STABLE ISOTOPE COMPOSITIONS OF ORGANIC CARBON AND CONTENTS OF ORGANIC CARBON AND NITROGEN OF LACUSTRINE SEDIMENTS FROM SUB-ARID NORTHERN TANZANIA

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ABSTRACT
The stable isotope compositions of organic carbon (OC), and contents of OC and nitrogen for four sediment cores recovered from lakes Makat (located in the Ngorongoro Crater), Ndutu and Masek (located in the Serengeti Plains) are used to document sources of organic matter (OM) and climatic changes in sub-arid northern Tanzania during the late Pleistocene-Holocene period. Accelerate mass spectrometer (AMS) 14C ages on total OM for sediments collected from the Ngorongoro Crater Lake indicate that the sedimentation rate is approximately 17 cm/ka. The δ13C values from the 20 cm long core (short core) show a downcore increase, whereas that of 500 cm long core (long core), show two peaks enriched in 13C and three peaks depleted in 13C. A general downcore increase in the δ13C values for the short core suggests changes in the relative proportion of C3 and C4 with C4 fraction increasing downcore. Similarly, low and high peaks in the long core suggest changes in the relative proportion of C3 and C4 with low values having high proportion of C3 type of material, probably indicating changes in precipitation and lake levels in the area. Deposition of OM depleted in 13C took place during periods of high precipitation and high lake levels. Although high content of OC and nitrogen in some core sections are associated with elevated C/N ratio values, diagenetic alteration of isotope signature is unlikely to have caused OC isotope enrichment in sections having high contents of OC and nitrogen. The OC isotope record from Lake Ndutu shows a general downcore decrease in δ13C values and contents of OC and nitrogen. Furthermore, this general trend is punctuated by a period of above normal enrichment in 13C, with δ13C values being as high as -6‰. A downcore decrease in δ13C values and contents of OC and nitrogen could be attributed either to climatic variability or diagenetic effect. Moreover, a peak enriched in 13C probably indicates a period of reduced precipitation, where phytoplankton used dissolved bicarbonate rather than dissolved atmospheric CO2. Lake Mesak record shows two peaks depleted in 13C that are flanked by near constant values of about -20‰. These two peaks (depleted in 13C), which most likely have high proportion of C3 type of OM, are associated with low contents of OC and nitrogen. Generally, the contents of OC and nitrogen for this lake are lowest relative to other lakes.

INTRODUCTION
Climate change is partly manifested through variability in precipitation and, over prolonged period of time, changes in vegetation cover. Depending on the level of precipitation, vegetation can change from C4 (mainly grassland) to C3 (mainly forest) dominant type of vegetation. Dense vegetation covers of higher land plants occurs during humid conditions while grasses, which are more tolerant to drought, are the major type of vegetation cover during dry episodes. Plants, which require a lot of water for growth, are generally C3 type and are characterised by stable carbon isotope values that range from -24 to -31‰ and averaging -27‰ (Deines 1980, Muzuka, 1999, Swap et al. 2004). Similarly, plants that are efficient users of water and adapted to high radiation and temperatures in the growing season (resistant to drought) such as many grasses are generally C4 types and are characterized by stable carbon isotope values that range from -10 to -16‰ and
averaging -12‰ (Deines 1980, Muzuka, 1999, Swap et al. 2004). Because of this, the stable isotopes of OC for C₃ vegetation are generally negatively correlated with rainfall (Swap et al. 2004). Furthermore, as the C₃ grasses out-compete C₄ plants when atmospheric CO₂ levels are low (Cerling et al. 1997, Ehleringer et al. 1997), variations in bulk δ¹³C of the terrestrial biomass in the tropics may reflect changes in atmospheric CO₂, temperature, moisture conditions and seasonality of rainfall (Street-Perrott et al. 1997).

In the East African region, several studies have been conducted to document variability in palaeo-precipitation and climate variability using various indicators such as diatoms, mineral magnetic, pollen, stable isotopes and lake levels (Hillaire-Marcel et al. 1986, Hillaire-Marcel and Cassanova, 1987, Johnson et al. 1996 & 2000, Olago et al. 2000, Stager et al. 1997, Karlén et al. 1999, Gasse, 2000, Talbot and Laerdel 2000, Thompson et al. 2002). Some of these studies have indicated that precipitation at the end of the last glacial period was low, and lake levels were at their lowest level, with shallower lakes like Lake Victoria being completely dry (Johnson et al. 1996, Stager et al. 1997, Talbot and Laerdel 2000). This dry phase was later followed by an increase in precipitation to a maximum level during the early Holocene that culminated at about 5 ka (Hillaire-Marcel and Cassanova 1987, Stager and Mayewski 1997, Stager et al. 1997, Gasse 2000). Although there is a significant amount of information on the climatic condition in the East African region, documentation of climatic changes in northern Tanzania is scanty and available information has been obtained using stromatolites (Hillaire-Marcel et al. 1986, Hillaire-Marcel and Cassanova 1987) and diatoms (Roberts et al. 1993). Furthermore, there is a great potential of using stable isotopes in paleoclimatic studies, but it is evident that only a few studies have used stable isotopes of OC and nitrogen to document climatic changes in Tanzania (Johnson et al. 2000, Talbot and Laerdal 2000). Thus, the present work documents the Pleistocene-Holocene climatic variability in sub-arid northern Tanzania as preserved in lacustrine sediments of lakes Magat (Ngorongoro Crater), Ndutu and Mesak (Serengeti plains) using the stable isotopes of sedimentary OC and contents of OC and nitrogen. The work also documents changes in the sources of organic matter preserved in these lakes.

**Study Area**

The Ngorongoro Crater, which is a large caldera, is located in the northern part of Tanzania at an altitude of more than 2000 m above sea level. The crater covering a total area of 250 km² is about 23 km wide and has an average depth of 600 meters. To the west of the crater lies the famous Serengeti Plains and the Olduvai Gorge, which are relatively at a lower altitude (910-1820 m above sea level). Furthermore, the crater houses thousands of wild animals creating very exciting scenery.
Figure 1: A map showing location of sampling sites of Ngorongoro Crater, Lake Ndutu and Lake Masek.
Lake Makat or Magadi lies within the Ngorongoro Crater (Fig. 1). The lake, which is alkaline in nature, is shallow and is only 3 meters deep during good rains and during dry season its levels drops dramatically. Sediments deposited in the lake are derived from the flanks of the Ngorongoro Crater.

Lakes Ndufu and Masek, which are about 1 km apart, are located about 90 km from the Ngorongoro Crater in the Serengeti Plains and Olduvai Gorge (Fig. 1). The two lakes are alkaline in nature with Lake Ndufu being frequented by flamingos during the rainy season when the lake is full. During the dry season, all of the water of Lake Ndufu evaporates and a thick crust of salt (trona) forms over the lake. Underneath the salt crust is mud; sticky, green, smelly, slimy mud. The nearby Lake Masek is relatively deeper and larger and holds more water so it lasts longer in the dry periods, however, there is no documented water depth.

Like other parts of Tanzania, which are climatically characterized by dry and wet seasons, this northern part of the country receives rain during the months of October through December and March through June. In Tanzania, rainfall is not evenly distributed, with central Tanzania (which include Dodoma and Singida regions) and a large part of Arusha region in the northern Tanzania receiving far less rainfall relative to other parts of the country. Currently, this northern part of Tanzania receives less than 1000 mm rainfall per year. The 19-year annual rainfall average at Ngorongoro Crater is 900 mm per year with less rain (about 750 mm per year) on the crater floor. The sedimentation rates in the crater as well as other lakes located in this region are poorly known.

Geologically, the study area is studded by Neogene volcanic rocks and Quaternary lake beds (Harris 1981). The volcanic rocks are basaltic in nature. In the Olduvai Gorge-Ndufu area seven major beds namely: Bed I, Bed II, Bed III, Bed IV, the Masek Beds, the Ndufu Beds, and Baisiusiu Beds have been identified. These beds are rich in skeletal remains of hominids.

**MATERIALS AND METHODS**

Sediment cores were obtained from Lake Makat in the Ngorongoro Crater, Lake Ndufu and Lake Masek (Fig. 1) using a flow-through type of corer. Two cores namely MG 0 (20 cm long) and MG 2 (500 cm long) were recovered in the Ngorongoro Crater Lake. Owing to hard crust at the surface, the upper 100 cm of MG 2 was not recovered. The sediments for core MG 2 are generally muddy in nature varying in colour from light grey to dark grey or black (Fig. 2). However, within the core section there are laminated layer, fine-grained sandy layer and pebbly layer intercalated with mud (Fig. 2).

Cores MES 1 (300 cm long) and NDU 2 (289 cm long) were retrieved from Lakes Masek and Ndufu respectively, and sediments are muddy in nature with varying colour and particle size (Fig. 2). During sampling, Lake Ndufu was dry and covered by a thick white layer of trona. Wherever possible, cores were sub-sampled every 10 cm, except Core MG 2 which was sampled every 5 cm. Each sample represents a homogenate that is 1 cm thick.

The stable isotope compositions of OC and contents of OC and nitrogen were determined at the GEOTOP, University of Quebec at Montreal and the Department of Geology and Geochemistry, Stockholm University. The stable isotopes were determined using a FINIGAN MAT mass spectrometer, while the contents of OC and nitrogen were determined using a C-H-N analyser. Sediment samples for the stable isotopes of OC and contents of OC were first acidified using 1M hydrochloric acid, washed of all salts and oven dried at 40°C. Nitrogen content was determined using unacidified sediment samples. OC stable isotope data are reported in δ-values relative to the PDB, while the contents of OC and
nitrogen are reported in dry weight percentage. Reproducibility of OC and nitrogen is within \( \pm 2\% \) and \( \pm 0.1\% \), respectively. Similarly reproducibility for \(^{14}C\) values is within \( \pm 0.1\% \).

**Figure 2:** Stratigraphy for cores MG 2 (right), NDU 1 (left top panel) and MES 1 (left bottom panel) collected from Lakes Makat, Ndutu and Masek respectively.

Geochronology of cores MG 0 and MG 2 was established using few \(^{14}C\) data from a nearby site (Core MG 1) located 1 m apart (Table 1, Fig. 3) under the assumption of equal sediment deposition rate in a radius of 1 m. The geochronology of cores MES 1 and NDU 1 is based on the \(^{210}Pb\) activity.

**Table 1** \(^{14}C\) ages determined on total organic matter

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>(^{14}C) age</th>
</tr>
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<tbody>
<tr>
<td>200</td>
<td>31335±880</td>
</tr>
<tr>
<td>300</td>
<td>10275±75</td>
</tr>
<tr>
<td>400</td>
<td>25720±635</td>
</tr>
<tr>
<td>500</td>
<td>28320±655</td>
</tr>
</tbody>
</table>
Figure 3: Downcore variation in the stable isotope composition of organic carbon for, and contents of organic carbon and nitrogen for core MG 0 and MG 2 collected from Lake Makat in the Ngorongoro Crater.

RESULTS
From the $^{14}$C data on total OM for a nearby site (~1 m apart; Table 1, Fig. 3), the sedimentation in the Ngorongoro Crater Lake is as high as 11 cm/ka. $^{210}$Pb activity for core MES 1 is nearly constant (Fig. 4) indicating that the surface sediments are either older than 100 years or have been homogenised by benthic organisms and wild animals. The activity of $^{210}$Pb for Lake Ndutu decrease exponentially and the estimated recent sedimentation rate (plot of Ln $^{210}$Pb activity Vs depth) is about 18.4 cm/yr (Fig. 4). Downcore trend in the activity of $^{210}$Pb at the two sites (Lake Masek and Ndutu) shows that the supported $^{210}$Pb is around 3 dpm/g (Fig. 4).
Lake Makat

The δ13C values for core MG 0 show a downcore increase, with δ-values ranging from -21 to -12.5‰ and averaging -16.9±3.8‰ (Fig. 2). Similarly, the C/N ratio values that range from 8.2 to 14.8 and averaging 11.8±3.0, increases downcore (Fig. 3). However, the OC content, which ranges from 0.35 to 1.06% and averaging 0.51±0.3%, is invariant downcore (Fig. 3). Near constant values are also observable for the nitrogen content that ranges from 0.027 to 0.13% and averaging 0.05±0.05 (Fig. 3). The C/N ratio values, which range from 1.1 to 112.2 and averaging 31.2±25.5, are generally elevated in cores sections that have high content of organic carbon and nitrogen (Fig. 3).

The δ13C values for core MG 2 show two zones enriched in 13C and 3 zones depleted in 13C when a line is drawn through -20‰ (Fig. 2). Zones enriched in 13C are centred at 300 cm and 420 cm (Fig. 2). The δ13C values for core MG 2 ranges from -25.1 to -14.3‰ and averages -20.6±2.2‰. The OC and nitrogen contents for core MG 2 are highly variable with low values corresponding to peaks depleted in 13C (Fig. 2). The OC content ranges from 0.17 to 16.7% and averages 4.074.04%. Similarly, the nitrogen content ranges from 0.0 to 0.42% and averages 0.13±0.11%.

Lake Ndutu

The isotope values of OC for core NDU 1 that range from -27.1 to -7.8‰ and averaging -19.64±6.4‰, shows a general downcore decrease (Fig. 5). This general downcore trend is punctuated with an interval enriched in 13C centred at approximately 180 cm (Fig. 5). The shift in 13C to higher values is associated with abrupt increase in the contents of OC (Fig. 5). The content of OC, which ranges from 0.04 to 3.68% and averages 0.54±1.0%, shows downcore decrease in the upper 100 cm, reaching near constant values below it (Fig. 5). Similarly the nitrogen content shows a downcore decrease in the upper 100 cm followed by near-constant values. Both OC and nitrogen lack a significant change at about 180 cm (Fig. 5). The nitrogen content at this site ranges from 0.00 to 0.66% and averages 0.01±0.02%. The C/N ratios values range from 11.1 to 170.0 and averages

Figure 4: Plots of 210Pb activity versus depth for core NDU 1 and MES 1 as well as ln(210Pb) activity versus depth for core NDU 1.
32.7±47.0. The C/N values are generally invariant downcore when two high values are excluded and the mean value changes to 14.9±2.3. (Fig. 5)

**Figure 5:** Downcore variation in the stable isotope composition of organic carbon for, and contents of organic carbon and nitrogen for core NDU 1 recovered from Lake Ndutu.

**Lake Masek**

The δ¹³C values for core MES 1 show two intervals depleted in δ¹³C at a depths of 120 cm and 230 cm that are flanked by near constant values of about -19‰ (Fig. 6). The carbon isotope values at this site range from -25.4 to -16.4‰ and averages -20.2±2.4‰. Although the contents of OC and nitrogen show high variability, they display a general downcore decrease and they co-vary (Fig. 6). The contents of OC at this site range from 0.06 to 0.41% and averages 0.10±0.07%, while that of nitrogen ranges from 0 to 0.015% and averaging 0.004±0.004%. This site has the lowest contents of both OC and nitrogen relative to other sites. The values C/N ratios for this core, which range from 15 to 60 and averaging 25.9±10.2, shows a near constant values downcore (Fig. 6).
Inter-Site Comparison
Mean isotope values of organic carbon for the three lakes range from -20.6 (Makat) to -19.6% (Ndutu), when mean isotope value for core MAG 0 is excluded. Owing to lack of good chronology for a core from Lake Ndotu, the zone enriched in $^{13}$C cannot be correlated with any of the Lake Makat zones. Also due to lack of good chronology the Lakes Makat and Masek records cannot be correlated. Lake Masek has the lowest contents of organic carbon and nitrogen.

![Graph showing C/N Ratios, Nitrogen Content, OC Content, and $\delta^{13}$C Values over depth](image)

**Figure 6:** Downcore variation in the stable isotope composition of organic carbon for, and contents of organic carbon and nitrogen for core MES 1 recovered from Lake Masek.

DISCUSSION
Lake Makat
As pointed out previously, the stable isotope compositions of OC for core MG 2 display two peaks enriched in $^{13}$C. Assuming that the two cores (MG 1 and MG 2) collected 1 m apart have similar chronology, the first $^{13}$C enriched peak fall in the time range of uncalibrated radiocarbon dates of 9708 to 12415, while the second one falls between 21400 and 23200 uncalibrated radiocarbon ages (Fig. 3). The first segments correspond to the Younger Dryas. Available information indicate that in the East African region, the Younger Dryas was associated with low lake levels resulting from aridity (Roberts et al. 1993, Gasse 2000). Similarly the 21-23 ka period, which is considered to be the beginning of the last glacial maximum, was associated with aridity and low lake levels in the East African region (Gasse 2000). Because of aridity during these two-time
periods where drought resistant C4 plants out-compete C3 type of vegetation, grass was most likely the most dominant type of vegetation. Therefore, the mechanism that led to OM enrichment in 13C in the two segments of Core MG 2 is preferential preservation of C4 derived plant material.

Another possible mechanism that could have caused enrichment in 13C for the two segments is utilization of bicarbonate by phytoplankton during photosynthesis. Phytoplanktons prefer to utilize dissolved CO2 during synthesis of OM. However, in a situation where demand for CO2 is high particularly during high primary productivity or where waters are highly alkaline, phytoplankton tend to utilize bicarbonate as source of carbon during synthesis of OM (Collister and Hays 1991). When bicarbonate is utilized in the synthesis of OM the resulting organic material will be enriched in 13C. Owing to shallowness of the studied lakes and their alkaline nature, this mechanism may contribute to the observed enrichments during Younger Dryas and 21-23 ka periods.

The mean difference in the isotopic compositions between depleted and enriched zones range from 3.2 to 4.9‰. The difference in the isotope compositions between the two zones could be attributed to differences in the relative proportion between C3 and C4 type of organic material and utilization of bicarbonate during photosynthesis. Currently areas surrounding the Ngorongoro Crater are semi-arid, and rainfall is less than 1000 mm per year. The Crater Lake, which is a shallow alkaline lake with pH >10, is a closed lake basin only with water inflow coming from springs and Munge river that originates from the Olmoti crater. A change in these water inflows most likely due to changes in the level of precipitation may easily change the chemistry of the lake. A decrease in inflow from these sources means higher rate of water loss during evaporation, and thus increase in the bicarbonate concentration. Such a process will cause waters to be enriched in 13C, and when such waters are utilized by phytoplankton during synthesis of OM the resulting material will be enriched in 13C. Therefore, core sections depleted in 13C could be a result of increase in input of freshwater owing to increase in rainfall in the area and high relative proportion of C3 type of organic material, while core sections enriched in 13C could be a result of high proportion of C4 type of organic material and utilization of bicarbonate during photosynthesis. Because phytoplanktonic materials are rich in nitrogen, the C/N ratios are usually less than 10 while that of cellulose rich materials such as land plants have higher C/N ratios that are greater than 20 (Meyers 1994, 1997, 2003). A scatter plot of C/N ratios versus δ13C values, which is a useful plot for easy discrimination of various sources (Meyers 1997, 2003), shows that contribution of phytoplankton to the total organic matter is minimal (Fig. 7).

The contents of organic carbon and nitrogen between 100 and 200 cm for core MG 2 is high and correspond to relatively low isotope values of OC and high C/N ratios averaging 40.71±6.8 (Figs. 3), an indication that the material is enriched in cellulose and is of C3 type of plants. Preferential preservation of OC and nitrogen during this time period could be attributed to increase in primary productivity in response to increase in nutrient during wetter conditions. Increase in the supply of nutrients could have resulted in high isotope discrimination and thus low isotope values.
Figure 7: Scatter plots of C/N ratios versus δ¹³C values for cores collected from lakes Makat, Ndutu and Masek.

Lake Ndutu
A downcore decrease in δ¹³C values for the Lake Ndutu sedimentary record could be attributed either to diagenetic alteration of OM or changes in the relative proportion between C₃ and C₄ type of organic material. Lower C/N ratios that averages 14.9±2.3 could be partly a result of diagenetic alteration owing to very low contents of organic carbon and nitrogen, (Fig. 5) Various workers have noted that diagenetic alteration of OM is associated with either small change or no change in the isotopic compositions of OC (Meyer 1994, Krishnamurthy et al. 1999). However, in areas where organic material has been subjected to high temperatures a significant effect has been noted (Meyers and Simoneit 1999). Because the analysed samples have not been subjected to high temperatures, a change of about 5‰ observed in this study cannot be attributed to diagenetic alteration.
alone. Most likely the results suggest progressive increase in the input of C₄ type of OM in recent times. This further suggests that the size of lake Ndutu has progressively declined owing to decrease in precipitation in the area.

**Lake Masek**

Core MES 1 is characterized by at least two zones depleted in ¹³C. These zones depleted in ¹³C can primarily be attributed to decrease in the relative proportion of C₄ type of OM and increase in lake primary productivity. This could have resulted from increase in phytoplanktonic production owing to increase in precipitation and thus lake levels. A scatter plot of C/N ratios versus δ¹³C (Fig. 7) shows that the organic material deposited in the lake are rich in cellulose thus derived from C₃ and C₄ types of land plants.

**Inter-Site Correlation**

Although the stable isotope compositions of OC at all three sites (Makat, Ndutu and Masek) have a wide range, they have similar mean value of -20‰. This suggests that mechanisms governing isotope distribution in the three lakes are similar. The stable isotope compositions of East African higher plants have been reported to be about -28‰, while that of grasses have been reported to be -12‰ (Koch et al. 1991; Muzuka, 1999). Therefore, mean δ¹³C values of -20‰ for organic material from this semi-arid area suggest at least 50% contribution of C₃ type of organic material into the sediments of these three lakes. Although the stable isotopic composition of OC for lake phytoplanktonic material ranges from -16 to -38‰ with most of δ¹³C values falling within and below the range of δ¹³C values of C₃ plants (Deines 1980, LaZerte and Szalados 1982, Aravena et al. 1992, Meyers 1994, de Giorgio and France 1996, Mitchell et al. 1996, Tenzer et al. 1997), a plot of C/N ratio versus δ¹³C values (Fig. 7) show that phytoplankton contribution is minimum. However, because of lower contents of OC and nitrogen particularly for cores collected from Lakes Ndutu and Masek, which can potentially be diagenetically altered and adsorbed to clay particles leading to lower C/N ratios (Muller, 1977), this parameter alone cannot exclude the possibility of the presence of phytoplanktonic material.

The OC and nitrogen content for Lake Makat in the Ngorongoro Crater is higher compared to the other two lakes (Ndutu and Masek) an indication of preferential preservation of OC and nitrogen in Lake Makat. Poor preservation of OM in Lake Ndutu and Masek could be attributed to frequent exposure of sediments to high concentration of oxygen when the lakes dry up. Furthermore, it could also be a result of low primary productivity and small input of OM from the catchment’s basin.

**CONCLUSION**

The stable isotope values for three lakes (Lake Makat, Ndutu and Masek) located in semi-arid northern Tanzania averages -20‰ suggesting that C₄ plants contribute at least 50% to the total OC preserved in the lake. The ¹³C record shows that Lake Makat experienced input of organic material enriched in ¹³C during the Younger Dryas and between 21 and 23 ka periods that can be attributed to deposition of high proportion of C₄ type of organic material and utilization of bicarbonate by phytoplankton. The stable isotopes of OC show major variations in the composition of C₃ derived OM material deposited in the three lakes. Although inter-core correlation is not possible owing to poor chronology, the isotope data may be interpreted to show that enriched sections were deposited during dry periods and vice versa.

Contents of OC and nitrogen for cores MES 1 and NDU 1are generally low and have been significantly affected by diagenetic processes. However, the stable isotope signatures seems to have undergone little alteration.
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