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AMS-^{14}C CHRONOLOGY OF A LACUSTRINE SEQUENCE FROM LAKE LANGANO (MAIN ETHIOPIAN RIFT): CORRECTION AND VALIDATION STEPS IN RELATION WITH VOLCANISM, LAKE WATER AND CARBON BALANCES

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ABSTRACT. Located in the Ziway-Shala Basin of the Main Ethiopian Rift, Lake Langano is part of an asymmetric half-graben, defined by a series of north-northeast–trending faults in the tectonically active zone of the rift. A 15-m deep succession of organic homogeneous muds, silts, bioclastic sands, and pyroclastic layers was cored in 1994. The definition of a certified radiocarbon chronology on these deposits required the indispensable establishment of modern hydrological and geochemical balances. The isotopic contents of the total dissolved inorganic carbon (TDIC) of surface water clearly show the influence of a deep CO_2 rising along the main fault crossing the lake basin. The 5.8 pMC disequilibrium existing in 1994 with the atmosphere likely produces the aging of authigenic materials developing at the lake surface. However, with a mean residence time of ~15 years, this apparent ^{14}C aging of Lake Langano water still integrates the ^{14}C produced by the nuclear tests in the 1960s. Reconstructing the natural ^{14}C activity of the lake TDIC allows for the quantification of the deep CO_2 influence, and for the correction of AMS-^{14}C datings performed along the core. The correction of the AMS-^{14}C chronology defined on Lake Langano allows for a better understanding of paleohydrological changes at a regional scale for at least the last 12,700 cal BP.

INTRODUCTION

We present here part of the geochemical and isotopic investigations of lake water and sediments performed on Lake Langano that belongs to the Ziway-Shala Basin, Main Ethiopian Rift (Figure 1). This study was conducted under the French-Ethiopian Project ERICA ("Environmental Research for Intertropical Climate in Africa") funded since 1994 by both specific research programs of INSU-CNRS (PNEDC/DYTEC/VARIENTE), the French-Ethiopian Cooperative Program in Earth Sciences (INSU-CNRS), the Ministry of Foreign Affairs (France), and the Department of Geology and Geophysics, University of Addis-Ababa (Ethiopia). This paper focuses on performing and correcting the accelerator mass spectrometry (AMS)-radiocarbon datings on authigenic materials taken from the LL-III sedimentary sequence collected in the north-eastern part of Lake Langano in 1994 (Figure 1), with the aim of:

1. defining more precisely the lake hydrological and geochemical balances in a very active geodynamic/geothermic context, i.e., taking into account deep gases and diagenetical processes influences,
2. validating the AMS-^{14}C corrections and chronology via the application of two successive geochemical correction models, and
3. trying to contribute to the reconstruction of paleoenvironmental evolution at a regional scale by comparing sedimentary rates of depositional sequences with paleoenvironmental phases already described in the Ziway-Shala Basin (Gasse and Street 1978; Street 1981; Bonnefille et al. 1986; Gibert et al. 1999).

Because ^{14}C excess has been produced in the atmosphere due to nuclear weapons testing in the mid 1950s and integrated in the biosphere, most of the studies conducted focused on the measurements of atmospheric ^{14}C activity as an accurate indicator of CO_2 exchanges between the different carbon

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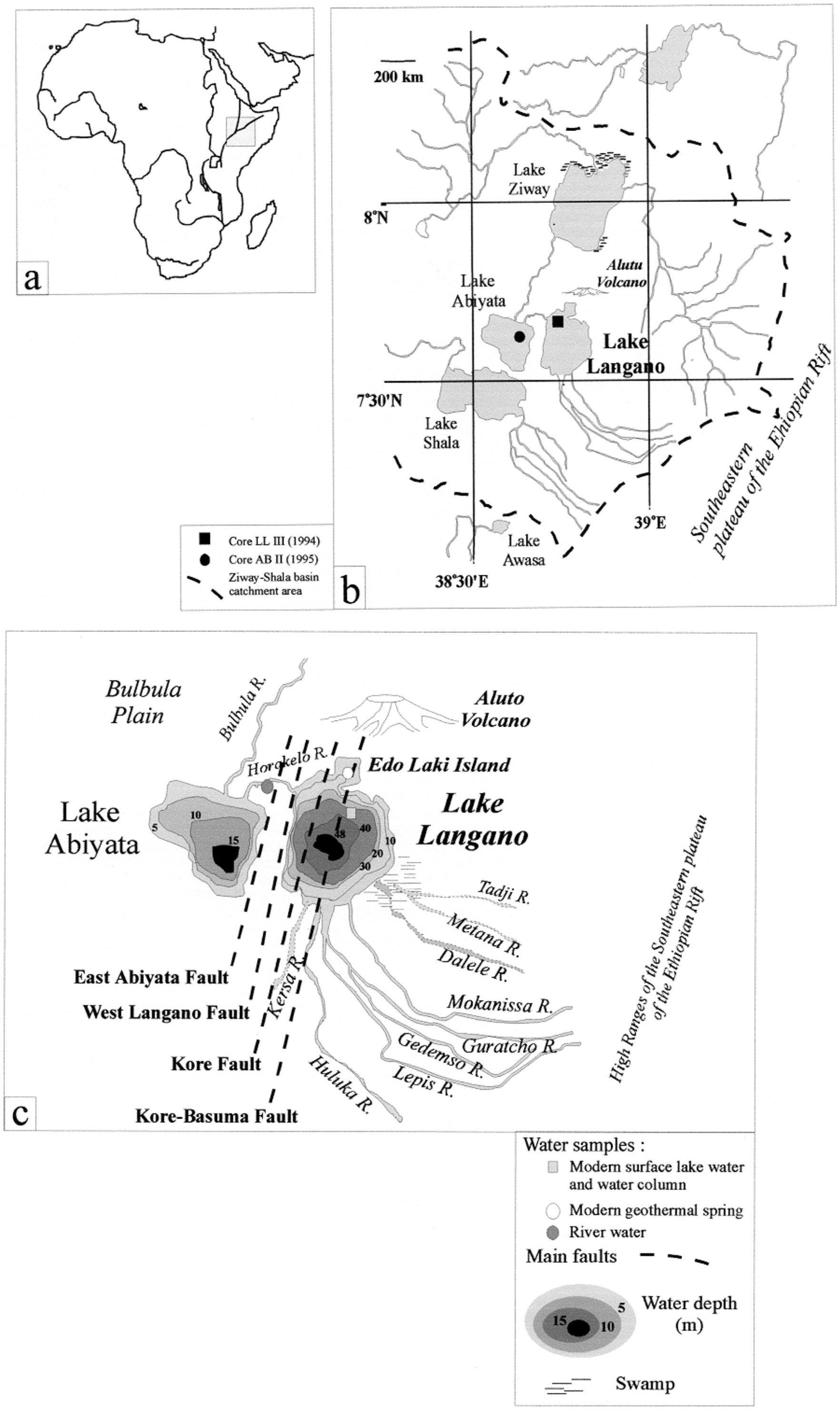


Figure 1 Parts a and b: location map of the Ziway-Shala basin and of Lake Langano (East Ethiopian Rift); part c: Bathymetry of Lakes Abiyata and Langano, location of water samples and of Lake Langano Core LL-III (see text and Figure 5 for description).

Table 1a (top) Measured AMS-^{14}C activities and associated $\delta^{13}C$ values of sediments from Lake Langano Core LL-III. Table 1b (bottom) AMS-^{14}C datings of sediments from Lake Langano Core LL-III. Key: A—Measured ^{14}C ages; B—^{14}C ages corrected from the TDIC aging, considering a mean residence time of 15 yr; C—^{14}C ages of column B corrected from post-sedimentary recrystallization; D—calibration of ^{14}C ages of columns A to C; E—^{14}C ages corrected from the TDIC aging, considering a mean residence time of 20 yr; F—^{14}C ages of column E corrected from post-sedimentary recrystallization; G—calibration of ^{14}C ages of columns A, E, and F.

Table 1a

Depth (cm)	Type	Analyse Nr (Orsay)	^{14}C Activity (pMC)	Measured ^{14}C Age (yr B.P.)	$\delta^{13}C$ (‰ vs PDB)
121.5	Charcoal	H1495	57.2 ± 0.8	4490 ± 70	-15.88
246.0	TOM	H1492	49.4 ± 1.3	5670 ± 100	-
412.9	Charcoal	H1420	47.5 ± 0.9	5980 ± 80	-18.17
645.6	TOM	H1421	40.4 ± 1.0	7280 ± 80	-25.16
817.1	Charcoal	H1217	30.8 ± 0.4	9460 ± 100	-24.60
958.0	Charcoal	H1220	30.3 ± 0.4	9590 ± 100	-20.98
970.3	Charcoal	H1369	30.1 ± 0.3	9640 ± 80	-
1048.0	Shell	H1189	21.7 ± 0.3	*12270 ± 100*	-
1185.0	Shell	H1190	24.3 ± 0.3	*11360 ± 110*	-

TOM : Total Organic Matter ; Error bars correspond to 1 sigma (1σ) deviation. Sampling date : November 1995.
Analytical uncertainties of ^{13}C measurements on TOM and biogenic carbonates are 0.05 and 0.02 ‰ vs PDB respectively.

Table 1b

		A	**B**	**C**	**D**	**E**	**F**	**G**
Depth (cm)	^{14}C Activity (pMC)	Measured ^{14}C Age (yr B.P.)	^{14}C Age (yr B.P.) Corrected from TDIC ageing (*TR = 15 yr)	^{14}C Age (yr B.P.) Corrected from TDIC (*TR = 15yr) and recrystallization	**Calibrated ^{14}C Ages (*) (cal. yr B.P.) (*TR = 15 yr)**	^{14}C Age (yr B.P.) Corrected from TDIC ageing (**TR = 20 yr)	^{14}C Age (yr B.P.) Corrected from TDIC (**TR = 20yr) and recrystallization	Calibrated ^{14}C Ages (*) (cal. yr B.P.) (**TR = 20 yr)
121.5	57.2 ± 0.8	4490 ± 70			***5120*** *(5315/4960)*			*5120 (5315/4960))*
246.0	49.4 ± 1.3	5670 ± 100	4880		***5600*** *(5670/5590)*	4690		*5385 (5585/5310)*
412.9	47.5 ± 0.9	5980 ± 80			***6800*** *(6895/6685)*			*6800 (6895/6685)*
645.6	40.4 ± 1.0	7280 ± 80	6495		***7425*** *(7460/7320)*	6310		*7250 (7315/7100)*
817.1	30.8 ± 0.4	9460 ± 100			***10690*** *(11060/10560)*			*10690 (11060/1056*
958.0	30.3 ± 0.4	9590 ± 100			***10870*** *(11165/10700)*			*10870 (11165/1070*
970.3	30.1 ± 0.3	9640 ± 80			***11110*** *(11170/10760)*			*11110 (11170/1076*
1048.0	21.7 ± 0.3	*12270 ± 100*	11560	9990	***11400*** *(11685/11235)*	11310	9710	*11165 (11200/10870)*
1185.0	24.3 ± 0.3	*11360 ± 110*	10580		***12725*** *(12875/12355)*	10390		*12330 (12770/11955)*

*, with Δ equal to 9.32, and **, with Δ equal to 12.42 pMC (see text for details).
(*) ^{14}C calibration method: CALIB 4.0 program, Stuiver et al. 1998a. *Radiocarbon* 40(3):1041–83.

reservoirs such as the different compartments of the atmosphere, the ocean, and the biosphere at a global scale. More recently, highly accurate studies have been performed on speleothems, considering 2- or 3-black box models for the reconstruction of e.g. vegetation conditions and CO_2 partial pressure in caves (Genty and Massault 1997, 1999). However, little was performed on the integration and recycling of this nuclear-induced ^{14}C in lakes, in relation with the lake water balance used as an indispensable reference system, for past environmental reconstructions in continental domains.

Overimposed to the recent history of ^{14}C at a global scale, the understanding and modeling of regional/local production and dissolution of deep gases in surface water bodies (such as CO_2 or CH_4 linked to underwater geothermal springs) are required in areas where global paleoenvironmental changes can be hidden by local hydrological and hydrogeochemical fluctuations linked to volcanic and/or tectonic evolution of the region. This is of high importance because the main problem encountered for paleoclimatic reconstructions at a global scale from cored lacustrine sequences remains the establishment of reliable ^{14}C time-scales especially in regions closely related to the monsoon evolution such as East Africa or Tibet (e.g. Gasse et al. 1990; Fontes and Gasse 1991; Fontes et al. 1993, 1996; Colman et al. 1996; Johnson 1996; Geyh et al. 1998; Gibert et al. 1999; Gasse 2000).

BACKGROUND

Climatological and Geological and Settings

The four lakes Ziway, Langano, Abiyata, and Shala belong to a 100-km-long and 40-km-wide, north-northeast–south-southwest trending faulted and caldera-bearing system located in the axial zone of the Main Ethiopian Rift between 7° and 8°30′N latitude (Figure 1). This complex basin is bound to the east by the Southeastern Plateau including the Arussi-Bale Massif, and in to west by the Ethiopian Shewan Plateau. Fluvio-lacustrine sediments (silts, clays, diatomites) interbedded with volcanic/volcanoclastic products form the 600-m-thick infill of the basin (Le Turdu et al. 1999).

The regional climate of the Ziway-Shala area is tropical monsoonal with mean annual precipitation and mean annual temperatures varying respectively from 1180 mm and 16.3 °C on the highlands (Addis-Ababa station; Figure 1a; WMO/IAEA Network 1998; Rozanski et al. 1996), to 600 mm and 25.0 °C on the drier part of the lowlands around the lakes (Chernet 1982). The pluviometric regime is driven by the yearly oscillation of the Inter-Tropical Convergence Zone (ITCZ), which determines a warm, wet summer (maximum rainfall from June to September), and a dry, cold, and windy winter. However, the study area is located south of the Addis-Ababa station, and is thus comprised between the unimodal (e.g. Addis-Ababa), and the bimodal annual cycles of rainfall (with a second, short rainfall season in March–April; Chernet 1998).

Lake Langano (7°40′N, 38°50′E; 1582 m asl) occupies a 20-km-long, asymmetric half-graben in a central basin (48-m maximum water depth) and western littoral plateau (34-m maximum water depth), both delineated by a set of three north-northeast–trending faults, i.e., the West Langano, Kore and Kore-Basuma Faults (namely WLF, KF, and KBF; Figures 1c and 2). Unlike neighboring Lake Abiyata, which occupies a rather stable depression (Gibert et al. 1999), Lake Langano basin is still tectonically active, as indicated by faulted modern sediments and natural gas bubbles of geothermal origin reaching the lake surface above the KBF (Le Turdu et al. 1999; Figure 1c).

Furthermore, degassing has been suspected to the north along the KBF, as well as along the WLF (Figure 2), and evidenced through isotopic measurements on groundwater and soil gases (Tables 2 and 4). Knowing that carbonated gas such as CO_2 or CH_4 may alter the ^{14}C-^{13}C system via apparent water aging, analyses of the ^{13}C signature of soil CO_2 have been performed around Lake Langano.

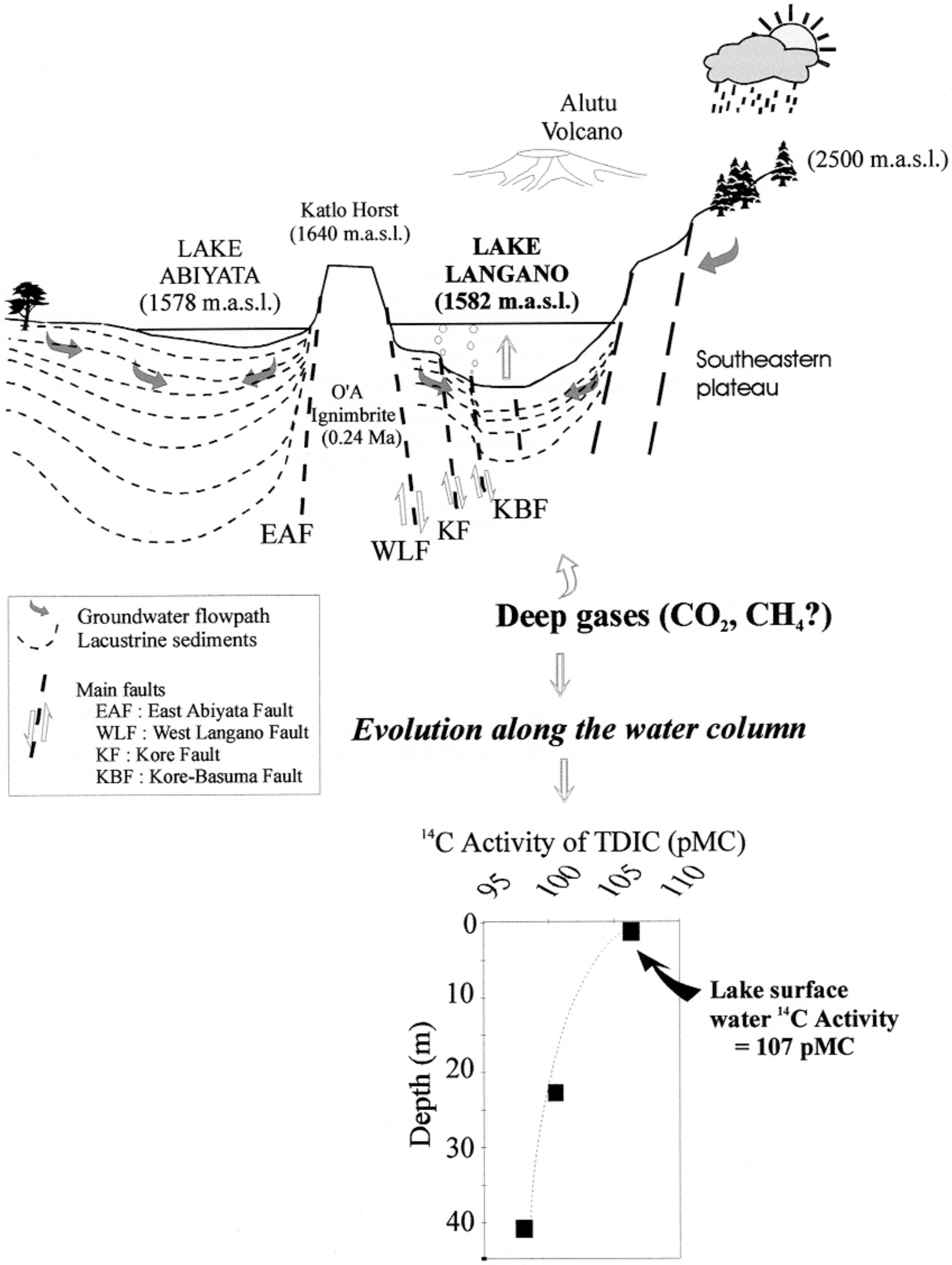


Figure 2 Schematic description of Lakes Abiyata and Langano sub-basin, and associated ^{14}C evolution of the total dissolved inorganic carbon (TDIC) of Lake Langano water (see Table 2 and Figure 1 for sample locations)

Four samples of soil gases were thus taken from three sites (Table 4 lists locations and results). The first three samples of soil gas were obtained at about 2 km from the active fault zone, respectively under natural vegetation and culture (site 8, Table 4). Both have a ^{13}C content in agreement with the mean $\delta^{13}C$ values of soil gas in sahelian vegetation zone, i.e., about –14‰ vs. PDB. In contrast, the fourth gas sample taken at the southern end of the WLF escarpment shows an enriched $\delta^{13}C$ value of –1‰ vs. PDB (site 7, Table 4). Such an enrichment in ^{13}C could be produced by CO_2 and/or CH_4 gases, via two geochemical pathways because their fractionation factors are quite different (Bottinga 1969; Friedman and O'Neil 1977). However, if we consider that CH_4 produced by organic matter degradation during burial will get a ^{13}C signature of about –70‰ vs. PDB, the mixing with atmospheric CO_2 in soil producing a $\delta^{13}C$ value of –1‰ vs. PDB requires the soil-CH_4 reservoir to be considered infinite with respect to the atmospheric reservoir (^{13}C fractionation factor of CO_2-CH_4: ~–70‰ at 20 °C). This is quite impossible in this arid, vegetation-free area. Moreover, because carbonate chemistry in hydrological systems is strongly influenced by deep CO_2 (Scripps Institution of Oceanography 1977), we assume that this gas mainly consists of CO_2. As a consequence, this feature will induce some complications 1) in the establishment of the lake carbon balance, and 2) in the interpretation of water residence time inferred from carbon chemistry and isotopic contents.

Table 2 Measured AMS-^{14}C activities, associated $\delta^{13}C$ values and in-situ measurements of surface water, groundwater, and thermal spring from the Lake Langano basin[a]

Sample	Depth	Analyses nr (Orsay)	^{14}C activity (pMC)	Measured ^{14}C age (BP)	$\delta^{13}C$ (‰ vs. PDB)	pH	T (°C)	EC ($mS.cm^{-1}$)
Lake water column	Surface	H1207	107.1 ± 0.9		−1.76	21.2	9.2	1503
	25 m	H1386	100.4 ± 0.6			21.6	9.2	1498
	40 m	H1389	97.8 ± 0.6			21.4	9.1	1496
Geothermal spring		H1381	4.8 ± 5.1			n.d.	>100	2580
Horakelo River	Surface	H1209	112.0 ± 0.8	Modern	−2.13	18.9	9.3	1845
Bekele Mola borehole			40.8 ± 0.6		−3.62			

[a] Sample date November 1994. See Figure 1 for sample locations.

The LL-III Core Sedimentary Sequence

High-resolution reflection seismic data acquired in 1994 (Sparker profiles; Jeudy 1995; Le Turdu et al. 1999) combined with core data (Mohammed and Bonnefille 1991; Mohammed 1992) indicate that recent sedimentation in the central basin is characterized by homogeneous muds and organic oozes with a high gas content of biogenic or hydrothermal origin. The 14.70-m long LL-III sequence was cored under 15-m water depth, on the northern end of the western littoral plateau (Figure 1c) using the Equarift stationary piston corer.

Sediment lithology is represented in Figure 3 (Le Turdu et al. 1999) and is characterized as follows: 1) from 1470 to ~1000 cm, 0.1- to 0.5-m-thick beds of ungraded to normally graded sand or gravelly sand are bound by flat, non-erosive surfaces, or diffusely bounded. These sands are overlain, from base to top, by massive dark-brown, silty muds, by medium- to coarse-grained sand, and by massive to laminated muds, 2) from 1000 cm to the core top, deposits consist of an alternation of dark-brown to grey-green diatom-rich, massive silty-clayey muds and green, silty sands. Air-fall pyroclastic layers from ~1 to 3 cm thick are situated between 960 and 820 cm indicating recent explosive volcanic activity. Very homogeneous muds are found between 150 and 345 cm, and from 580 to 730 cm. The core top is marked by more thick pyroclastic layers (532–537 cm; 385–390 cm; 348–352.5 cm; 139–150 cm), interbedded with greyish homogeneous marls.

Table 3 Chemical contents of some surface water and groundwater from Lake Langano basin

Sample	Sampling	TDS Time	pH	Na^+ (mg.L^{-1})	K^+ (mg.L^{-1})	Ca^{2+} (mg.L^{-1})	Mg^{2+} (mg.L^{-1})	HCO_3^- (mg.L^{-1})	CO_3^{2-} (mg.L^{-1})	Cl^- (mg.L^{-1})	SO_4^{2-} (mg.L^{-1})	F^- (mg.L^{-1})	Br (mg.L^{-1})	NO_3 (mg.L^{-1})
LAKE LANGANO														
Lake surface ***(1)***	**1995**		**9.2**	**361**	**34**	**4.6**	**6.5**	**649**	**72**	**151.0**	**11.2**	**14.0**		
Shebelle (L. suface) ***(2)***	**1994**	1346	9.2	386	28	4.5	0.8	622	72	214.0	18.3	0.0	0.65	0.00
Bekele Mola (L. suface) ***(3)***	**1994**		9.2	361	34	4.6	6.5	649	72	151.0	11.2	14.0		
Island (L. surface) ***(4)***	**1994**	1335	9.2	375	28	4.3	6.7	665	72	156.4	11.4	14.9	0.60	0.15
Along the water column (5)														
Fault (L. surface)	**1994**	1425	9.2	398	28	4.67	6.27	736	72	151.9	11.9	14.2	0.59	0.61
Fault (10 m depth)	**1994**	1524	9.2	426	28	4.37	6.38	810	72	150.5	11.5	14.5	0.59	0.11
Fault (25 m depth)	**1994**	1402		392	28	4.90	6.45	720	72	151.3	11.7	14.6	0.59	0.53
Fault (40 m depth)	**1994**	1382	9.2	386	28	5.66	6.78	704	72	151.4	12.2	14.6	0.59	0.51

With sites located as follows :

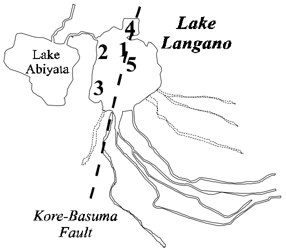
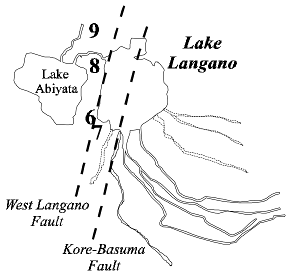


Table 4 Measured AMS-^{14}C activities and associated $\delta^{13}C$ values of modern vegetation and soil gases from Lake Langano basin

Type*	Analyse Nr (Orsay)	^{14}C Activity (pMC)	$\delta^{13}C$ ($^o/_{oo}$ vs PDB)
Modern plants			
Wood ***(6)***	H1785	109.0 ± 0.6	-23.1
Wood ***(6)***	H1787	109.9 ± 0.7	-23.8
Soil Gases under:			
Natural vegetation-Fault zone ***(7)***			-1.2
Natural vegetation ***(8)***			-13.0
Cultivated field ***(9)***			-14.4

*, Samples taken from trees located nearby the southern bank/beach of Lake Langeno (see Figure 1 for sample location).

With sites located as follows :



Lake Langano Modern Hydrological System

The modern hydrological and water geochemical balances were investigated first, to provide a reference system for lake water residence time and carbon recycling over the whole catchment (e.g. Travi et al. 1997; Chernet 1998).

Hydrological Balance

Lake Langano is an open lake with a mean surface of about 230 km^2. Water inflow mainly comes from small, intermittent rivers that drain a catchment consisting mostly of ignimbrites and some acidic volcanic rocks, and reach the lake on its southern and southeastern shores (Figure 1). Waters entering the lake are sodium-carbonated-dominated such as $[Na+K] > [Ca+Mg]$ and $[Ca+Mg] < [HCO_3]$ (Table 3). The lake output is concentrated on the Horakelo River (long time-series of gauging data in Chernet 1998) that flows from the northeastern shore of the lake towards Lake Abiyata (Figure 1). For a maximum water level fluctuation of about 1 m registered between 1971 and 1994 (Chernet 1998), Lake Langano volume varied between 5400 and 5700 Mm^3.

Chemical models showed that the water mineralization is mainly influenced by the evaporative concentration process of a unique source of elements (silicate hydrolysis) producing $NaHCO_3$ in water with high pH values (Table 3; Chernet 1998; Chernet, Travi and Valles 2001). This evaporative process is observed all over the basin and implies homogeneity of the water chemical characteristics at the basin scale. As a result, there is a relative stability of the HCO_3 content (with respect to the present-day lake level), associated with very low calcium contents (Chernet 1998).

The mean residence time of Lake Langano water is calculated according to hydrological measurements conducted during the last 20 years, according the definition of Pourriot and Meybeck (1995) as follows:

$$t = V/I \quad \text{or} \quad t = V/Q \tag{1}$$

with t = mean residence time; V = lake volume; I = total inputs, and Q = total outputs.

Using a mean lake volume of 5550 Mm^3, a mean outflow value of about 120 Mm^3.yr^{-1} as represented by the Horakelo River flows for the 1979–1994 period, and an evaporation rate close to 2 m.yr^{-1} (Chernet 1998; Vallet-Coulomb et al. 2000), the mean residence time of Lake Langano waters is estimated between 10 and 15 years.

Carbon balance: In the water balance, the "evaporation" term is dominant. However, dissolved carbon species (i.e. dissolved CO_2, HCO_3–, CO_3^{2-}) are not removed from the lake through evaporation. The carbon cycle and carbon residence time in Lake Langano water have to be considered. The estimation appears to be possible since there is a linear trend in carbonate concentrations in Lake Langano water during the evaporative concentration process (Chernet 1998). This implies both a very low rate of $CaCO_3$ chemical precipitation and a relatively constant stock of carbon for the same lake level.

As demonstrated by a long time series of in-situ chemical and gauging measurements, the Horakelo River water presents the same carbon concentration as that of Lake Langano water, i.e. 600–700 mg.L^{-1} (Chernet 1998). We thus can state that:

$$t = V \times [C_{\text{Lake}}] / Q \times [C_{\text{River}}] = V/Q \sim 5550/120 \tag{2}$$

with V = lake volume, Q = total outputs (i.e. Horakelo River), and $[C_{\text{Lake}}]$ and $[C_{\text{River}}]$ = carbon concentrations of lake and river waters, respectively, giving a mean residence time of about 45 years.

However, the relative hydrological steady state does not fully exclude carbonate precipitation as shown by the calcium content decrease. Moreover, the contribution of carbon brought to the lake by deep CO_2 and its associated degassing at the lake surface are not taken into account. Assuming that deep CO_2 production remains constant, these contributions might be important especially during lowstands. The value of 45 years is a maximum estimate and we can reasonably assert that the mean carbon residence time in Lake Langano would be between 10 and 30 years. The mean values of 15 and 20 years will thus be used below for the calculation and correction of the ^{14}C chronology of lacustrine deposits.

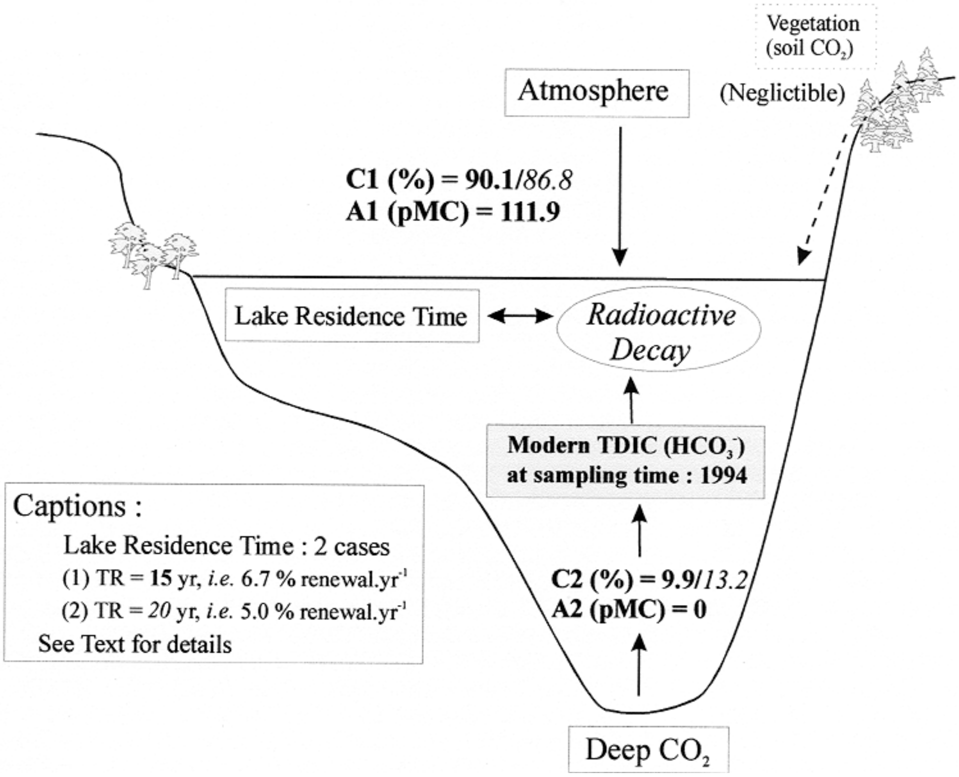


Figure 3 Representation of the 2-black box model used for ^{14}C datings correction

Isotopic Contents of Modern Water

Isotopic measurements (^{13}C content and ^{14}C activity) were performed on the TDIC of 1) samples from the water column at three depths: 40 m, 25 m, and the lake surface, 2) the lake outflow, i.e. Horakelo River, and 3) the geothermal spring rising on the small Edo Laki Island at the northern end of the lake (North Bay) (Figure 1). Sample locations and analytical results are reported in Table 2.

The ^{14}C activity of the 40-m deep water sample collected at about 2 km from the KBF is 97.8 (±0.6) pMC, and confirmed the underwater geothermal activity. Phenomena of dispersion and diffusion of carbon within the water column are not sufficient to maintain the isotopic equilibrium between the TDIC and the atmospheric reservoir. At sampling time, the ^{14}C activity of surface water only is 107.1 (±0.9) pMC compared to the 111.9 pMC activity of atmospheric CO_2 recorded in 1994, and as measured on the Horakelo River sample where re-equilibration with the atmosphere is totally reached (i.e. 112.0 (±0.8) pMC; Figure 3; Table 2). Datings performed on phyto-planktonic organic matter and shells living in the surface lake water thus need to be corrected.

RESULTS

AMS-^{14}C Chronology of Lake Langano Core LL-III

Authigenic materials are required for the establishment of the ^{14}C chronology and their selection has been based on microscopic observation of charcoal and macrophyte remains. Zones with an important detrital fraction or presenting gas bubbles, even rich in charcoal, have been eliminated. The chronology of Core LL-III is then based on 9 AMS-^{14}C datings as performed on authigenic charcoal, total organic matter (TOM), and surface-living shells (*Melanoides tuberculata*; J C Plaziat, personal communication).

All the samples obtained by hand-picking directly after the core opening were subjected to the standard chemical protocol for AMS analyses 1) acid-alkali-acid chemical treatment for organic matter, and 2) cleaning with slightly acidic solution for biogenic carbonates. AMS-^{14}C and associated ^{13}C analyses were conducted on aliquots prepared according to the AMS protocol: 1) organic material: burning at 860 °C for 30 mn, under vacuum, in presence of a mixing of copper-(II)-oxide/copper-(III)-oxide and silver thread, and 2) shells by H_3PO_4 destruction under vacuum overnight. The CO_2 gas obtained was graphitized on powdered iron with hydrogen at 650 °C for 100 min, and graphite was compressed in analytical plots. Aliquot of the CO_2 gas was then used for stable isotope measurements and/or stored for ^{14}C-dating duplicates. Graphite sources were prepared in Orsay (Laboratory of Hydrology and Isotope Geochemistry, Orsay, France), and counted by the accelerator mass spectrometer at Gif-sur-Yvette (Tandetron facility, France). Analytical uncertainties, including laboratory errors, are ± 0.1‰ for δ^{13}C and between 0.5 and 0.8 pMC for ^{14}C activity. All the dates are converted to calendar ages according to the revised calibration program CALIB 4.0 (Stuiver et al. 1998; Table 1b, section C), considering the mean 15-yr residence time of lake water.

The interpretation of the datings are discussed within the framework of the internal consistency of the whole chronology as well as according to the hydrological and geochemical balances of the basin. All the ^{14}C datings performed are in agreement with the stratigraphy, except the two lowermost ages defined on biogenic carbonates. The ^{14}C discrepancies correspond to datings of originally aragonitic *Melanoides tuberculata* shells, i.e. 12,270 (±100) BP and 11,360 (±110) BP, at 1048.0 and 1185.0 cm depth, respectively. Semi-quantitative analyses using X-ray diffractometry show that the deepest shell sample is still made of pure aragonite while the more fragile 1050-cm sample presents 17% (± 1%) of secondary calcite (Table 4). These two samples of the same species develop in shallow aquatic environments, and the recrystallization can only have happened during burial. Thus, a second correction has to be applied.

Deep CO_2 and Diagenetic Processes on the Carbon Content of Lake Langano Deposits—First ^{14}C Correction

The first correction to be considered corresponds to the imbalance of carbon species with respect to normal geochemical conditions and carbon acquisition, in both soils and water.

1. *Deep CO_2 influence processes on the initial carbon content of Lake Langano deposits*

A first source of ^{14}C aging of authigenic materials (such as charcoal and plant remains) corresponds to the influence and assimilation of ^{14}C-free soil CO_2 linked to active faults by living plants. Bruns and co-authors (1980) described the specific δ^{13}C/A^{14}C evolution of organic materials exposed to ^{14}C-free CO_2 fluxes in geothermal contexts, and showed that higher plants can have apparent (older) ages due to the possible admixture and assimilation during photosynthesis of up to 16% of dead CO_2. Two woody samples from modern vegetation (benches and leaves from *Pinus/Acacias*) were taken in 1995 and 1996 from trees located right on the WLF on Lake Langano Southern beach (point 7; Table 4). They present ^{14}C activities of 109.0 (±0.9) and 109.9 (±0.9) pMC, respectively, lower than that of the atmosphere at sampling time. Considering the fractionation equation as follows: $\Delta^{14}C = 2.3\ \varepsilon^{13}C$, with ε, the fractionation factor between ^{13}C and ^{14}C (Saliège and Fontes 1984), the maximum 3-pMC difference observed with the atmosphere corresponds to a ^{13}C variation of 16‰ vs. PDB. One can note that this is exactly what is observed between the mean $\delta^{13}C$ value of the woody samples analyzed (i.e. –23‰ vs. PDB) and the ^{13}C content of the atmosphere (i.e. –7‰ vs. PDB). For ^{14}C activities comprised between 20 and 60 pMC, a 3-pMC variation of the initial ^{14}C activity gives a maximum age discrepancy of only about 250 years. Moreover, the mixing of deep CO_2 in soil gases is localized nearby the lake shores, and influences only a part of the vegetation of the catchment area. Such a phenomenon of apparent aging of plant debris via ^{13}C-depleted soil gases does not have to be considered around Lake Langano.

2. *Geochemical evolution of the ^{14}C cycle in the lake*

Following the estimation of the lake water mean residence time, the above-mentioned apparent aging of 5.8 pMC of the lake surface water integrates the ^{14}C produced by nuclear weapon tests in the atmosphere during the 1960s. Reconstructing the evolution curve of the natural ^{14}C activity in the lake will allow for 1) the establishment of the single influence of the deep CO_2 on the initial TDIC ^{14}C content before the 1960s, and 2) the correction of AMS-^{14}C datings for the authigenic materials along the lacustrine sequence. The calculation of the dead carbon proportion before the influence of the ^{14}C produced in the atmosphere by nuclear weapon tests and still present in the lake in 1994 is required to allow for the reconstruction of ^{14}C initial curves.

The system can be described with a two-box model (Figure 3).

$$A^{14}C_{\text{ TDIC of lake water}} = [C1 \times \Sigma_{(i=1\text{ to }i=n)}\ A^{14}C_{\text{ Atmospheric CO2}}] + [C2 \times A^{14}C_{\text{ Deep CO2}}] \qquad (3)$$

and

$$C1 + C2 = 100\% \qquad (4)$$

with i, single considered year, n, mean residence time of lake water, C1, percentage of atmospheric CO_2 dissolving in the lake per year (assumed as constant for each of the n years), and C2, percentage of deep CO_2 bubbling at the lake bottom per year (assumed as constant for each of the n years).

The dead carbon proportion refers to the following conditions:

1. using equation (1);
2. considering no Suess effect (Suess 1955), which means a constant atmosphere activity during the pre-bomb period (100 pMC), and a pre-bomb year, i.e. 1950;
3. assuming that this deep CO_2 is of crustal origin and thus, ^{14}C-free ($A^{14}C_{\text{ Deep CO2}} = 0$ pMC).

Equation (1) becomes:

$$A^{14}C_{\text{ TDIC of lake water}} = C1 \times \Sigma_{(i=1\text{ to }i=n)}\ A^{14}C_{\text{ Atmospheric CO2}} \qquad (5)$$

The atmospheric ^{14}C activity has been reconstructed using already published data (e.g. Rafter and Ferguson 1957; Levin et al. 1992, 1995; Levin and Kromer 1998; Nydal and Lovseth 1983; Genty and Massault 1999; Figure 4).

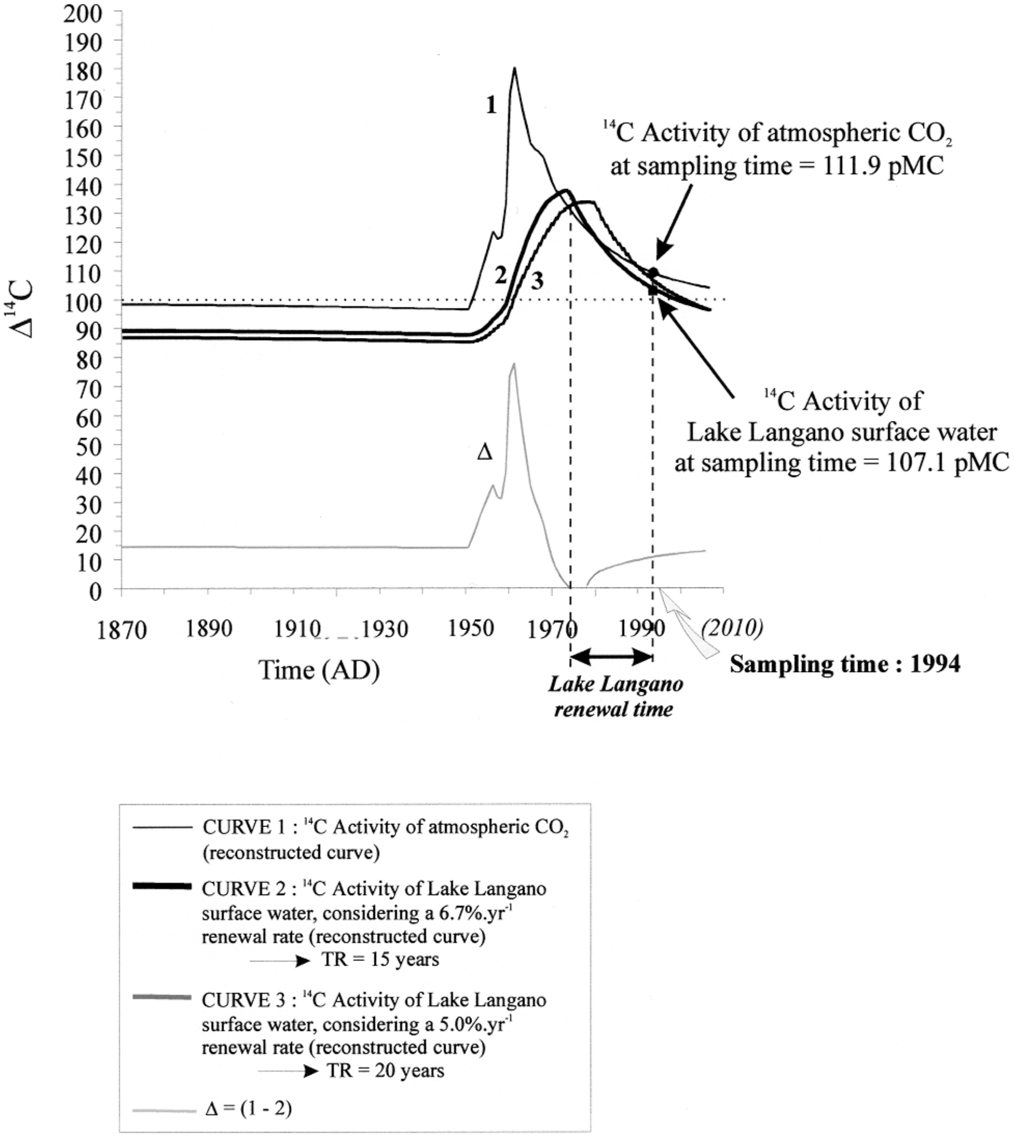


Figure 4 Comparison of the reconstructed ^{14}C activity of Lake Langano surface water with that of atmospheric CO_2 (Curve 1; after Libby et al. 1949; Levin et al. 1980, 1992, 1995; Kromer and Becker 1993; Levin and Kromer 1998); two specific cases are considered: Curve 2 for a mean residence time of 15 yr, and Curve 3 for a mean residence time of 20 yr.

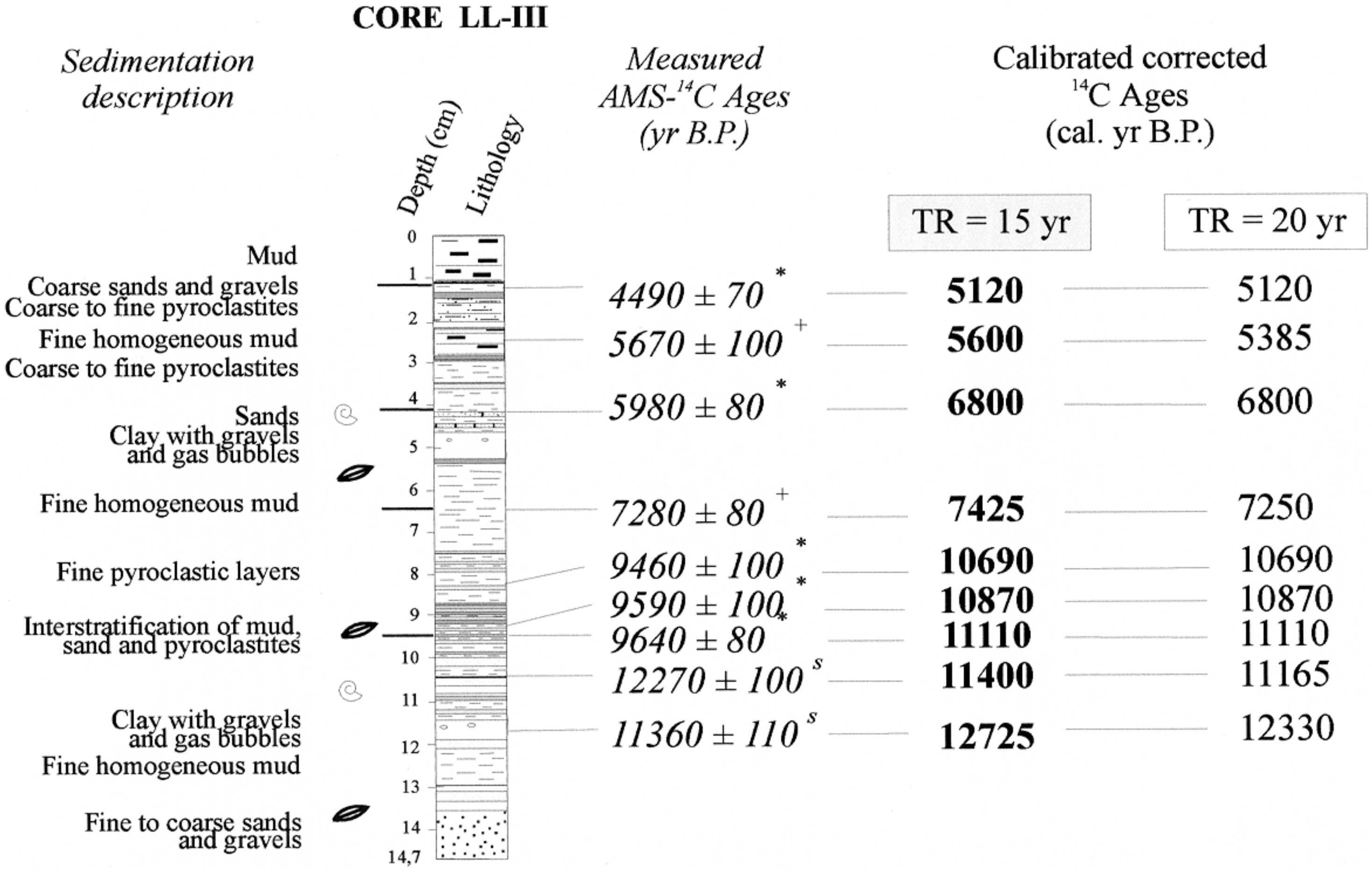


Figure 5 Stratigraphic log of Lake Langano Core LL-III and associated measured and corrected ^{14}C chronologies (see text for calibration methods)

In order to fit the measured ^{14}C activity of the lake water TDIC (107.1 (±0.9) pMC) with the evolution of the atmospheric ^{14}C concentration (i.e. true $A^{14}C_{\text{Atmospheric CO2}}$ in 1994 = 111.9 pMC), a step-by-step incrementation has been applied on parameter C1. This brought to the calculation of the respective parts of every end-member of the model:

- For a mean residence time (TR) of 15 years: C1 = 9.9% and C2 = 90.1%;
- For a mean residence time (TR) of 20 years: C1 = 13.2% and C2 = 86.8%.

Curves (2) and (3) have been reconstructed by extending the above-mentioned C1/C2 ratio to the past (Figure 4). The two scenarios of a 15-yr and a 20-yr residence time show differences of respectively 9.32 and 12.42 pMC before the 1960s between the atmospheric ^{14}C concentration and the lake TDIC.

Despite the fact that the TDIC activity of lake surface waters has obviously fluctuated through time in response to lake level variation, the ^{14}C diffusion rate in the lake water column must be considered unchanged at the sampling site and within the period reached in core LL-III. Indeed, this proposition is likely correct when Lake Langano is disconnected from the three other lakes of the basin, since its level is controlled by the Horakelo River. However, the hypothesis of an unchanged deep-^{14}C production at the lake bottom and diffusion rate in the water column (due to increasing dilution processes?) becomes unpredictable during phases of lacustrine highstands.

Deep CO_2 and Diagenetical Influence Processes on the Carbon Content of Lake Langano Deposits—Second ^{14}C Correction (Diagenetical Processes on Biogenic Carbonates)

As described above (# Isotopic contents), the post-sedimentary recrystallization of the 1048-cm shell is likely due to preferential interstitial water circulations, assuming that this interstitial water has a ^{14}C-free TDIC due to deep CO_2 partial dissolution while rising. Since the first correction to be applied on this shell sample corresponds to the surface water TDIC aging (Table 1b, section A), the second correction varies according to the mean residence time of the lake water (Table 1B, section B). The correction is based on a simple mass balance model, as follows:

$$A^{14}C_{\text{recrystallized shell}} = \mathrm{LN}(2) \,/\, T \times \mathrm{LN}[((A_{\text{o [corrected]}} \times 0.17/100) + A_{\text{o [corrected]}})/A] \qquad (6)$$

with T = half-life of ^{14}C, $A_{\text{o [corrected]}}$ = initial ^{14}C activity of the sample after correction from the lake surface water apparent aging, and A = measured ^{14}C activity of the sample.

For a mean residence time of 15 yr, the two-step correction of the 1048-cm depth shell gives a minimum age of 9990 (± 100) BP (11,400 cal BP; Table 1).

DISCUSSION AND CONCLUSION

1. The successive geochemical corrections applied on ^{14}C datings performed on Lake Langano sediments are based on the establishment of the hydrological and chemical balances of the lake, considering a 15-yr residence time for the lake water, and taking into account both the nuclear-induced ^{14}C in the atmosphere and the deep ^{14}C-dead CO_2 production rising along active faults at the lake bottom. This allows for the definition of a reliable ^{14}C chronology along Core LL-III (Table1). The corrected ^{14}C time-scale indicates that Lake Langano sediments have registered the Late Pleistocene and Holocene periods, with a global mean sedimentation rate (msr) of 1.12 $m.ka^{-1}$.
2. The inflection points defined with the msr curve are obviously linked to the specific sedimentary levels dated due to the few datable materials available in Core LL-III. Nevertheless, these msr fluctuations are important and relatively well-correlated with the lithostratigraphy (Figure 5).

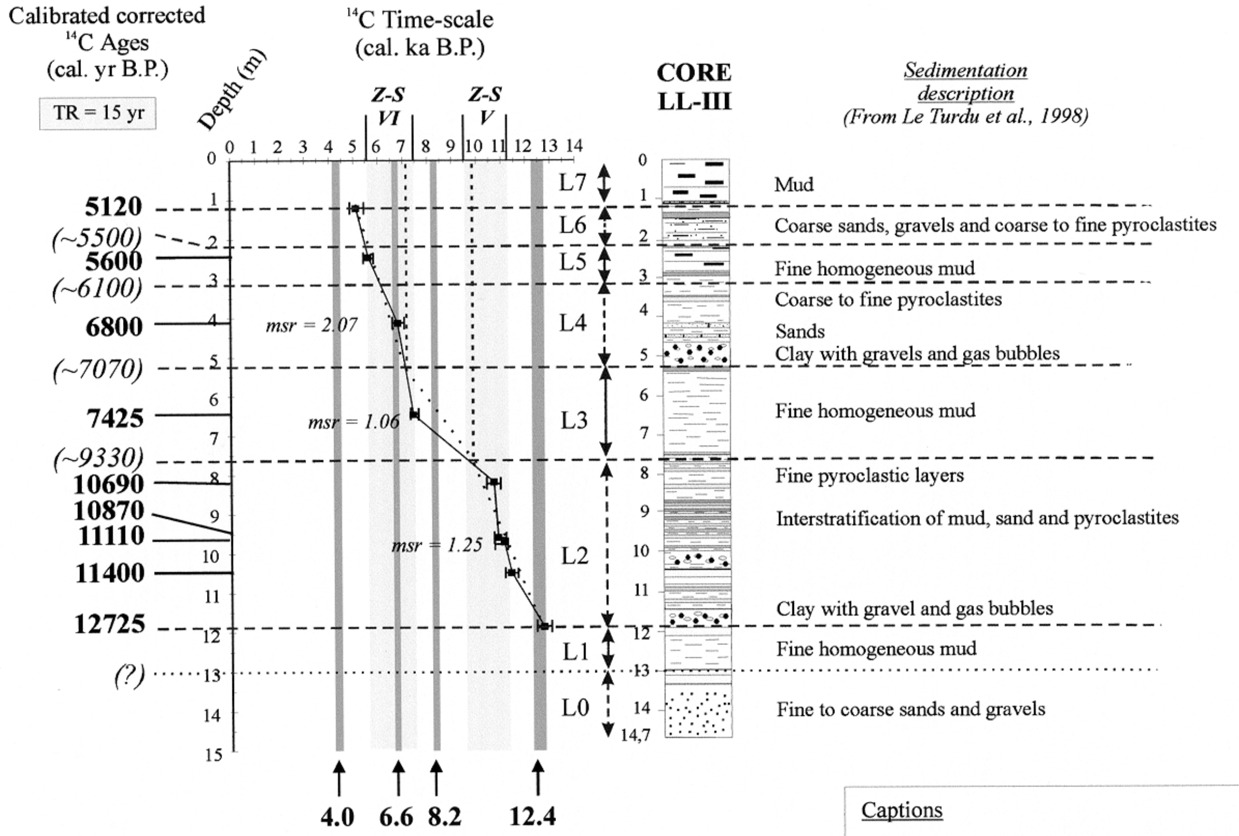


Figure 6 Attempt at reconstructing paleoenvironmental conditions of Lake Langano, with calculation of the mean sedimentary rates (msr; dashed lines) defined on Core LL–III–1994, with respect to previous works of Gasse and Street (1971), Street (1981) and Gillespie et al. (1983).

Captions

Z-S = Ziway-Shala lacustrine highstands (Street 1981)
Z-S V = 9950-8500 yr BP ; ***11,300–~9500 cal. yr BP***
Z-S VI = 6500-4800 yr BP ; ***7400–~5520 cal. yr BP***

⟷ Fine homogeneous sedimentation mainly
◄- - -► Detrital and volcanoclastic sedimentation mainly
msr = mean sedimentation rate (mm.yr^{-1})
↑ = weak monsoon episodes (Gillespie et al. 1983; Gasse 2000)

3. The comparison between the specific sedimentation facies (Le Turdu et al. 1999) and the AMS-^{14}C dates allows for the distinction of several major phases along core LL-III from base to top (Figure 6). These seven intervals, i.e. from L0 to L6, respectively, are not all marked by ^{14}C-dated levels and most of them have been calendar-^{14}C dated (in italics and brackets in Figure 6; see Table 1) by extrapolation between measured levels and seem to be relevant to deduce the paleoenvironmental history of Lake Langano with respect to previous works of Gasse and Street (1971) and Street (1981):
    - *Phases L0* (14.70-13.00m depth) and *L1* (13.00-12.72 m depth) at the very core base are characterized by a drastic difference in sedimentation: zone L0 (coarse sands and gravels) could be likely related to the crater rim erosion;
    - *Phase L2* (12.72–7.60 m depth; 12,725–~9330 cal BP) is mainly detrital-deposited (fine to coarse sands, gravels and pyroclatites), and is characterized by a high sedimentation rate of 1.25 mm.yr^{-1};
    - Although based on the stratigraphic description of Le Turdu and co-authors (1999) and only one single ^{14}C age, *Phase L3* is comprised between 7.60 and ~5.25 m depth (~9330–~7070 cal BP), and consists exclusively of finely homogeneous muds with a low msr, i.e. 1.06 mm.yr^{-1}; this sedimentation may reflect a calm deposition medium, with some shell development (Le Turdu et al. 1999);
    - *Phase L4* (~7070–~6100 cal BP) begins at ~5.25 m depth, and extends up to 3.15 m depth (core top); this interval is characterized by a high deposition rate, the increase in msr having been already began at the top of the L3 interval (mean msr = ~2.07 mm.yr^{-1});
    - *Phase L5* is defined between 3.15 and 2.10 m depth (~6100–~5500 cal BP) and consists on a high detrital fraction, except a small event of fine homogeneous mud between 2.9 and ~2.3 m depth;
    - *Phase L6* is comprised between ~2.30 and 1.25 m depth (~5500–5120 cal BP) and consists mainly in coarse sands, gravels and pyroclatites;
    - Chronological uncertainty, due to coring problems and any corresponding ^{14}C dates, remains for the core top (*i.e. Phase L7*) which corresponds to a very fine, smooth sedimentation.
4. At first glance, Lake Langano seems to react relatively in agreement with the lacustrine highstands previously determined by Street in 1981. The fluctuations of the lake level are marked by an important increase in the sedimentation rate occurring at the beginning of those highstands, e.g. especially for the Z-S VI stage (Z-S V: 11,300–~9500 cal BP, and Z-S VI: 7400–5520 cal BP, respectively; Figure 6). No clear links appear between the sedimentation/^{14}C time scale and the arid phases defined by Gillespie et al. (1983) at 12.4, 8.2, 6.6, and 4.0 cal ka BP (Figure 6). The 8.2 cal ka BP event falls into the Lake Langano L3 interval characterized by a rather low msr.
5. In conclusion, Lake Langano can be “summarized” in three major phases, i.e. the L2, L3, and L4-to-L6 intervals. As demonstrated, the Ziway-Shala high lake levels agree with the lithostratigraphy and the chronology. However, a decrease in msr during lacustrine highstands is generally admitted due to the decrease in river inputs, and/or to minor erosional processes on the catchment area that allow for 1) the core site to be far from the lake shores, and 2) the detrital particles to be filtered by the development of a vegetation belt. Nevertheless, the geomorphology of the Ziway-Shala basin likely induced a low “lake surface increase/surface detrital input” ratio due to the presence of the eastern plateau and relief of the Ethiopian Rift to the east (Street 1981; Le Turdu et al. 1999). In fact, the site of Lake Langano Core LL-III could have been localized not too far from the river and the Rift-slope depositional areas. Further studies involving other environmental indicators (e.g. pollen and diatoms) will allow for discussion and improved accuracy of the chronology and associated paleoenvironmental phases through cross-checking of sedimentary rates and lake level variations, taking into account other major factors such as volcanism and tectonics.

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