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Isotopically distinct modern carbonates in abandoned livestock corrals in northern Kenya

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ABSTRACT

We report $\delta^{18}O$ and $\delta^{13}C$ data from modern carbonate in soils and dung samples from 3 recently abandoned livestock corrals in northern Kenya. Calcium carbonate content is higher within ∼5 cm depth that contains a mixture of dung and surface soils of corrals than in soils below 5 cm depth. We radiocarbon dated carbonates from 0.5 to 40 cm depths in two corrals and one control site. Surface carbonates (0.5 cm) from the two corrals were formed from modern carbon (>1955) when the corrals were active, while all other carbon is >16,000 years (BP) old. Shallow carbonate is also enriched in ^{18}O ($\delta^{18}O$ up to 3.0‰) and depleted in ^{13}C ($\delta^{13}C$ up to −12.0‰) with respect to carbonate at deeper levels and at two control sites. The $\delta^{18}O$ and $\delta^{13}C$ of soil carbonates ($\delta^{18}O_{SC}$ and $\delta^{13}C_{SC}$ respectively) in corrals are inversely correlated for depths up to about 15 cm where organic carbon is greater than 0.5%. Below that depth, there is a positive correlation between $\delta^{18}O_{SC}$ and $\delta^{13}C_{SC}$ values, similar to that observed in a control site.

In concordance with the increase in $\delta^{18}O_{SC}$ and the decrease in $\delta^{13}C_{SC}$ values in corral surface soils, the $\delta^{15}N$ of soil organic matter (SOM) ($\delta^{15}N_{SOM}$) decreases with depth in corral soils, but in a control site shows a slight increase within the first 5 cm and then becomes relatively constant with depth. Dung-laden organic matter at corral surfaces is enriched in ^{15}N by ∼5‰ relative to surface SOM of control sites. The $\delta^{15}N_{SOM}$ values imply that dung enriches the surface soils of livestock corrals in ^{15}N.

The observed $\delta^{15}N_{SOM}$ and $\delta^{18}O_{SC}$ trends suggest microbially-mediated carbonate precipitation in the dung, a conclusion that is supported by $\delta^{13}C_{SC}$ and $\delta^{18}O_{SC}$ trends and the radiocarbon data. The calcium carbonate from the dung is released in the soil as dung mixes with the mineral phases of the soil.

Changes in land use have resulted in more sedentary lifestyles among many pastoral communities, so corrals are likely to become increasingly important in conferring long-lasting transformations of the organic and inorganic components of soils that may lead to shifts in soil properties. The $\delta^{13}C_{SC}$ and $\delta^{18}O_{SC}$ therefore add to the toolbox for identifying former animal encampments in archaeological sites occupied by pastoral communities.

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1. Introduction

Stable isotopes have been used to identify and study modern and prehistoric impacts of pastoral cultures of corralling livestock on landscapes (Treydte et al., 2006; Shahack-Gross, 2003; Shahack-Gross et al., 2008). For instance, the isotopic abundance of organic nitrogen has been successfully used to identify livestock corrals abandoned over two millennia ago (Shahack-Gross et al., 2008), and the results are consistent with other geochemical methods, phytolith assemblages, and mineral assemblages. In understanding isotopic effects, knowledge about geochemical transformations that take place during the active and abandoned phases of livestock corrals is essential. Such knowledge helps identify potential isotopic tracers, and also explains how such tracers can be used to infer geochemical processes that take place in modern corrals.

Materials that accumulate within livestock corrals are derived largely from herbivore excrement. Consequently, geochemical interpretations of isotopic signatures depend on understanding processes that take place while corrals are in active use, and also following their abandonment. Although there is good information about the effects of corralling livestock on the $\delta^{13}C$ of soil organic

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matter (SOM) ($\delta^{13}C_{SOM}$) and the $\delta^{15}N$ of soil organic matter (SOM) ($\delta^{15}N_{SOM}$) values, effects of corralling on the $\delta^{13}C_{SC}$ and $\delta^{18}O_{SC}$ have never been elucidated. However, Canti (1997) described the structure of spherulites in dung via X-ray diffraction, SEM, polarized light microscopy, and FTIR Spectroscopy. Canti (1997) shows that carbonate spherulites, minute (typically 5–15 μm) spheres of radially crystallized calcium carbonate surrounded by an organic coating, in herbivore dung are precipitated through microbially-mediated activities. Laboratory experiments indicate that live bacterial cells are a prerequisite for the formation of spherulites that are coated a mucilaginous biofilm (Chekroun et al., 2004). Bacterially induced calcium carbonate precipitation is an outcome of common microbial metabolic processes such as photosynthesis, urea hydrolysis, or oxidative deamination of amino acids (Rodriguez-Navarro et al., 2003), that increase the pH and ionic strength in the microenvironment around bacteria and promote carbonate precipitation (Knorre and Krumbein, 2000; Rodriguez-Navarro et al., 2003). Bacteria in the herbivore gut and the dung-rich soils have been reported to enhance carbonate precipitation through urea hydrolysis (Stewart and Smith, 2005; Abdoun et al., 2007; Reynolds and Kristensen, 2008; Ferris et al., 2003), degradation of calcium oxalate to $CaCO_3$ by oxalotrophic bacteria (e.g., Zaitsev et al., 1998; Sahin et al., 2002, 2008, 2009) and dissimilatory sulfate reduction by sulfate reducing bacteria (SRB) (Deplancke et al., 2000; Nakamura et al., 2009; Cook et al., 2008). The $\delta^{15}N_{SOM}$, and occurrence of calcium carbonate spherulites have also been reported in abandoned livestock corrals of Maasai pastoralists in Kajiado, Kenya (Shahack-Gross, 2010).

This study uses stable isotopes and radiocarbon dating to better understand the effects of carbonate precipitation and nitrogen cycling in livestock corrals. The corrals investigated were constructed by local Turkana people, who herd goats, sheep, camels, and donkeys, but do not herd cattle in this area because it is too dry. Herd animals are taken out in the early morning, and returned in the evenings, and normally watered every other day. The local vegetation is dominated by *Indigofera* sp. on the plains, with *Acacia* sp., *Grewia* sp., *Cadaba* sp., and *Salvadora persica* and *Hyphenae thebaica* along watercourses. The principal grasses are *Aristida* sp., *Dactyloctenium* sp., and *Sporobolus* sp. We did not observe the feeding preferences of the animals. Corrals are used for several years before abandonment, and they are probably abandoned because of infestation with ticks or insects. We use $\delta^{15}N_{SOM}$, $\delta^{13}C_{SOM}$, $\delta^{13}C_{SC}$, and $\delta^{18}O_{SC}$, and radiocarbon dating of soil carbonate to show that microbial activities in the gut lead to higher carbonate concentrations in recently active corrals. Data from a non-corral (control) site do not show evidence for enhanced carbonate accumulation. The trends are attributable to microbial-mediated calcium carbonate precipitation within the herbivore gut.

2. Materials and methods

Soil sampling was undertaken in July 2003 and 2007 near the lower course of the Lokalalei wash west of Lake Turkana (Fig. 1), where the mean annual temperature and precipitation are ~ 29 °C and 234 mm, respectively. Vegetation is sparse in the region except along ephemeral watercourses; plains between these are covered principally with *Indigofera* sp. that support short grasses (e.g., *Aristida* sp.) following rains. Topographically the area is quite flat, with streamcourses seldom incised as much as 3 m. The initial (2003) soil sampling contained only mineral soils at depths of 0 cm, 5 cm, 10 cm, and 25 cm excluding the dung layer. The latter samples (2007) were obtained at depths of 0.5 cm, 2.5 cm, 5 cm, 10 cm, 15 cm, 25 cm, and 40 cm in three recently abandoned corrals of which the samples within the top 5 cm contained dung or a mixture of dung and mineral soils. The three corrals, B1, B2, and B3, were abandoned in January, 2005; January, 2003; and July, 2000, respectively. Undisturbed soil was collected from two nearby control sites, NB4 and B0, in 2003 and 2007 respectively about 250 m from the corrals. Aliquots of about 1 g were taken from each soil sample, placed in a ceramic mortar, and crushed with a pestle.

Subsamples for analysis of soil organic matter were put into 50 ml beaker. Excess 0.1 N HCl was added to remove soil carbonates and left to react for 48 h. The samples were then transferred into 1.7 ml centrifuge vials, placed into a centrifuge, and spun at 4000 rpm for 5 min, following which the supernatant was decanted. Remaining acid was rinsed from the soils by adding distilled water, centrifuging, and decanting the supernatant. Rinsing was repeated with distilled water until the pH became neutral (pH ≈ 7.0). The soils were then dried in an oven at 60 °C for 48 h.

For stable isotope analysis of carbonates, a second subsample was taken from the crushed soil samples, sieved through 140 μm mesh, and transferred into a 5 ml centrifuge vial.

2.1. Stable isotope analysis of soil organic matter (SOM)

Treated soils for analysis of $\delta^{15}N_{SOM}$, and $\delta^{13}C_{SOM}$ were combusted in a Costech 4010 Elemental Analyzer at 1650 °C and inlet to a Finnigan® MAT 252 Isotope Ratio Mass Spectrometry (IRMS) in continuous flow mode. Isotope values were calculated as shown in Eq. (1).

$$\delta X(‰) = 1000^{*}\left(R_{\text{sample}}/R_{\text{standard}} - 1\right) \tag{1}$$

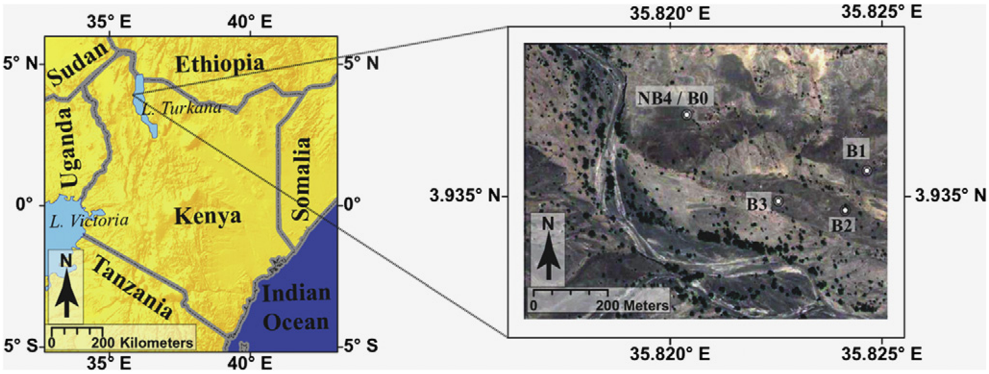

Fig. 1. Map of the study area. The livestock corrals are located in Lokalalei, west of Lake Turkana. The sites include an active corral (B1), a corral that was active for two years (B2), a corral that was abandoned in 1999 (B3), and the two control sites (B0 and NB4).

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where '*X*' is either ^{15}N or ^{13}C, *R* is $^{15}N/^{14}N$ or $^{13}C/^{12}C$, respectively, and δX is expressed in permil (‰) relative to internationally agreed standards; VPDB for both carbon and oxygen, and atmosphere (AIR) for nitrogen $\delta^{15}N$, respectively. Carbon and nitrogen yields were determined from the preliminary samples, optimum sample sizes established, and samples run in duplicate with newly determined masses. The analytical precision of isotopic analysis of $\delta^{15}N_{SOM}$, and $\delta^{13}C_{SOM}$ are 0.1‰ and 0.2‰, respectively.

2.2. Stable isotope analysis of soil carbonate

Soil carbonates were analyzed for $\delta^{18}O$ and $\delta^{13}C$ via dual inlet with a Carboflo (Finnigan) and via continuous flow with a GasBench (Thermoscientific Inc.). Both peripherals were coupled to a Finnigan MAT 252 IRMS. UU Carrara (carbonate) of grain size < 140 μm was used as an internal standard for all analyses. Soil samples analyzed with the Carboflo were weighed into 3.5 mm × 5 mm silver capsules and reacted in a common acid bath at 90 °C for 10 min, and yielded ~2–6 V on the major mass (44) Faraday cup. The carbonate analysis in Gas Bench was done by weighing about 5 mg of soil samples were weighed into 25 ml screw-top vials with septa, purged with helium to remove atmospheric gases in the headspace, injected with phosphoric acid to evolve for carbon dioxide and left to react overnight at 72 °C. UU Carrara (carbonate) was used as an internal standard. The fraction of carbonate in the soil samples is expressed as the ratio of the yields (voltage per unit mass) of soil samples to those of UU Carrara (pure carbonate), with errors estimated from replicated measurements of the Carrara standard approximating 5% of the amount of carbonate present. The soil masses analyzed ranged from ~280 μg for the dung containing samples to ~2200 μg for the deeper levels and at the control sites. The standard deviations (1σ) of isotope measurements of $\delta^{13}C$ and $\delta^{18}O$ were ≤0.07 and ≤0.02‰, respectively.

2.3. Radiocarbon dating of soil carbonate

Soils from 0.5 to 40 cm depths were selected from corrals B2 and B3, and the control site (NB4). Corral B2 was abandoned in January, 2003 and B3 was abandoned in July, 2000. Sample mass varied from 85 to 950 mg based on carbonate content. Soils were treated with excess 30% H_2O_2 to remove organic matter. Reaction times varied based on SOM content. Samples were centrifuged and the H_2O_2 supernatant was decanted and fresh H_2O_2 was added until effervescence ceased to ensure all organic matter was removed. Samples were then rinsed with distilled water and centrifuged three times, and dried overnight at 60 °C. Samples were reacted under vacuum with phosphoric acid at 90 °C for 4 h. CO_2 was cryogenically collected into 6 mm pyrex tubes, flame sealed, and sent to the University of Arizona where they were graphitized and then analyzed by Accelerator Mass Spectrometry. Data are expressed in fraction of modern carbon ($F^{14}C$), and for those that are older than 1950, an age (in years BP) is given. Modern ages were calculated using Calibomb (Reimer and Reimer, 2010), and all error estimates are 2σ.

3. Results

The $\delta^{13}C$ values of SOM across all corrals range between −24‰ and −19.7‰ indicating a significant contribution of C_3 plants (Fig. 2, Table 1). Variations in $\delta^{13}C$ values with depth are unique at each site and no global systematic trends are evident.

In contrast, $\delta^{15}N$ of the SOM from corrals (B1–B3) all have similar trends of decreasing values with increase in depth. This trend contrasts sharply with the SOM $\delta^{15}N$ trends of the control site (NB4). The $\delta^{15}N$ values of the control site (NB4) vary from 8.8‰ at 0.5 cm (at the surface) to 11‰ at 10 cm and decrease to ~7.0‰ at 25 cm depth. In contrast, corral soils are more positive (between 10‰ and 15‰) near the soil surface, and decrease steadily with increase in soil depth.

The soil carbonate content in surface soils of corrals is higher than in deep soils (>5 cm) and all soils at the control site (Fig. 4). For instance, the corral abandoned in 1999 (B3) has a soil carbonate content of ~12% at 0.5 cm, that increases to ~14% at 2.5 cm from the surface, before declining to ~8% at 15 cm depth. The soil carbonate concentration at 5 cm depth in B3 is highest (26%). In contrast, the carbonate content of the control site (B0) is ~3% at the surface and increases steadily to ~10% at 15 cm depth and then decreases to 7% at 40 cm depth.

Soil carbonates of corral sites are enriched in ^{18}O and depleted in ^{13}C at the surface with respect to values from the control sites, NB4-04 and B0-07 (Fig. 4). The $\delta^{18}O_{SC}$ values become more negative and $\delta^{13}C_{SC}$ values become more positive with increase in depth. From ~15 cm and below, there is a positive correlation between $\delta^{18}O_{SC}$ and $\delta^{13}C_{SC}$ values. The positive correlation occurring below 15 cm in corrals is similar to that through the soil profile at the control site (NB4). A notable observation is that among the corral sites, the corral that was abandoned two and a half years before sampling (B1) has less positive $\delta^{18}O_{SC}$ values (−0.3‰) and less negative $\delta^{13}C_{SC}$ values (−10.8‰) than B2 and B3 that were abandoned four and a half years, and seven years before sampling, respectively.

Radiocarbon data from soil carbonates show that surface carbonate (0.5 cm) in the recently abandoned corrals B2 and B3 is derived from modern carbon, which is carbon fixed from the atmosphere since 1950 (Table 2). The 0.5 cm carbonate from corrals B2 and B3 have $F^{14}C$ values of 1.0428 ± 0.0023 (2σ) and 1.0817 ± 0.0023, respectively. These values likely correspond to ages more recent than the year 2000 ($F^{14}C = 1.0980$), which is the most recent published date for the Northern Hemisphere zone 3 (NH3) bomb curve (Hua and Barbetti, 2004). Two more recent northern hemisphere data sets (Levin and Kromer, 2004; Levin et al., 2008) extend the tropospheric CO_2 data set through 2006. The data sets are applicable to equatorial East Africa because tropospheric CO_2 has been globally well-mixed for the past few decades. Based on the two Levin data sets, the $F^{14}C$ value from the 0.5 cm carbonate at corral B3 corresponds to 2002 ± 1 yr, while the $F^{14}C$ value from the 0.5 cm carbonate at corral B2 was formed after >2007. The latter age date probably does not reflect the actual date formation since the corral was abandoned in 2003. The presence of any non-dung derived carbonate in the sample, which we assume has an $F^{14}C$ value < 1, would lead to a younger age. The alternative NH3 bomb-curve ages of 1957.6 ± 0.08 for B2 and 1958.0 ± 0.13 for B3-0.5 carbonates cannot be ruled out. All carbonate from 40 cm depth and the surface carbonate from the control site have $F^{14}C$ values that range from 0.0731 to 0.1301 (±0.0007), which correspond to ages ranging from 21,020 ± 60 to 16,380 ± 50 years BP.

4. Discussion

The observed trends in $\delta^{15}N_{SOM}$, $\delta^{13}C_{SOM}$, $\delta^{13}C_{SC}$, and $\delta^{18}O_{SC}$ values in the carbonates, and in the %C and %N in corrals indicate that domestic livestock have great impact on nitrogen and carbonate cycling in corrals. The enrichment in ^{18}O and ^{15}N coupled with higher carbonate content in surface soils relative to those at deeper levels and the control site is a clear manifestation that livestock dung influenced both the nitrogen and carbonates on the surface of corrals. We discuss the causes of observed isotopic trends

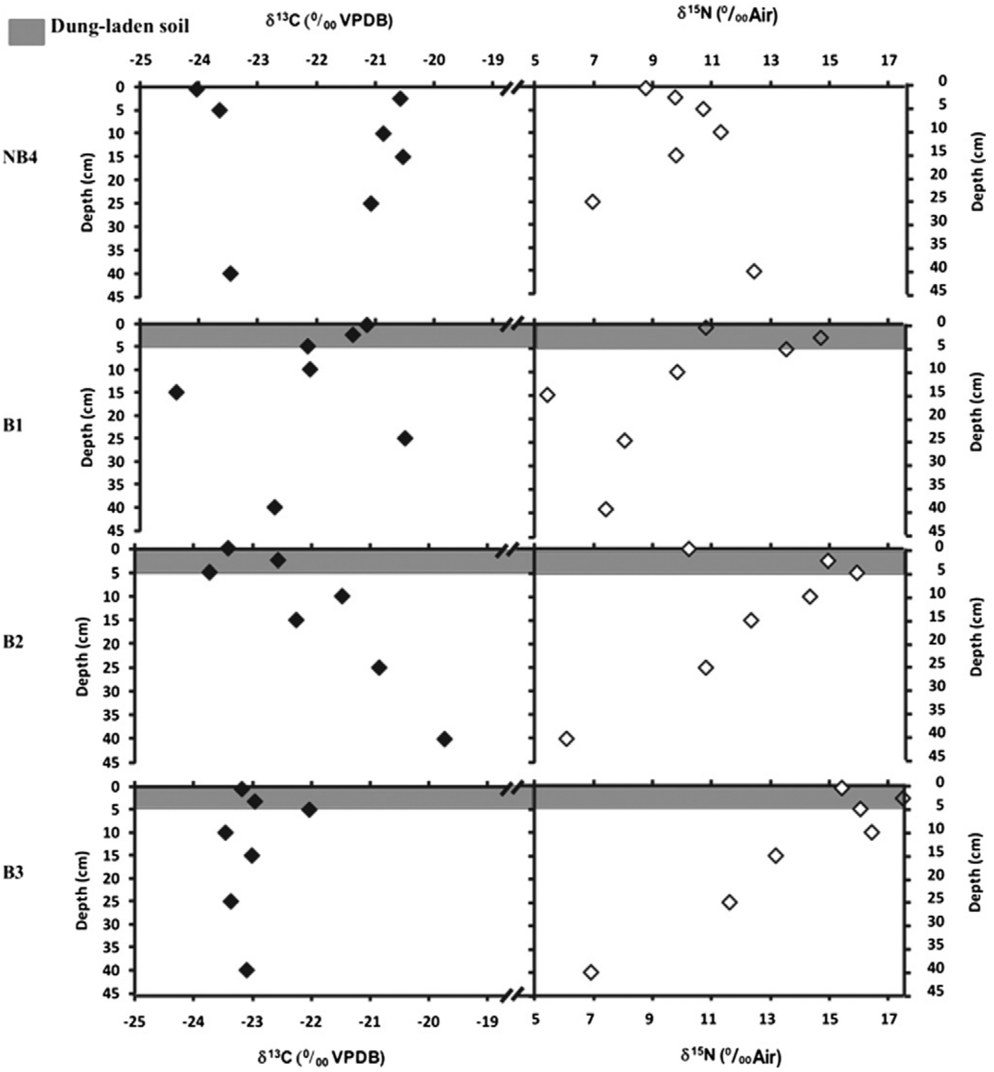

Fig. 2. The $\delta^{13}C$ and $\delta^{15}N$ profiles of SOM of the control site (NB4) and the livestock corrals (B1–B3) for 2007 samples.

in soil carbonate and their implications in archeological investigations on livestock corrals.

4.1. Radiocarbon and stable isotope evidence of modern carbonates

Radiocarbon dates provide evidence (Table 2) that carbonate in the upper 0.5 cm is a result of the corral occupation. Carbonates from 40 cm depth and the surface of the control site, that yielded older ages may be authigenic or alternatively, allochthonous (e.g., detrital). Carbon in authigenic soil carbonates can be sourced from soil respired CO_2 or atmospheric CO_2. The presence of vesicular A horizons in undisturbed soils in this area support eolian deposition as a possible source of allochthonous carbonates. Determining the carbon source of the older carbonates is not possible, but their age (>16,000 BP) indicates formation prior to the establishment of the corrals. In this region, the earliest livestock keeping is estimated to be about 4500 BP (Gifford-Gonzalez, 1998).

We used the following mass balance equation to determine the proportion of soil carbonates in surface soils (up to 2.5 cm deep) of corrals that is derived from dung:

$$\delta_{\mathrm{orig}}M_{\mathrm{orig}} + \delta_{\mathrm{new}}M_{\mathrm{new}} = \delta_{\mathrm{total}}M_{\mathrm{total}}, \qquad (2)$$

where δ_{orig}, δ_{new}, and δ_{total} are the mean $\delta^{13}C_{SC}$ values of the upper 2.5 cm of the control site and the value of carbonate derived from dung (Table 1: $-11.2‰$), and M_{orig}, M_{new}, and M_{total} is the % carbonate of the upper 2.5 cm of the control site, the carbonate derived from dung, and the total carbonates in corrals respectively. The mass balance approach indicates that 76%, 85%, and 91% of surface carbonates in corrals B1, B2, and B3 respectively, are derived from dung. High carbonate accumulation in surface soils of corrals that increase with the age of corral may be viewed as a manifestation of a rapid time-integrated carbonate precipitation process. The inverse correlation between $\delta^{13}C_{SC}$ and $\delta^{18}O_{SC}$ from the surface to a depth of about 15 cm establishes that carbonates at the surface are isotopically distinct from pedogenic or detrital carbonates in the soil (see Fig. 4). Carbonates that form at the surface of corrals are the most depleted in ^{13}C ($\delta^{13}C < -10‰$) and most enriched in ^{18}O ($\delta^{18}O > 1‰$). These isotopically distinct values indicate that a novel carbonate precipitation process occurs in the gut prior to dung deposition at the soil surface of corrals. The $\delta^{15}N_{SOM}$ also shows that the soil organic matter is depleted in ^{15}N with depth (Fig. 2), which also points to addition of ^{15}N of soil organic matter by dung (Steele and Daniel, 1978; Sponheimer et al., 2003).

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Table 1
Stable isotope values of carbon and oxygen and carbonate content of soil and goat feces carbonates and stable isotope values of carbon and nitrogen of soil organic matter and goat feces.

Site	Depth (cm)	Carbonates			Organic matter				
		$\delta^{13}C$ (VPDB)	$\delta^{18}O$ (VPDB)	%$CaCO_3$	$\delta^{13}C$ (VPDB)	$\delta^{15}N$	% C	% N	C/N
K07-B0	0.5	−6.1	−4.9	2.86	−24.0	8.8	0.18	0.02	8.1
Collected: July 2007	2.5	−3.9	−3.9	3.08	−20.6	9.8	0.14	0.11	6.6
Undisturbed	5	−2.9	−1.8	6.09	−23.6	10.7	0.11	0.01	10.6
	10	−4.2	−1.7	9.85	−20.9	11.3	0.08	0.01	9.4
	15	−4.3	−2.6	8.20	−20.5	9.8	0.10	0.01	8.6
	25	−4.1	−1.9	7.22	−21.1	7.0	0.11	0.01	9.3
	40	−5.5	−3.1	5.24	−23.5	12.5	0.09	0.01	11.3
K07-B1	[a]0.5	−10.2	0.4	9.34	−20.2	9.9	0.08	0.01	8.2
Abandoned: Jan 2005	[a]2.5	−10.1	0.3	9.25	−21.4	14.7	7.24	0.76	9.6
Collected: July 2007	5	−5.7	−2.8	4.29	−22.1	13.5	0.45	0.06	7.8
	10	−3.1	−7.8	5.18	−22.1	9.8	0.22	0.03	7.1
	15	−6.0	−4.0	4.33	−24.4	5.4	0.25	0.03	10.1
	25	−5.6	−4.5	4.69	−20.5	8.1	0.13	0.02	7.8
	40	−5.0	−3.9	8.07	−22.7	7.4	0.16	0.01	15.5
K07-B2	[b]0	−11.2	0.6	9.08	−23.4	10.2	12.19	1.12	10.9
Collected: July 2007	[a]0.5	−11.2	4.4	17.58	−23.9	13.9	21.69	1.93	11.2
Abandoned: Jan 2003	[a]2.5	−9.8	3.8	12.11	−22.6	15.0	15.26	1.45	10.5
	5	−11.2	6.3	25.84	−23.7	15.9	9.73	1.00	9.7
	10	−6.4	−2.5	8.03	−21.5	14.3	0.19	0.03	6.4
	15	−6.1	−2.4	9.34	−22.3	12.3	0.13	0.02	7.5
	25	−4.7	−3.1	8.92	−20.9	10.8	0.24	0.03	9.2
	40	−5.5	−2.0	8.48	−19.7	6.1	0.21	0.02	9.0
K07-B3	[a]0.5	−10.8	2.9	18.91	−23.2	15.4	27.19	2.75	9.9
Collected: July 2007	[a]2.5	−11.1	3.2	22.48	−23.1	17.5	22.35	2.20	10.2
Abandoned: July1999	5	−10.7	2.1	15.25	−22.0	16.0	25.10	2.69	9.3
	10	−7.4	−1.6	8.39	−23.5	16.4	1.46	0.20	7.4
	15	−5.6	−2.9	6.79	−23.0	13.2	0.18	0.03	6.8
	25	−5.5	−3.6	8.98	−23.4	11.6	0.17	0.02	6.7
	40	−5.5	−3.6	11.39	−23.1	6.9	0.14	0.02	8.3
NB4-03	0	−6.9	−5.7	2.37	−20.3	5.8	0.20	0.01	22.5
Collected: July 2003	5	−6.5	−5.0	1.93	−20.0	5.3	0.30	0.01	24.6
Undisturbed	10	−6.7	−5.2	2.35	−19.5	5.3	0.21	0.01	19.2
	15	−6.4	−5.7	2.01	−18.8	5.3	0.16	0.01	16.6
	25	−7.3	−5.4	1.83	−19.4	4.2	0.20	0.01	22.8
B1-03	[a]0	−10.9	3.4	17	−23.3	16.0	31.15	2.82	11.1
Collected: July 2003	[a]5	−7.3	−5.8	0.55	−20.5	15.7	0.77	0.06	13.1
Abandoned: In current use?	10	−8.1	−7.6	0.61	−20.2	5.5	0.47	0.02	31.3
	15	−3.9	−4.6	2.01	−19.8	4.1	0.49	0.01	36.0
	25	−2.5	−4.7	7.76	−19.7	3.6	0.31	0.01	39.7
B2-03	[a]0	−7.1	−1.5	5.01	−20.0	17.7	0.71	0.07	9.6
Collected: July 2003	[a]5	−3.9	−2.0	8.76	−20.2	11.4	0.39	0.02	19.4
Abandoned: January, 2003	10	−5.2	−2.6	30.06	−20.4	9.1	0.24	0.01	23.7
	15	−4.2	−1.3	7.41	−20.2	4.9	0.18	0.01	16.9
	25	−5.1	−1.7	7.09	−20.0	6.3	0.28	0.01	27.4
B3-03	0	−4.1	−3.6	5.31	−20.1	16.4	0.44	0.04	11.3
Collected: July 2003	5	−6.1	−3.2	9.07	−20.1	12.7	0.26	0.02	16.8
Abandoned: 1999	10	−6.1	−3.1	4.72	−20.0	10.9	0.24	0.01	18.6
	15	−7.4	−0.5	6.92	−19.3	9.5	0.22	0.01	15.5
	25	−4.7	−1.6	7.25	−18.5	5.6	0.18	0.01	18.8

Note: The C:N ratios differ from the %C and %N because of rounding in the reported values for %C and %N.

[a] Signifies the samples that had a high organic matter content and also most enriched in ^{18}O and ^{15}N relative to samples with low organic matter content (%C).

[b] Signifies goat feces.

4.2. *Implications of isotopically distinct values on carbonate sources*

Microbially-mediated carbonate precipitation enhances soil carbonate formation in situations where spontaneous carbonate precipitation is unfavorable (Laiz et al., 1999; Braissant et al., 2002, 2003; Combes et al., 2006; Jimenez-Lopez et al., 2007). Consequently, a large proportion of terrestrial and marine carbonates arise through biologically mediated precipitation (Lee et al., 2008). In livestock corrals, microbial communities from the herbivore gut and in the soil can alter equilibrium conditions of carbonate precipitation. This occurs through provision of nucleation surfaces for carbonate crystal formation, increase in soil pH by metabolizing organic acids (Ellis et al., 2008), and enzymatic degradation of certain compounds (e.g., calcium oxalate) that result in $CaCO_3$ precipitation (Garvie, 2006).

Microbial processes associated with carbonate precipitation include degradation of calcium oxalate (Zaitsev et al., 1998; Sahin et al., 2002, 2009; Schoonbeek et al., 2007; Khammar et al., 2009), sulfate reduction (Deplancke et al., 2000; Nakamura et al., 2009; Cook et al., 2008), and urea hydrolysis (Ferris et al., 2003; Fidaleo and Lavecchia, 2003). All these processes may contribute to carbonate precipitation in the gut. For instance, calcium oxalate, produced in over 200 plant families, and is the most abundant insoluble mineral in plants (Korth et al., 2006) and its abundance in animal diet corresponds to levels of calcium oxalate in urine (Holmes et al., 2001). However the presence of carbonate in dung from microbial precipitation in the gut is well established.

Microbial activities in the gut result in the formation of spherulites, calcareous crystal aggregations common in the dung of

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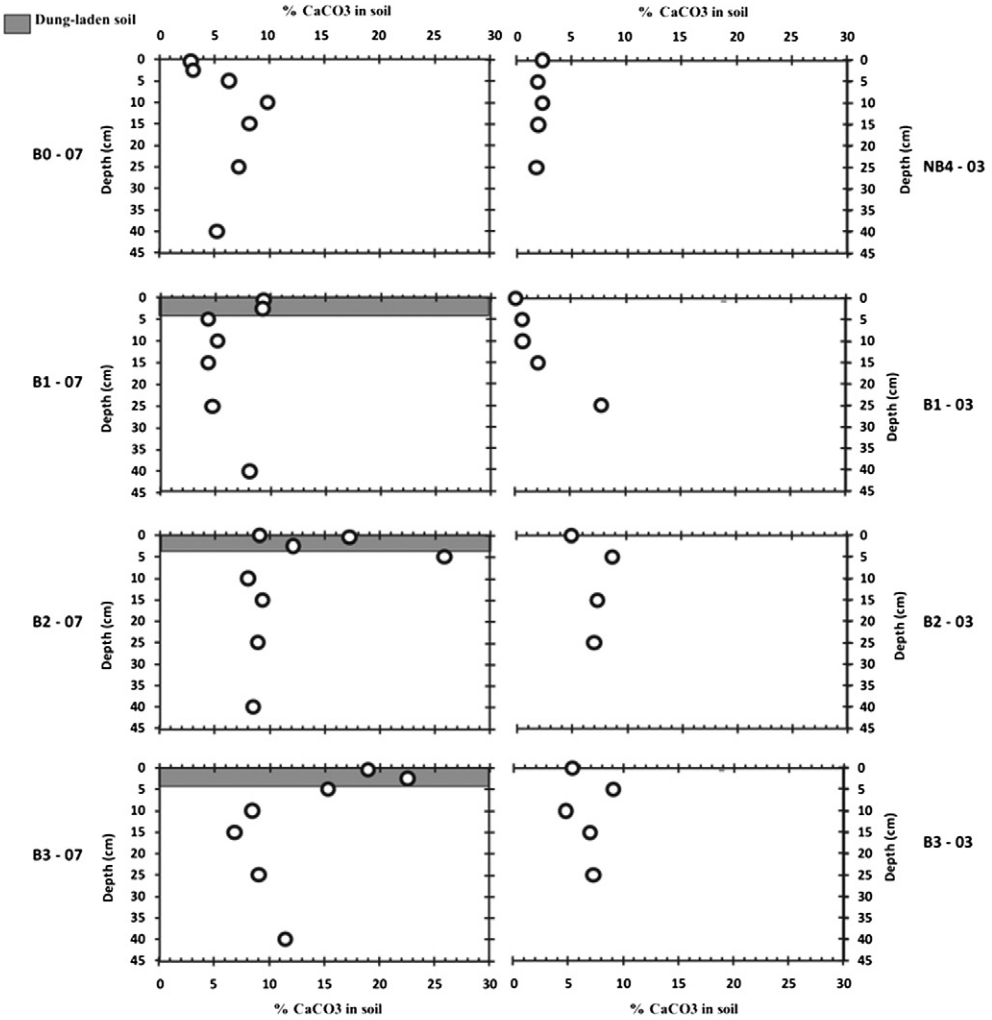

Fig. 3. Scatter plots of carbonate fraction of the soils within livestock corrals (B1–B3) and the two control sites (B0 and NB4). The surface soils of corrals have higher levels of calcium carbonate ($CaCO_3$) than soils below 15 cm and soils of the control site.

a range of herbivores grazing on what Canti (1997) referred to as the "calcareous pastures", but that they also form regardless of bedrock type so they should be expected in herbivores in Turkana where the soils are formed on volcanic and siliciclastic parent materials. The spherulites appeared as minute (5–10 μm) thick spheres under a phase-contrast microscope and have also been reported in coprolites of other animals including hyena (Horwitz and Goldberg, 1989). Bacterially induced alkalinization is a prerequisite for the development of spherulites (Chekroun et al., 2004). Shahack-Gross (2003) attributed the occurrence of monohydrocalcite in abandoned livestock corrals to sphelurites in the dung. The isotopic signatures associated with the biocalcification processes can help elucidate the mechanism leading to carbonate precipitation. In this regard, the observed trends in $\delta^{13}C_{SC}$, $\delta^{18}O_{SC}$, and $\delta^{15}N_{SOM}$ values in livestock corrals may be attributed to carbonates in the dung (see Figs. 2–4). Further, the consistency of the $\delta^{13}C_{SC}$ and $\delta^{18}O_{SC}$ trends across all three corrals is an indication that the carbonates arise from similar sources.

In this study we show that $\delta^{13}C_{SC}$, and $\delta^{18}O_{SC}$ in the soil carbonates in corrals reflect contribution of carbonates from dung and can be used to identify recently abandoned livestock corrals. Considering the impacts that corrals have on ecosystem processes, it would be beneficial to consider the changes in soil microbial communities in future studies in order to understand how microbial dynamics influence the soil $\delta^{15}N_{SOM}$, $\delta^{13}C_{SOM}$, $\delta^{13}C_{SC}$, and $\delta^{18}O_{SC}$. In this respect, further investigation is necessary to explain how the $\delta^{13}C_{SC}$, $\delta^{18}O_{SC}$, and $\delta^{15}N_{SOM}$ trends come about, what microbial processes are involved (e.g., calcium oxalate degradation or urea hydrolysis). For instance, Millo et al. (2009) performed experiments using *Bacillus pasteurii* cultures and reported a 3‰ decrease in soil DIC during ureolysis but offered no explanation of the observation. To corroborate trends observed in this study, control studies in field and laboratory conditions are necessary. However, this study has established that dung carbonates are isotopically distinct from carbonates derived from other processes in the soil and may therefore be used to identify and study abandoned livestock encampments in historic and prehistoric times.

Nonetheless, to use these findings as an indicator of corrals in the archeological record, the investigator must consider the possible effects of diagenesis, possible dissolution of spherulites, and possible admixture of local carbonate in sites located on calcareous bedrock. It is likely that the carbonate isotopic signature will be best preserved in hot, dry areas with little rainfall, and where soil pH is ≥8.2. Application of the method in archaeological sites will require evaluation the type(s) of carbonates present in the soil sample: geogenic, pedogenic, aeolian, dung, etc. For such evaluation microscopic techniques will be most likely of the utmost importance.

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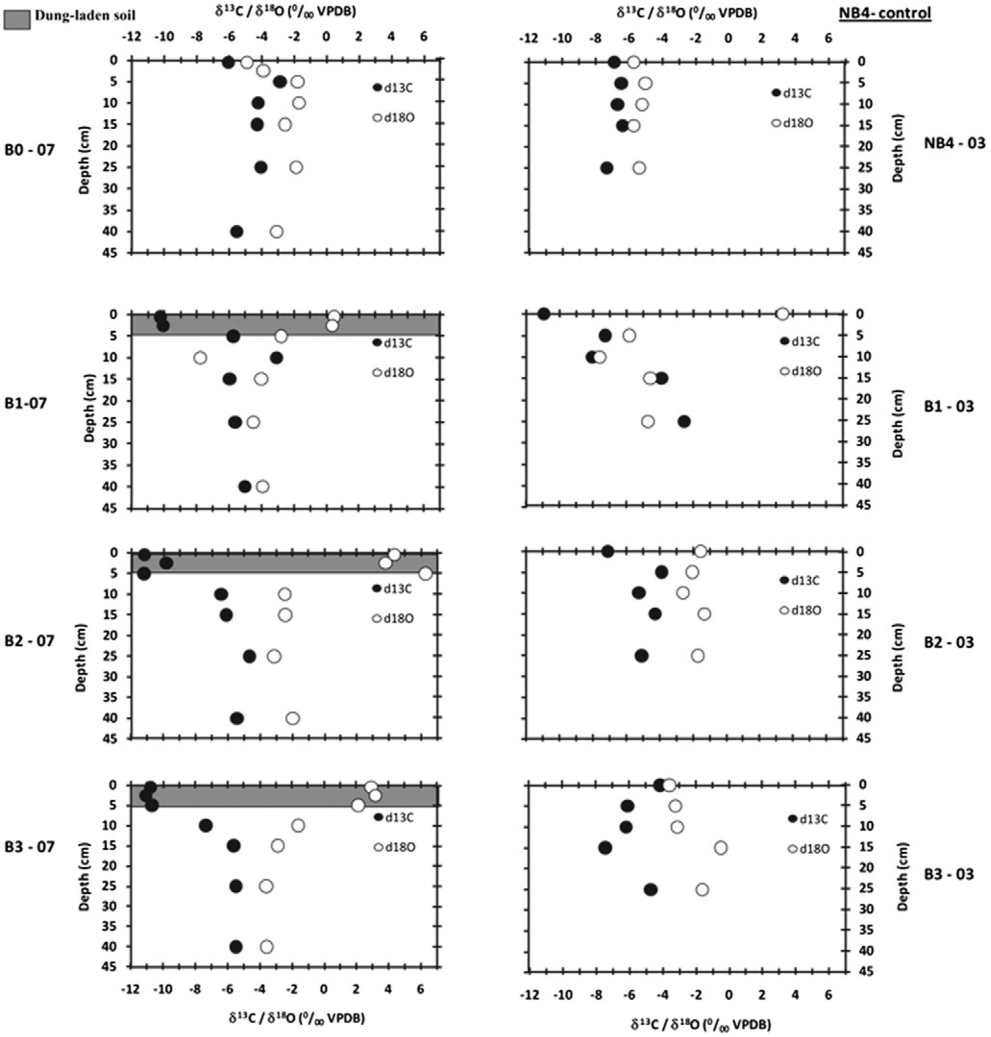

Fig. 4. Scatter plots of $\delta^{13}C_{SC}$ and $\delta^{18}O_{SC}$ within livestock corrals (B1–B3) and the two control sites (B0 and NB4).

The $\delta^{13}C_{SOM}$ and $\delta^{15}N_{SOM}$ values of the corrals soils in this study indicate goats occupied the corrals. Shahack-Gross et al. (2008) showed in a study conducted in Rombo area, southern Kenya indicates that caprine enclosures had a more positive $\delta^{15}N_{SOM}$ (12.8–19.7‰ in goat exclosures and 12–16.3‰ in cattle exclosures) and more negative $\delta^{13}C_{SOM}$ values (−14–19.2‰ for goat enclosures and −14.6–17.2‰ for cattle enclosures) than cattle enclosures. They attributed these findings to the dietary preferences (i.e., grazers vs. browsers for goats and cattle respectively). These workers used the results to show abandoned corrals of Elementaita Neolithic site of Sugenya, southern Kenya radiocarbon dated to ca. 2000 BP (uncalibrated) were occupied by cattle. The surface soils of the control sites had $\delta^{15}N_{SOM}$ values <9.0‰, which is similar to the value reported by Shahack-Gross et al. (2008).

Table 2
^{14}C dates of soils sampled at 0.5 cm depth and at 40 cm depth for livestock corrals (B2–B3) and the control site (NB4). Age dates for modern carbonates were calculated from the Levin dataset (Levin and Kromer, 2004; Levin et al., 2008) available from Calibomb (Reimer and Reimer, 2010).

Sample ID	$F^{14}C$	$+/-2\sigma$	^{14}C age (y)	Error (y)	Date	Description
K07-B0-0.5	0.0882	0.0007	19,500	60	NA	Control soil
K07-B0-40	0.0731	0.0006	21,020	60	NA	Control soil
K07-B2-0.5	1.0428	0.0023	Post-bomb	–	>2007	Boma soil
K07-B2-40	0.1301	0.0008	16,380	50	NA	Boma soil
K07-B3-0.5	1.0817	0.0023	Post-bomb	1	2002	Boma soil
K07-B3-40	0.0810	0.0006	20,190	60	NA	Boma soil

5. Conclusion

The $\delta^{13}C_{SOM}$, $\delta^{15}N_{SOM}$, $\delta^{13}C_{SC}$, and $\delta^{18}O_{SC}$ values show marked distinctions between livestock corrals and control site (non-corral) soils. The former have higher concentrations of soil carbonate in the surface layers that are enriched in ^{18}O and depleted in ^{13}C relative to carbonates in the control site (non-corral) soils. Microbially-mediated carbonate precipitation in the herbivore gut is most likely the source of the abundant carbonates in dung that accumulate in corral soils, and these carbonates are isotopically distinct from other soil carbonate in the environment.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jas.2012.02.005.

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