red Latosol</td>
</tr>
<tr>
<td>WRBb</td>
<td>Ferralsol</td>
</tr>
<tr>
<td>Elevation</td>
<td>1281 m</td>
</tr>
<tr>
<td>Slope positionc</td>
<td>Lower slope</td>
</tr>
<tr>
<td>Depth to groundwater table</td>
<td>± 7 m (rainy season)</td>
</tr>
<tr>
<td>± 12 m (dry season)</td>
<td>± 12 m (dry season)</td>
</tr>
<tr>
<td>Morphological evolution of selected termite moundsd</td>
<td>Advanced stage</td>
</tr>
<tr>
<td>a</td>
<td>Sys and Schmitz (1959).</td>
</tr>
<tr>
<td>c</td>
<td>FAO (2006).</td>
</tr>
<tr>
<td>d</td>
<td>Aloni (1975).</td>
</tr>
</tbody>
</table>
The 13C/12C ratios of soil carbonate were measured by analysis of CO2 evolved by dissolution in 100% phosphoric acid at 25 °C during 24 h (McCrea, 1950). Helium gas was used instead of vacuum. The produced CO2 was measured using a trace gas preparation unit (ANCA TG11, PDZ Europa) coupled to the isotope ratio mass spectrometer. Oxalates were extracted from the samples using 1 N HCl to obtain the highly soluble acid form; after centrifugation the supernatant was dried by evaporation under reduced pressure. The oxalates were precipitated as calcium oxalate by suspending the residue in a Ca2+ solution. After being washed with water the obtained residue was analyzed using the same mass spectrometry system as for analysis of SOC fraction.

The results of the isotope analyses are expressed as δ values (‰) relative to the Pee Dee Belemnite (PDB) standard (Gonfiantini, 1978):

$$\delta^{13}C = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

where $R_{\text{sample}}$ and $R_{\text{standard}}$ refer to the 13C/12C ratios in the sample and the standard, respectively.

The mineralogical composition of bulk soil samples and carbonate concentrations was studied by X-ray diffraction (XRD) using powder samples. XRD patterns were recorded with a Philips diffractometer (PW3710) using Cu Kα radiation (40 kV, 30 mA) in the 3° to 70° 2θ interval with 0.02° 2θ steps size and 2.5 s counting time per step.

The amount of Mg incorporated into the calcite lattice ($M_{\text{calcite}}$) was calculated by measuring the shift of the $d_{202}$ of calcite following the procedure of Goldsmith and Graf (1958), with the $d_{202}$ value being chosen because of its higher sensitivity to Mg incorporation (Lippmann, 1973). Mg incorporation was calculated as $M_{\text{calcite}}(\%) = \left( \frac{d_{202} - d'_{202}}{100} \right) \times 100 / (d_{202} - d''_{202})$, where $d_{202}$ is the lattice spacing of pure calcite (2.094 Å; ICSD code 88–1807), $d'_{202}$ is the lattice spacing of magnesite (1.942 Å, ICSD code 88–1804), and $d''_{202}$ is the lattice spacing of the Mg-bearing calcite under investigation.

Undisturbed soil samples were air-dried and impregnated with a polyester resin. After hardening, large (90 × 120 mm) thin sections were prepared for all main intervals that were recognized in the field, for both sites, according to standard methods (Murphy, 1986). Thin sections were analyzed according to the concepts and terminology of Stoops (2003). Undisturbed subsamples were carbon-coated for SEM–EDS analysis.

The variation in CaCO3 content and pH value within the termite mound and adjacent soil (Site 2) has been estimated using the natural neighbor interpolation technique (ArcGIS 9.2). Correlation analyses were tested by means of Pearson’s correlation coefficient using Microsoft Excel’s for Windows 7.

3. Results and discussion

3.1. Field morphology and distribution of carbonate features

Three morphological types of carbonates are recognized in the field for both mound profiles studied: soft powdery masses, nodules, and coatings on ped faces. Their occurrence in the profiles is summarized in Tables 3 and 4. The variation in CaCO3 and pH at Site 2 is illustrated in Figure 3a and b.

At Site 1, the profile shows an increase in carbonate coalescence and aggregation with increasing depth, as well as a thickening of carbonate coatings, followed by the appearance of nodules. When tested with 1 N HCl, effervescence was obtained for all units from the MF1–IS2 unit downwards, with increasing intensity of the reaction with depth (Table 3). In the MF1–IS2 unit, many soft powdery masses, common coatings and few nodules occur. In the underlying MF2 unit, the main morphological forms of carbonate features are white and light greenish gray coatings on ped faces and rare hard nodules. The MF2 unit, which has a higher pHH2O (7.6 vs 6.8) than the MF1 unit, is marked by many medium to coarse pale yellow (2.5Y 8/2) hard carbonate nodules. The SL–MF2 unit is transitional, with common hard and soft nodules and some fine soft powdery carbonate masses. In the SL unit, few light greenish gray (10GY 8/1) carbonate coatings occur on stone fragments. Some carbonate occurrences appear to have associated manganese oxide concentrations (dark mottles in Table 3). Manganese oxide concentrations occur in the MF1–IS2 unit and in all lower units, with a downward increase in abundance. Below 210 cm depth, the manganese concentrations are darker, iron oxide concentrations are more abundant, and rock fragments are present. Outside the Mn–Fe oxide mottles, the mound material has the same type of color as in other parts of the profile (Table 3).

In the termite mound at Site 2, the CaCO3 content is high in the inner cone (≈25–38%), intermediate in the middle cone (≈6–25%), low in the outer cone (0–5%), and absent in the adjacent soil (Figure 3a). In contrast to the spatial distribution observed by Watson (1962), the carbonate concentration is thus higher in the inner cone of the mound and gradually decreases away from the center. The pH predictably shows a similar pattern, with pH values up to 8.4 in the inner cone (Figure 3b). The great difference in pH between the mound and the adjacent soil concurs with earlier results (Mujinya et al., 2010). In the central vertical section at this site, effervescence when tested with HCl is observed for all intervals from the near-surface CH1 unit downwards. The strongest reaction is observed in the IS2 and MF units. In the central hive (CH1, CH2), carbonates are mainly concentrated in the form of soft powdery masses. Carbonate coatings on the surface of coarse pedds are abundant in the MF, MF–IS2 and IS2 units. Hard and soft carbonate

![Fig. 1. Schematic representation of the sampling strategy at Site 1.](image-url)
nodules appear in the CH2 unit and are distributed throughout the underlying IS2, MF–IS2, MF and SL units. Nodules are more abundant (± 15% vol.) in the IS2 and MF units, and they are larger in the IS2, MF and SL units. Rare carbonate coatings occur on stone fragments present in the SL–SP unit. Carbonate features are paler in the MF–IS2 and MF units than in all other units. The mound material has color between a 7.5YR 5/6 (strong brown) and 10YR 5/8 (yellowish brown), but it displays mottles with lower chroma (Table 4). The matrix contains Mn-oxide concentrations and Fe-oxide depletion features throughout the profile, up to 300 cm above the soil surface. The Fe-oxide depletion features are more abundant below the soil surface, where they are associated with Fe-oxide concentrations.

At both studied sites, the mound material in the MF units was moist during excavation of the profiles in the dry season, which has also been observed in other studies (Hesse, 1955; Konaté et al., 1999; Watson, 1967). During the rainy season, rainfall sheds from the mound, charging perched and permanent water tables by penetrating in the more permeable soils between the mounds. These can finally drain back to the mound site, if the top of an impermeable layer forms a depression below the mound (Turner, 2006).

In summary, carbonate coatings occur mainly between 1 m above the soil surface and 1 m below that level in both mound profiles. Carbonate nodules do show a different distribution pattern at each site, occurring mostly in the mound foot at Site 1 and nearly throughout the profile at Site 2. In both profiles, a strong color contrast exists between the mound material and the carbonate features, particularly the coatings and nodules (Tables 3 and 4). Distribution patterns and modes of carbonate occurrence provide field evidence for a pedogenic origin rather than inheritance from the parent material.

### 3.2. Microscopic characteristics

#### 3.2.1. Calcium carbonates

At Site 2, carbonates occur in all main units, except the SL–SP and OCR units. For bulk samples from Site 1, carbonates are only recognized in the stone layer and in the MF1–IS2 transitional zone, but only for one

Table 3

<table>
<thead>
<tr>
<th>Profile parts</th>
<th>Height/depth (cm)</th>
<th>Matrix color (dry)</th>
<th>Mottling*</th>
<th>Texture*</th>
<th>Carbonates</th>
<th>pHsoil of</th>
<th>Forms and abundance$^{a,c}$</th>
<th>Color (dry)</th>
<th>Contrast with soil-matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>OC</td>
<td>520–570</td>
<td>7.5YR 5/6</td>
<td>HC</td>
<td>N</td>
<td>m5 CH</td>
<td>N</td>
<td>10GY 8/1</td>
<td>Prominent</td>
<td>4.3 (7.5$^*$)</td>
</tr>
<tr>
<td>IS1</td>
<td>440–520</td>
<td>7.5YR 5/6</td>
<td>C</td>
<td>N</td>
<td>f5 BN</td>
<td>N</td>
<td>10GY 8/1</td>
<td>Distinct</td>
<td>4.8</td>
</tr>
<tr>
<td>CH</td>
<td>250–440</td>
<td>5YR 6/6</td>
<td>C</td>
<td>N</td>
<td>f3 CH</td>
<td>N</td>
<td>10GY 8/1</td>
<td>Distinct</td>
<td>7.3</td>
</tr>
<tr>
<td>MF1–IS2</td>
<td>0–70</td>
<td>5YR 4/6</td>
<td>v5 5GY2.5/1</td>
<td>HC</td>
<td>SL</td>
<td>N</td>
<td>10GY 8/1</td>
<td>Distinct</td>
<td>7.9</td>
</tr>
<tr>
<td>MF1</td>
<td>0–76</td>
<td>5YR 5/8</td>
<td>v3 5GY 2.5/1</td>
<td>SIC</td>
<td>SL</td>
<td>M</td>
<td>10GY 8/1</td>
<td>Distinct</td>
<td>7.6</td>
</tr>
<tr>
<td>MF2</td>
<td>76–210</td>
<td>7.5YR 5/8</td>
<td>f3 5GY 2.5/1</td>
<td>C</td>
<td>MO</td>
<td>N</td>
<td>10GY 8/1</td>
<td>Distinct</td>
<td>8.0</td>
</tr>
<tr>
<td>SL–MF2</td>
<td>210–280</td>
<td>5YR 4/6</td>
<td>f3 10YR 6/8</td>
<td>SIC</td>
<td>MO</td>
<td>N</td>
<td>10GY 8/1</td>
<td>Distinct</td>
<td>8.0</td>
</tr>
<tr>
<td>SL</td>
<td>280+</td>
<td>5YR 4/6</td>
<td>f3 10YR 6/8</td>
<td>C</td>
<td>MO</td>
<td>N</td>
<td>10GY 8/1</td>
<td>Distinct</td>
<td>8.0</td>
</tr>
</tbody>
</table>

$^a$ v = very few, f = few, c = common, m = many; 1 = very fine, 2 = very fine to fine, 3 = fine, 4 = fine to medium, 5 = medium, 6 = medium to coarse, 7 = coarse.

$^b$ HC = heavy clay, C = clay, SiC = silty clay.

$^c$ N = non-calcareous, SL = slightly calcareous, MO = moderately calcareous, ST = strongly calcareous.

$^d$ CH = humus-rich carbonate coating, CC = calcium carbonate coating, DC = discontinuous circumgranular coatings, BN = soft and hard nodules, HN = hard nodules, SP = soft powdery.

$^e$ pH of carbonate-rich microsites.
of two available samples of each of these intervals; carbonates are predictably abundant in samples of carbonate nodules occurring in the MF1 unit at this site, but not in a sample with common white aggregates from the IS2 unit.

In all samples, carbonates are never present as part of the groundmass, in the form of micromass components, coarse mineral grains, or rock fragment constituents. This implies that the carbonates are clearly not derived directly from the local bedrock.

### Table 4
Field description of carbonate features and selected characteristics for Site 2.

<table>
<thead>
<tr>
<th>Profile parts</th>
<th>Height/depth (cm)</th>
<th>Matrix color (dry)</th>
<th>Mottling</th>
<th>Texture</th>
<th>Carbonate Reaction with HCl</th>
<th>Forms and abundance</th>
<th>Color (dry)</th>
<th>Contrast with soil-matrix</th>
<th>pH_Watsoil-matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCR (IS2)</td>
<td>400–500</td>
<td>7.5YR 5/6</td>
<td>HC</td>
<td>N</td>
<td>v1 SP</td>
<td>v1 SP</td>
<td>10Y 8/1</td>
<td>Faint</td>
<td>6.0</td>
</tr>
<tr>
<td>CH1</td>
<td>300–400</td>
<td>7.5YR 5/6</td>
<td>HC</td>
<td>MO</td>
<td>v1 SP</td>
<td>v1 SP</td>
<td>10Y 8/1</td>
<td>Faint</td>
<td>8.1</td>
</tr>
<tr>
<td>CH2</td>
<td>200–300</td>
<td>7.5YR 5/6</td>
<td>c7 10Y 8/1</td>
<td>MO</td>
<td>v1 SP</td>
<td>v1 SP</td>
<td>10Y 8/1</td>
<td>Faint</td>
<td>8.1</td>
</tr>
<tr>
<td>IS2</td>
<td>100–200</td>
<td>7.5YR 5/8</td>
<td>f7 5PB 8/1</td>
<td>ST</td>
<td>c CC</td>
<td>c CC</td>
<td>10Y 8/1</td>
<td>Faint</td>
<td>8.3</td>
</tr>
<tr>
<td>MF–IS2</td>
<td>0–100</td>
<td>7.5YR 6/6</td>
<td>f3 10B 3/1</td>
<td>MO</td>
<td>c CC</td>
<td>c CC</td>
<td>N 8/0</td>
<td>Distinct</td>
<td>8.5</td>
</tr>
<tr>
<td>MF</td>
<td>0–100</td>
<td>7.5YR 6/6</td>
<td>v3 10B 3/1</td>
<td>SiC</td>
<td>m CC</td>
<td>m CC</td>
<td>N 8/0</td>
<td>Distinct</td>
<td>8.6</td>
</tr>
<tr>
<td>SL</td>
<td>100–200</td>
<td>7.5YR 5/6</td>
<td>v3 10B 3/1</td>
<td>MO</td>
<td>c CC</td>
<td>c CC</td>
<td>10Y 8/1</td>
<td>Distinct</td>
<td>8.6</td>
</tr>
<tr>
<td>SL–SP</td>
<td>200–300</td>
<td>10YR 5/8</td>
<td>f3 10R 4/6</td>
<td>C</td>
<td>v DC</td>
<td>v DC</td>
<td>10Y 8/1</td>
<td>Faint</td>
<td>6.0</td>
</tr>
</tbody>
</table>

**a** v = very few, f = few, c = common, m = many; 1 = very fine, 2 = very fine to fine, 3 = fine, 4 = fine to medium, 5 = medium, 6 = medium to coarse, 7 = coarse.

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**d** CC = calcium carbonate coating, DC = discontinuous circumgranular coatings, BN = soft and hard nodules, SP = soft powdery.

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![Fig. 3. Variation in (a) CaCO3 and (b) pH within a cross-section of the termite mound and adjacent soil at Site 2.](image-url)
The carbonates mainly occur in the form of orthic micritic nodules with gradual to sharp boundaries (Figure 4a). The degree of carbonate impregnation is variable, also between nodules in the same sample. The nodules commonly enclose small, rounded, non-calcareous aggregates, with a size similar to that of pellets (Figure 4b), the basic construction units of Macrotermes mounds (Jungerius et al., 1999; Lee and Wood, 1971a; Mermut et al., 1984; Miedema et al., 1994; Stoops, 1964). The carbonate nodules are clearly impregnative features, formed in situ from interstitial solutions. The enclosed non-calcareous zones are pellets that were protected from carbonate impregnation by a slightly different nature.

Within the micritic carbonate nodules, small pores are commonly lined or filled by microsparitic carbonates (Figure 4c). These coatings and infillings probably formed at the same time as the impregnative
part of the nodule, whereby calcite developed as larger crystals where space was available. Diagenetic formation at a later stage would have resulted in occurrences that are less strictly confined to the nodule.

In some samples, calcareous pellets occur as part of pellet infillings that are mainly composed of non-calcareous aggregates (Figure 4d). These occurrences record the occasional use of calcareous material by the termites for construction. This most likely represents local reworking of soil materials within the mound, whereby soft calcareous material was sometimes randomly selected, rather than representing an input of materials from a distant source. This is suggested by the roughly disorthic nature of these features relative to associated non-calcareous pellets and to the surrounding groundmass.

Some pellet infillings consist almost entirely of calcareous pellets, with minor to strong welding. Non-calcareous pellets that are part of these infillings are invariably lined by carbonates (Figure 4e). The infillings consist either of transported calcareous material (Liu et al., 2007) or of non-calcareous material that was subsequently calcified along conducting pores. The former option is most likely, in view of the absence or limited occurrence of carbonate impregnation along the sides of the calcareous infilling. Carbonates along the sides of the non-calcareous pellets seem to have formed by local dissolution–reprecipitation processes. Microsparitic coatings do appear to be intrusive features in rare occurrences as the dominant carbonate type in reprecipitation processes. Microsparitic coatings also occur in samples from Site 1 (MF1, MF1m, with some variations between aggregates).

In the lower part of the profile at Site 2, at the level of the stone layer, carbonates occur predominantly in the form of coatings, with associated hypocoatings, along the sides of irregular planar voids (Figure 4g). Similar occurrences, besides more abundant nodules, are recognized for the IS2 and CH2 units with nodular occurrences. Coatings with associated hypocoatings, along the sides of irregular planar voids, with parallel orientations at the outer borders of the pellets, are considered to be calcareous pellets, with different states of preservation, occurring in a part of the mound where the structure consists of strongly welded pellets. The disorthic aggregates are smaller and less common than the orthic nodules described above.

In summary, micromorphological observations demonstrate that the carbonates in the studied profiles occur predominantly in the form of orthic nodules, which are the likely source material for calcareous pellets produced by termites and indirectly for coatings that formed along fissures at a later stage. No features are recognized that are indicative of direct biogenic carbonate precipitation.

3.2.2. Calcium oxalates

White aggregates in the IS2 unit at Site 1, as observed for a sample composed of undisturbed fragments (up to 1 cm), are identified as weddelite occurrences (CaC₂O₄·2H₂O), based on crystal morphology and optical properties. The mineral occurs as abundant loose continuous infillings of pores, including compound packing pores between pellets (Figure 5a).

The oxalate crystals are elongated prismatic, with common pyramidal terminations, to acicular (Figure 5b). The length of the crystals is less than 20 μm, with some variations between aggregates. The crystal size is occasionally greater in the central part of the aggregate, with a concomitant greater relative amount of non-acicular habits. The observed tetragonal prismatic morphology, with [110] and [101] forms, is one of the habits that is frequently reported for weddelite from various settings (e.g. Griffin et al., 1984; Mandarino and Witt, 1983). In the IS2 sample, they occur both as isolated crystals, which are generally non-acicular prismatic, and as radial aggregates of predominantly acicular crystals (Figure 5c). Another mode of occurrence consists of mainly acicular and rare wider crystals that are oriented perpendicular to the axis of a central thread (Figure 5d). These threads are generally fungal hyphae, for which an association with calcium oxalates has frequently been documented (e.g. Cromack et al., 1979), yielding elongated prismatic crystals (e.g. Braissant et al., 2004) as well as bipyramidal forms (e.g. Borrelli et al., 2009) or a combination of different habits (e.g. Malajczuk and Cromack, 1982).

In summary, the occurrence of oxalates is detected in thin sections for one level, above an interval with recognizable calcite accumulations. Oxalate formation is related to fungal activity, which might be common inside the mound of fungi-growing termite species. Calcium oxalates, in the form of whewellite, have previously been reported for Macrotermes mounds as xenomorphic microcrystalline aggregates and possible pellet cements (Dias Pereira and Leal Gomes, 2010), which is different from the occurrence documented by the present study. For the latter, local transformation to calcite is recognized, but no direct relationship exists between these pore-filling oxalate occurrences and the impregnative carbonate accumulations in lower parts of the same profile.

3.3. Mineralogical characteristics

XRD analysis demonstrates that all carbonate features consist exclusively of calcite (Figure 6a and b). On the basis of the difference between d₁₀₂ values for each site and those for pure calcite, the amount of magnesium (mol% MgCO₃) in the calcite lattice is estimated to be 4.9 to 8.7 mol% at Site 1 and 9.0 to 12.3 mol% at Site 2, which corresponds to high-Mg calcite (>4 mol% MgCO₃; Flügel, 2004). In both profiles, the d₁₀₄ peak intensities (3.035 Å) indicate variations in the relative abundance of high-Mg calcite that are in agreement with CaCO₃ patterns (Figure 8a and b) and pH patterns (Tables 3, 4). SEM–EDS analyses show variations in Mg content that are unrelated to variations in Si and Al contents, demonstrating that Mg occurs at least largely as part of the carbonate fraction and not as part of silicate minerals. Both termite mounds were built on deeply weathered soils subject to intensive leaching. At Site 1, on a Kakontwe limestone substrate that can be assumed to be dolomitic in the study area, carbonates in the termite mound should consist of dolomite if they are part of the material that is derived from the substrate during mound building. At Site 2, Mg-bearing calcite is identified in a termite
mound on a Ferralsol derived from shale, in which carbonates are absent, also in the surrounding soil (Figure 6a and b). XRD analysis of the underlying lateritic weathering materials shows the presence of quartz, kaolinite, muscovite and anatase. Calcium could be derived from plant tissue imported by termites (Lee and Wood, 1971b; Trapnell et al., 1976; Watson, 1975). Wood and litter can also be the source of magnesium that is part of the high-Mg calcite occurrences, as indicated by chemical data for this type of material in the miombo woodland (e.g. Musvoto et al., 2000; Young and Gollegde, 1948).

X-ray diffraction analysis confirms the occurrence of weddellite in the IS2 sample at Site 1 (Figure 7). Furthermore, XRD analysis corroborates the occurrence of calcite-bearing microsites (pH 7.5) in the acidic MF1–IS2 soil matrix (Site 1; Table 3; Figure 6a). The MF1–IS2 unit is the interval with the highest Corg content (1.5%) and the lowest pH (4.3) for the bulk soil matrix (Table 3; Figure 8a). The low pH in this interval can be attributed to the formation of organic acids (e.g. oxalic acid) during organic matter decay (Gadd, 1999). Oxidation of oxalate by oxalotrophic bacteria can locally increase the soil pH, making CaCO3 precipitation possible in an overall acidic environment (Braissant et al., 2004; Cailleau et al., 2005, 2011; Verrecchia et al., 2006). The pH increase is due to the transformation of oxalic acid into carbonic acid, that is of a relative strong acid (pK1 = 1.25, pK2 = 4.27) into a weak acid (pK1 = 6.35, pK2 = 10.33) (Braissant et al., 2002). Therefore, carbonate occurrences within the interval with weddellite are probably a product of microbial transformation of oxalate.

Other components detected by XRD analysis are quartz, kaolinite and subordinate goethite at Site 1, and quartz, muscovite and kaolinite at Site 2 (Figure 6a and b).

3.4. Carbon isotopic signature

The stable carbon isotope composition of SOC (δ13Corg) and bulk soil carbonate (δ13Ccarb-b) in each termite-mound profile are shown in Figure 8a and b. δ13C signatures of Ca-oxalate (δ13Coxal, from the IS2 and MF1–IS2 units at Site 1), and some carbonate segregations (δ13Ccarb-s, from both sites) are also included.

3.4.1. Organic matter

The δ13Corg in both mound profiles is within the range for C3 plants (woody species) (−32‰ to −22‰, Boutton, 1996). The average δ13Corg for the epigenous parts is similar for both mound profiles (−23.5‰ for Site 1, −23.1‰ for Site 2, S.E.’s of 0.3 for both sites). Site 2 shows a downward increase in δ13Corg in the upper part of the sequence, which is less clearly expressed at Site 1. At Site 1, the lowest δ13Corg values are
observed for the IS2 and MF1–IS2 units. Below the soil surface, $\delta^{13}C_{\text{org}}$ increases with increasing depth at Site 1 (from $-22.9\%$ to $-20.9\%$), whereas it is nearly constant with depth at Site 2. $\delta^{13}C_{\text{org}}$ for the 0–50 cm interval of the soils around the termite mounds ($-21.2\pm0.0\%$ at Site 1, $-20.4\pm0.1\%$ at Site 2) is less negative than those for the mound materials, except for the lower intervals at Site 1 (SL–MF2, SL). This difference in $\delta^{13}C_{\text{org}}$ between the termite mounds and their surrounding top soils is attributed to the preferential consumption of C3 woody materials by Macrotermes sp (Lepage et al., 1993; Spain and Reddell, 1996), whereas the SOM of the surrounding surface soil records a mixed C3/C4 plant carbon input, $\delta^{13}C$ of C4 plants clustering around $-13\%$ (Boutton, 1996).

Fig. 6. Powder XRD patterns of carbonate features segregated in termite-mound profiles at (a) Site 1, and (b) Site 2. All patterns are reproduced with the same intensity of the d$_{110}$ peak of quartz (3.34 Å).

Fig. 7. Powder XRD patterns of soft (humus-rich) powdery masses segregated in the IS2 unit at Site 1.

3.4.2. Calcium oxalates
At Site 1, $\delta^{13}C$ values of Ca-oxalates ($\delta^{13}C_{\text{oxal}}$) extracted from the humus-rich IS2 unit ($-23.4\pm0.6\%$) and the MF1–IS2 interval ($-23.7\pm0.1\%$) are within the range for occurrences in plant tissue ($-19.5$ to $-29.3\%$, excluding cacti), but they are different from those obtained for lichens ($-9.4$ to $-11.7\%$) (Hofmann and Bernasconi, 1998). Compared to the coexisting organic matter, Ca-oxalates are enriched by 0.5 to 1.2$\%$ in the IS2 and MF1–IS2 units. This difference is much smaller than for the mentioned occurrences in lichens and higher plants (ca. 5$\%$; Hofmann and Bernasconi, 1998). The fractionation leading to this $^{13}C$-enrichment must be the result of microbial degradation of oxalate in dissolved form prior to mineral crystallization (Hofmann and Bernasconi, 1998).

Fig. 8. Stable isotopic compositions ($\delta^{13}C$) of organic matter, bulk calcium carbonate and carbonate segregations (right), and CaCO$_3$ and organic carbon (C$_{\text{org}}$) contents (left), for termite-mound profiles at (a) Site 1, and (b) Site 2. At Site 1, $\delta^{13}C$ signatures of Ca-oxalate are also included. Error bars represent the standard deviation (n = 2).

3.4.3. Carbonates
There is a significant correlation ($r=0.9, P<0.01$) between $\delta^{13}C_{\text{carb-b}}$ and $\delta^{13}C_{\text{org}}$ values above the stone layer for both profiles. The significant correlation indicates that in all cases, except for the IS2 and MF1–IS2 units
at Site 1 (see further), carbonates precipitated in equilibrium with soil CO₂ produced during decomposition of soil organic matter (Nordt et al., 1996).

At Site 1 (Figure 8a), the average δ¹³C_carb-b is −15 ± 0.8‰ (mean ± S.E.) in the upper part (OC, IS1, CH), −27 ± 0.3‰ in middle part (IS2, MF1–IS2, MF2), and −9.0 ± 0.5‰ in the lower part (MF1, MF2, SL–MF2, SL). Carbonate coatings yield a δ¹³C_carb-b value of −12.6 ± 0.6‰ (MF1–IS2) and for nodules a value of 11.9 ± 0.4‰ is obtained (MF1, MF2), which are about 11‰ heavier than the coexisting SOC. At Site 2 (Figure 8b), the δ¹³C_carb-b averages are −8.7 ± 0.9‰, below a depth of 200 cm (SL–SP, SP) and −11.9 ± 0.3‰ for the rest of the profile. δ¹³C signatures of segregated carbonate nodules (δ¹³C_carb-b, Figure 8b) are between −13.2 and −12.1‰. Carbonate nodules are 9.8 to 11.5‰ heavier than associated SOC, and they have δ¹³C values similar those of the bulk soil carbonate. The δ¹³C offsets between carbonate segregations and coexisting SOC are very similar at both sites. They are, however, smaller than the value of 14–16‰, predicted by Cerling et al. (1989). Other investigators have also reported smaller than expected δ¹³C differences between SOM and pedogenic carbonate (e.g. Humphrey and Ferring, 1994; Nordt et al., 1996). This deviation from the theoretical δ¹³C differences is probably related to the superimposition and partial preservation of soil organic matter from different sources (Nordt et al., 1996) in termite mounds.

The IS2 and MF1–IS2 units at Site 1 have exceptionally low δ¹³C_carb-b values (Figure 8a). Soft powdery masses (humus-rich) from the MF1–IS2 unit show a similar δ¹³C_carb-b signature (−25.71 ± 0.5‰), whereas carbonate coatings from the same unit exhibit δ¹³C_carb-b values comparable to those observed for other carbonate segregations from both sites. These very low δ¹³C_carb-b values indicate that the bulk soil contains carbonates precipitated from a highly δ¹³C-depleted source. One available source of this type is calcium oxalates in the same part of the profile, which have a strongly negative δ¹³C signature in the studied samples (Figure 8a). Formation of strongly depleted carbonates by transformation of isotopically light oxalates has previously been reported by Hofmann and Bernasconi (1998). The difference in δ¹³C signatures between bulk carbonate and associated oxalate in the IS2 and MF1–IS2 units (−3.2‰; −4.0‰) could be related to fractionation during oxidation of oxalates by bacteria, but no experimental data seems to exist for this. An alternative explanation for the occurrence of highly δ¹³C-depleted carbonates is oxidation of methane, which is a compound known to be produced inside Macrotermes mounds and to have highly negative δ¹³C values (−78.7‰ to −40.7‰; Sugemoto et al., 1998). However, if methane production had been an important factor, extremely low δ¹³C values should not be confined to a single interval, at a single site.

The δ¹³C_carb-b values for the bottom units (below 0.8 m at Site 1, below 2 m at Site 2) fall within the range of values (−9.9 to −7.0‰) reported for dolomitic bedrock in the region (Mucchez et al., 2008). As hypothesized by Liu et al. (2007), this could be interpreted that part of the CaCO₃ being lithogenic. However, mineralogical, macro- and micromorphological observations indicate that carbonate features in both bottom and aboveground units are pedogenic.

In general, carbonate precipitated mainly in equilibrium with soil CO₂ provided by decomposition of SOM. For two intervals with high organic matter content and the occurrence of calcium oxalates, carbonates appear to be locally derived from the transformation of an oxalate precursor.

4. Conclusion

Macromorphological, micromorphological, mineralogical (XRD, SEM–EDS) and isotopic (δ¹³C) data generally confirm the pedogenic origin of carbonate accumulation in Macrotermes mounds. Nodules, coatings and soft powdery materials are the field-identified carbonate forms. Carbonate pedofeatures mainly occur in the form of impregnative orthic nodules, which are the likely source material for coatings that formed along fissures at a later stage. All isolated carbonate features consist exclusively of high-Mg calcite with δ¹³C signatures ranging from −13.2‰ to −11.5‰. One specific interval contains calcium oxalates (weddellite), which is locally transformed into calcite. The stable carbon isotope composition of bulk carbonate (δ¹³C_carb-b) and SOC (δ¹³C_carb-s) suggests that carbonates mainly precipitated in equilibrium with soil CO₂ generated during the decomposition of soil organic matter. Calcite with exceptionally light δ¹³C_carb-b values is most likely derived from microbial oxalate oxidation. Dolomite, expected to occur as part of the bedrock at one site, is absent as inherited component within the mound. The occurrence of secondary carbonates in a termite mound on a shale-derived Ferralsol implies that Ca²⁺ is derived from plant tissue conveyed by termites.

The results of this study imply that both indirect biotic processes (C derived from microbial decomposition) and abiotic processes (dissolution–precipitation) were involved in the formation of pedogenic carbonates in the studied termite mounds.

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