REFINING THE SARLIÈVE PALEOLAKE (FRANCE) NEOLITHIC CHRONOLOGY BY COMBINING SEVERAL RADIOCARBON APPROACHES

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ABSTRACT. Dating sedimentary series spanning the past few tens of thousands of years is often problematic due to the quality of radiocarbon data obtained from organic matter (OM), including bulk OM. This problem recently arose when establishing the chronology of a sediment infill at the Sarliève paleolake (French Massif Central). In the studied section of the cores that covers the Neolithic, *Ruppia* seeds yielded consistent ages for the lower part (7195 ± 75 to 6050 ± 60 yr BP). A reservoir age of 82 ± 42 ^{14}C yr was estimated through the comparison of ages derived from charcoal, *Ruppia* seeds, and charophyte oogonia sampled on a single level. The upper part of the cores lacks macrofossils and bulk OM dating yields unusable data because of a significant contribution of aged OM derived from the Oligocene substratum in the catchment. We therefore performed dating of lipids extracted from the sediments. The age of the lipids was 2880 ± 30 yr BP near the top of the section, i.e. much younger than the age estimated from previous correlations based on pollen assemblages. These new data call into question previous paleoenvironmental interpretations. The combined dating methodology used for the Neolithic series of Sarlième is a rather uncommon approach that may help to refine chronologies of Holocene sedimentary series.

INTRODUCTION

Accurate radiocarbon chronologies of lake sedimentary archives are necessary for unraveling the timing of environmental changes estimated from various proxies. Organic matter (OM) is generally used in this respect in preference to carbonates that result exclusively from aqueous biogenic activity. There may be a significant discrepancy between the ^{14}C of carbonates and atmospheric ^{14}C activity at the time of deposition due to the unconstrained hardwater effect. While terrestrial plant macroremains can be used for this purpose, they are usually infrequent or even absent in lake sediment cores (Yansa and Long 2007). Another common approach is to use bulk sediment containing dispersed OM. Lake sedimentary OM, however, can originate from multiple sources. Allochtonous OM from the catchment derives either directly from vascular plants, from the erosion of soil OM, or from fossil OM eroded from the geological substratum. OM can also be produced in the water column from algae or aquatic macrophytes (either sessile or floating). All of these carbon sources could have different ^{14}C activities: (i) the contemporaneous atmosphere ^{14}C activity for vascular plants; (ii) depleted ^{14}C activity due to the lake "hardwater effect," for aquatic and semi-aquatic plants; (iii) slightly depleted ^{14}C activity due to a partial hardwater effect, for floating plants that use a mixture of atmospheric CO_2 and CO_2 evaded from the lake degassing for photosynthesis; and (iv) highly depleted ^{14}C activity for geological and eroded OM (MacDonald et al. 1991; Fontana 2005; Hatté and Jull 2007). A mixture of some or all these carbon sources can introduce a ^{14}C offset from the actual time of carbon deposition in the sediment, and hence result in potentially spurious ages.

The previously described problems in obtaining suitable material for ^{14}C dating arose during the study of a sedimentary core spanning the Neolithic extracted from the Sarliève paleolake, located in

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the Limagne rift of the French Massif Central (Bréhéret et al. 2003; Fourmont 2005; Trément et al. 2007; Fourmont et al. 2009). The challenge therefore was to chronologically constrain the evolution of the Neolithic population in the catchment for which abundant archaeological data are available (Trément et al. 2007; Macaire et al. 2010). These previous studies used terrestrial macrophyte remains, bulk organic matter, and wigeongrass (*Ruppia*) seeds.

Lipids extracted from the Sarliève lake sediments, in the SARL 17b core, are mainly higher plants in origin, indicated by the predominance of long-chain *n*-alkyl lipids (*n*-alkanes, *n*-alkanols, and fatty acids), with minor macrophyte and cyanobacterial contributions (Disnar et al. 2011). Additionally, the predominance of *n*-alkanols over *n*-alkanes was interpreted as excellent preservation of higher plant remains that resulted from their short residence time in soils, accompanied by rapid transport to the lake via runoff or aerial transport and limited postdepositional decomposition. The lipid fraction extracted from the Sarliève lake sediments can therefore be considered a suitable ^{14}C target for refining the age model and providing a robust chronological framework for the Neolithic period in the newly investigated Sarliève lake core.

MATERIALS

Study Site and Lacustrine Deposits

The Sarliève paleolake is located 5 km SSE of Clermont-Ferrand (France) in the Limagne rift. Its catchment area has a total surface area of 29 km^2 and is mainly composed of Oligocene to Miocene marl and limestone covered with soil (Figure 1). Previous studies on sedimentary archives showed that this lake records environmental changes from 13,500 BP until the 18th century, when it was drained (Fournier 1996). A detailed evolution of the environment when Neolithic settlements were established at the lake was reconstructed from a study of stratigraphic levels corresponding to the Neolithic period (Trément et al. 2007; Fourmont et al. 2009; Macaire et al. 2010). This corresponds more or less to the Atlantic chronozone, i.e. 8000–5000 yr BP (de Beaulieu et al. 1988; Fourmont 2005). The sediments deposited during this time are composed of fine-grained silty marls, greenish gray to brown, mainly calcitic, that display numerous laminated layers rich in pristine Ca-dolomite, with small amounts of aragonite, which are clearly autochthonous (Bréhéret et al. 2003). These layers correspond to the fossilization of microbial mats developed at the bottom of a saline pan environment (Bréhéret et al. 2008; Disnar et al. 2011) as a consequence of excess evaporation from the restricted system. The homogeneous, physically mixed, and bioturbated intervals that separate these laminated layers result from more humid episodes that could have induced the opening of the system. The maximum depth reached by the lake was about 6 m, therefore implying large fluctuations in lake level during the interval studied. The sedimentation rate is not regular because of climate changes (alternation of wet and dry phases) and anthropogenic impact (Macaire et al. 2010) leading to catchment erosion. However, for events of short duration (<100 yr), the impact of erosion on sediment accumulation is difficult to assess given the precision of dating.

The investigated section is overlain by 2 m of lacustrine sediments composed of greenish gray to brown silty marls that are covered by a gray clayish soil belonging to the so-called *terres noires* of the Limagne rift. This soil, which is heavily waterlogged most of the year, is currently used for cereal cultivation. The catchment is covered by a variety of soils derived from the weathering of different geological formations (Oligocene-Miocene marls and limestones, Miocene basalts, and Holocene alluvia): rendzines, calcic brown soils, and clayey calcareous black soils (Bornand et al. 1968).

Currently, crops and especially cereals dominate the catchment. Non-cultivated areas are found above 450 m on the slopes of the Gergovie Plateau, whereas urban zones dominate the low-lying areas around the lake (Figure 1). Human settlements have been in the catchment since the Neolithic, with different episodes (Trément et al. 2007; Fourmont et al. 2009). The anthropogenic impact affected the entire lake area due to erosion, bringing organic matter of various origins and modifying the hydrology (Fourmont 2005; Fourmont et al. 2009; Macaire et al. 2010).

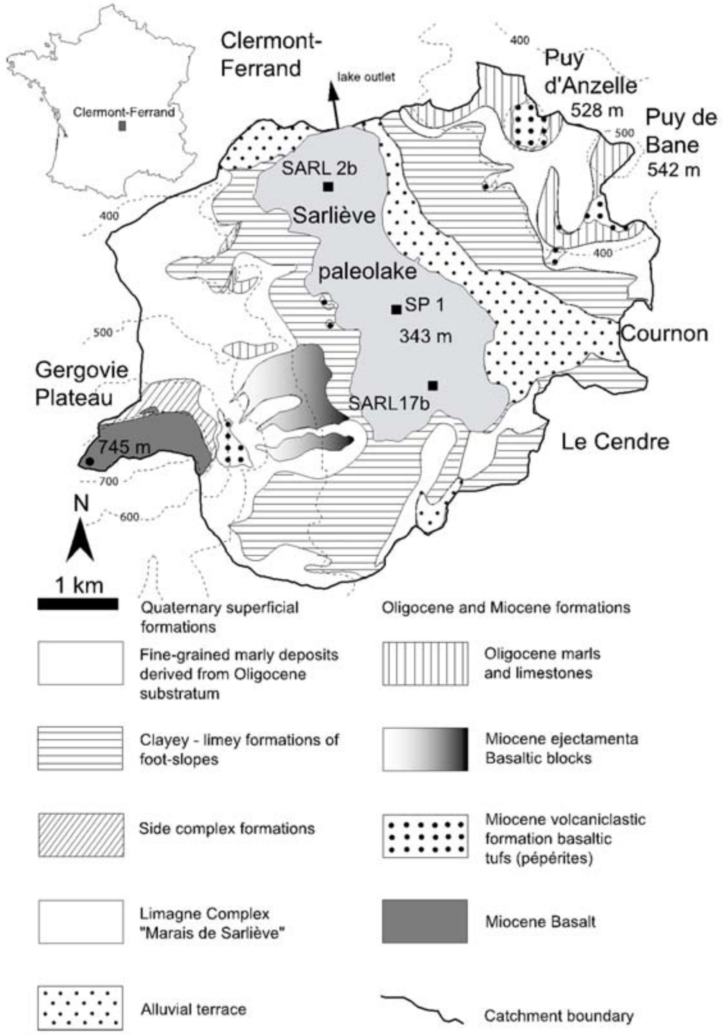

Figure 1 The Sarliève paleolake in its catchment area (Limagne rift, French Massif Central), from the geological map 1/50,000, no. XXV-31 Clermont-Ferrand (Aubert et al. 1973).

Sampling

Core SARL.17b (Figure 1) was extracted between 2.00 and 3.87 m depth below the present-day soil surface (Figure 2), using a percussion corer (Eijelkamp FB 60; Atlas Copco Berema AB, Stockholm, Sweden). For dating purposes, 15 samples of *Ruppia* seeds found in the lower part (2.93–3.68 m) of the section were collected and placed in plastic boxes. They have the advantage of being deposited and preserved *in situ* in laminated layers, without reworking. Since seeds, as well as other macroremains, were lacking in the upper part (2.00–2.92 m), 4 bulk samples (10 mm thick) were also sampled and placed in plastic bags. Two additional samples (of the same thickness) were also collected in the upper part of the section from organic-rich layers and packaged in aluminum foil, in order to analyze lipid fractions.

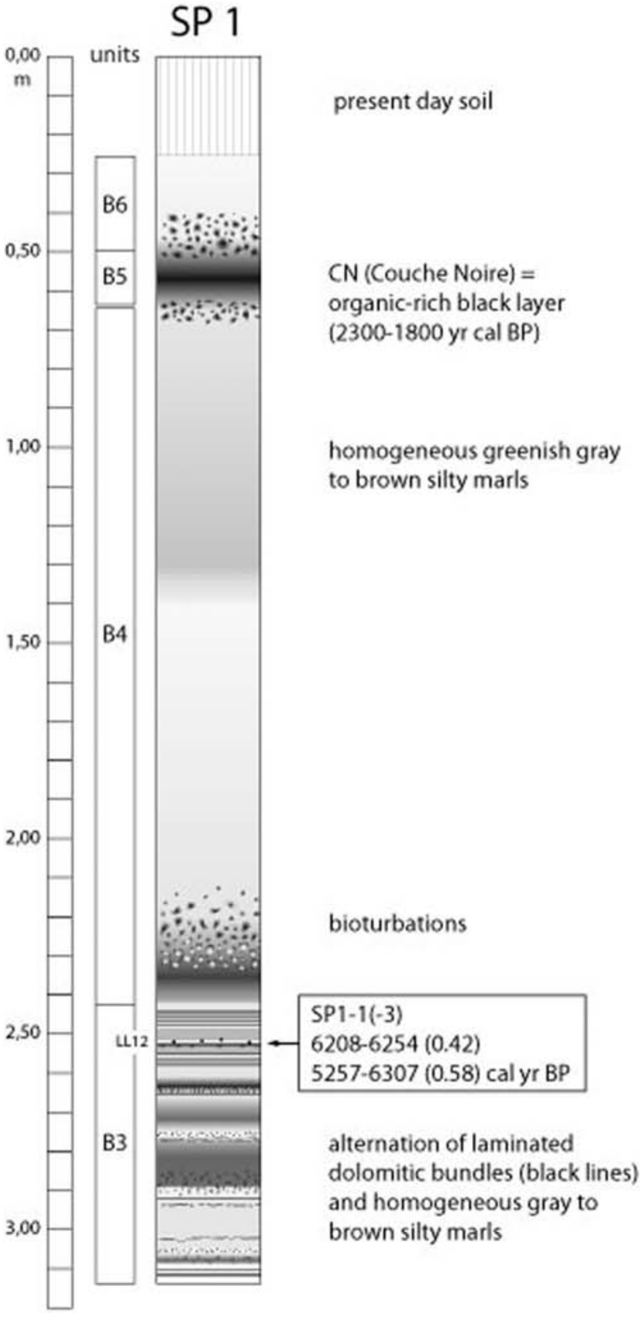

Figure 2 Lithology of the SP1 pit. The position of the sample SP1-1-3 at LL12 level (2.63 m) is indicated with dating. Sedimentary units are according to Fourmont et al. (2009) and Macaire et al. (2010). White to gray intervals: homogeneous silty marls that are more or less dark layers with irregular bioturbated patches; continuous to discontinuous lines: laminae; centimetric white layers with small black spots and lines are composed of microbial dolomite with *Ruppia* seeds. The *Couche Noire* is a key bed for all deposits of the Sarliève lake.

To clarify the dating of the sediments studied and evaluate the reservoir age effect, further sampling was performed on a laminated horizon observed from a pit (SP 1) dug in the same context ~1350 m north of SARL.17b (Figures 1 and 2). The sample taken at 2.6 m depth in this pit can be correlated according to lithostratigraphy with the LL12 level at ~2.70 m in SARL.17b. Charcoal, charophyte oogonia (organic membranes of *Chara braunii* and *Chara* cf. *canescens*; cf. Bréhéret et al. 2003), and *Ruppia* seeds were recovered from the same layer in the SP1 pit, thus offering the opportunity to compare ^{14}C ages from carbon of different origins.

Main Characteristics of Macroremains

Wigeongrass (*Ruppia*) is a shallow hydrophyte phanerogame (0–4.5 m depth according to Kantrud 1991; see also Verhoeven 1979) adapted to brackish to saline waters. *Ruppia maritima* has the widest known salinity tolerance of any submerged angiosperm (Kantrud 1991; Murphy et al. 2003) and extracts photosynthetic carbon from dissolved inorganic carbon (DIC) (e.g. Beer et al. 2006).

Charophytes are shallow freshwater algae fixed to the substrate by rhizoids (Soulié-Märsche 2002). They are characterized by female fructifications, oosporanges, usually mineralized in carbonate: the gyrogonites, a kind of shell that encapsulates the organic oospore. Several species are adapted to brackish to saline waters as is the case for *Chara* cf. *canescens* Loiseleur and, to a lesser extent, *Chara braunii* Gmelin. *Ch. canescens* is adapted to very shallow environments (down to several decimeters), whereas *Ch. braunii* is found between 3 and 5 m depth (Hutchinson 1975). In addition to photosynthesis using CO_2, charophytes assimilate bicarbonate ions (Smith 1968; Raven 1970; Hutchinson 1975).

HCO_3^- is abundant, particularly in alkaline environments (Steeman Nielsen 1947; Madsen and Sand-Jensen 1991) and is not a limiting factor in the Sarliève lake. This DIC comes from 3 potential sources: (1) atmospheric CO_2 diffusion across the lake surface; (2) soil gas CO_2 (root respiration and the decay of organic material release CO_2) from the catchment; and (3) old carbon from Oligocene-Miocene carbonates in the catchment subsurface. The first source involves an almost instantaneous equilibrium with atmospheric ^{14}C. The second introduces a delay depending on the proportion and of the age (older from some decades to some centuries than contemporaneous atmosphere) of the source organic matter, but the third could introduce significant biases due to the dilution of the DIC by the ^{14}C-dead carbon that comes from the dissolution of ancient carbonates.

METHODS

A combination of ^{14}C approaches was used for this study. Several types of ^{14}C analyses were investigated here: bulk organic matter, macroremains (*Ruppia* seeds, charophyte oospores, charcoal), deasphalted lipids, and asphaltenes extracted from bulk sediments.

Bulk Organic Matter and Macroremains

Bulk organic matter, charcoals, *Ruppia* seeds, and charophyte oospores underwent the classical acid-alkali-acid (AAA) treatment (HCl 0.5N at 80 °C for 1 hr, NaOH 0.1N at 80 °C for 1 hr, HCl 0.5N for 1 hr at 80 °C) and rinsed with ultrapure water after each step. The residue was then dried in an oven under vacuum at 40 °C. Some 100 mg of dried sample (evaluated to provide ~1 mg C) was introduced in a precombusted quartz tube with 500 mg of CuO, heated at 850 °C under vacuum just prior the use, and 1 cm of silver wire. The tube was evacuated and flame-sealed. It was then placed in a furnace at 900 °C for 6 hr and cracked under vacuum. The evolved CO_2 was passed through a –80 °C dry-ice trap to remove H_2O, cryogenically isolated, the amount of CO_2 measured, and then flame-sealed into the quartz tube.

Lipid Extraction and Preparation for ^{14}C Dating

Some 49 g (SARL.17b/48bis) and 21 g (SARL.17b/44) of dried (50 °C overnight in an oven) and crushed sediment were ultrasonically extracted with 250 mL of a mixture of dichloromethane-methanol (DCM:MeOH 9:1). The operation was repeated in order to maximize lipid extraction. After filtration, the extracts were combined and evaporated under vacuum. Precipitation of asphaltenes was achieved by diluting the total extract in few drops of DCM and then adding cold heptane in excess. After centrifugation, the supernatant was collected and evaporated under vacuum. Asphaltenes and deasphalted lipids were recovered with DCM, collected in precombusted (450 °C overnight) Pyrex® tubes, and DCM was evaporated under nitrogen. The deasphalted lipid extract was diluted in 2.5 mL and introduced into glass tubes and the solvent was removed under a stream of nitrogen. The deasphalted lipids and the asphaltenes of samples SARL.17b/48bis and SARL.17b/44 were converted to CO_2 by flame combustion under pure O_2 atmosphere (about –500 mm Hg) in a pre-evacuated (10^{-6} Torr) vacuum line devoted to small samples (typically <500 µg of C). The evolved gas was passed through water and Cu traps to remove H_2O, O_2, nitrogen, and sulfur oxides, and was then quantified. Pure CO_2 was flame-sealed in a Pyrex tube until graphitization and ^{14}C measurements at the LMC14 laboratory, as described above. Pure O_2 was chosen instead of CuO as oxygen source in order to minimize potential contamination by modern carbon, e.g. adsorbed on CuO. Some grayish components remained on the combustion tube of the SARL.17b/44 asphaltene after combustion. These residues might correspond to the heaviest part of the asphaltene fraction or residues of incomplete combustion of asphaltene. Residues were then enclosed with O_2 precombusted CuO under vacuum following the classical procedure for large AMS samples (see above).

Graphitization and ^{14}C Measurement

Evolved CO_2 were graphitized by reduction with H_2 on iron with a Fe/C ratio of 3 (Arnold et al. 1987, 1989). The Fe/C powder was pressed in a target holder and ^{14}C measured on ARTEMIS, the AMS of the LMC14 facility (Cottereau et al. 2007). ^{14}C activity is calculated by comparison with standard prepared from oxalic acid HOx I and normalized to δ^{13}C. ^{14}C ages are calculated according to the Mook and van der Plicht (1999) recommendations. The resulting ^{14}C activity is corrected from background ^{14}C evaluated on both a ^{14}C-free carbonate (“C1”) thermically decomposed into CO_2 to assert the line itself and on a ^{14}C-free charcoal (“Afrique du Sud” extracted from the Paleolithic level of Border Cave, South Africa, and dated to >70 kyr) that underwent the same chemical protocol as the bulk OM and seeds. Mass dependent background correction was applied to all samples. We used the same background correction for lipid fractions as we do not have any ^{14}C-free and known-age standards for this type of material. As recorded on the LMC14 result sheet, final ^{14}C uncertainties result from statistical error, results variability, and background subtraction.

RESULTS AND DISCUSSION

Bulk Organic Matter

^{14}C dates derived from bulk OM yielded ages of 6000–6700 yr BP, irrespective of depth (Table 1), and show clear chronological inversions (Figure 3). This can probably be attributed to the contribution of exogenous carbon, since pollen analysis shows a significant proportion of pollen grains from the weathering of Oligocene-Miocene rocks in the catchment (Argant and Lopez-Saez 2004; Trément et al. 2007). Therefore, a massive input of carbon derived from the catchment into the lake, including the surrounding soil erosion, which can be suspected, would induce an aging effect.

Table 1 ^{14}C dates on SARL 17b samples, sample and laboratory references, in raw ^{14}C ages. *Ruppia* seed ^{14}C dates are then further corrected by the 85 ± 42 yr BP estimated reservoir age so as to be compared with the contemporaneous atmospheric record. ^{14}C results for terrestrial are calibrated according to IntCal09 (Reimer et al. 2009) with CALIB 6.1.0 for Macintosh OSX (http://calib.qub.ac.uk/calib/). The 2 major calibrated intervals are reported. Modeled *a posteriori* age distribution for lipids and *Ruppia* seeds are obtained by OxCal v 4.1.7 (Bronk Ramsey 2009).

					Unprocessed data			Modeled data			
Sample nr	Lab code	Facies	Depth (m)	Material	C mass (µg)	$\delta^{13}C^a$ (‰)	^{14}C age (yr BP)	Reservoir effect corrected (corr. yr BP)	IntCal09 via CALIB 6.1 (probability) (cal yr BP)	Age at median probability (cal yr BP)	OxCal modeled age
SARL.17b/50	SacA-9355	Marl	2.10	bulk OM		–26	6500 ± 35				
SARL.17b/48bis lipids	GifA-091118/ SacA-17604	bioturbated silty marl	2.12	lipids	450	–37	2880 ± 30		[2922–3081] (0.93) [3092–3112] (0.03)	3009	[2889–3142]
SARL.17b/47	SacA-9354	Marl (faintly laminated)	2.21	bulk OM		–25	6320 ± 35				
SARL.17b/46	SacA-9353	Dolomitic marl	2.23	bulk OM		–26	6090 ± 35				
SARL.17b/44 asphal.	GiA-091116-2/ SacA-17602	bioturbated silty marl	2.47	asphaltene	1160	–33	5265 ± 35				
SARL.17b/44 residue	GifA-09504/ SacA-17678	bioturbated silty marl	2.47	residues	1470	–32	5435 ± 45				
SARL.17b/43bis-44 lipids	GifA-091117-1/ SacA-17603	bioturbated silty marl	2.47	lipids	750	–36	3570 ± 30		[3824–3933] (0.84) [3939–3971] (0.08)	3871	[3731–3973]
SARL.17b/35	SacA-6712	Dolomitic marl (faintly laminated)	2.93	*Ruppia* seeds		–16	6135 ± 40	6050 ± 60	[6741–7029] (0.93) [7108–7156] (0.05)	6905	[6897–7061]
SARL.17b/33bis	SacA-9356	Laminated dolomitic marl	2.96	bulk OM		–29	6655 ± 35				
SARL.17b/33	SacA-6711	Laminated dolomitic marl	2.97	*Ruppia* seeds		–11	6220 ± 35	6135 ± 55	[6860–6871] (0.01) [6881–7171] (0.99)	7034	[6934–7090]
SARL.17b/28	SacA-6005	Laminated dolomitic marl	3.11	*Ruppia* seeds		–14	6510 ± 35	6425 ± 55	[7260–7430] (1)	7354	outlier
SARL.17b/27	SacA-6004	Laminated dolomitic marl	3.12	*Ruppia* seeds		–16	6310 ± 60	6225 ± 75	[6941–7295] (0.99) [7296–7305] (0.01)	7122	[6991–7173]
SARL.17b/20	SacA-6003	dolomitic marl (faintly laminated)	3.28	*Ruppia* seeds		–17	6180 ± 60	6095 ± 75	[6754–6763] (0.01) [6778–7168] (0.99)	6973	[7057–7250]
SARL.17b/19	SacA-6002	Laminated dolomitic marl	3.34	*Ruppia* seeds		–15	6510 ± 60	6425 ± 75	[7175–7217] (0.04) [7241–7471] (0.96)	7354	[7181–7410]
SARL.17b/18	SacA-7400	homogeneous marl	3.38	*Ruppia* seeds		–10	6450 ± 40	6365 ± 60	[7173–7223] (0.12) [7233–7421] (0.88)	7303	[7261–7414]
SARL.17b/15b	SacA-6709	Laminated dolomicrite	3.45	*Ruppia* seeds		–15	6450 ± 70	6365 ± 80	[7029–7043] (0.01) [7156–7435] (0.98)	7299	[7280–7435]

Table 1 ^{14}C dates on SARL 17b samples, sample and laboratory references, in raw ^{14}C ages. *Ruppia* seed ^{14}C dates are then further corrected by the 85 ± 42 yr BP estimated reservoir age so as to be compared with the contemporaneous atmospheric record. ^{14}C results for terrestrial are calibrated according to IntCal09 (Reimer et al. 2009) with CALIB 6.1.0 for Macintosh OSX (http://calib.qub.ac.uk/calib/). The 2 major calibrated intervals are reported. Modeled *a posteriori* age distribution for lipids and *Ruppia* seeds are obtained by OxCal v 4.1.7 (Bronk Ramsey 2009). *(Continued)*

					Unprocessed data			Modeled data			
Sample nr	Lab code	Facies	Depth (m)	Material	C mass (µg)	$\delta^{13}C^a$ (‰)	^{14}C age (yr BP)	Reservoir effect corrected (corr. yr BP)	IntCal09 via CALIB 6.1 (probability) (cal yr BP)	Age at median probability (cal yr BP)	OxCal modeled age
SARL.17b/15	SacA-6708	Laminated dolomicrite	3.47	*Ruppia* seeds		–32	6630 ± 90	6545 ± 100	[7266–7592] (1)	7452	[7322–7558]
SARL.17b/12	SacA-6707	Laminated dolomicrite	3.49	*Ruppia* seeds		–13	6670 ± 40	6585 ± 60	[7418–7582] (1)	7488	[7426–7564]
SARL.17b/7b	SacA-5997	Laminated dolomitic marl	3.55	*Ruppia* seeds		–19	6910 ± 60	6825 ± 75	[7566–7834] (1)	7667	[7583–7763]
SARL.17b/6b	SacA-7399	Laminated dolomitic marl	3.58	*Ruppia* seeds		–14	7005 ± 40	6920 ± 60	[7674–7839] (1)	7755	[7672–7818]
SARL.17b/6	SacA-6706	Dolomicrite	3.60	*Ruppia* seeds		–16	7005 ± 40	6920 ± 60	[7674–7839] (1)	7755	[7684–7829]
SARL.17b/5	SacA-6705	Dolomitic marl (faintly laminated)	3.65	*Ruppia* seeds		–34	7190 ± 40	7105 ± 60	[7794–7814] (0.02) [7819–8023] (0.98)	7933	[7854–8007]
SARL.17b/4	SacA-6008	Dolomitic marl	3.68	*Ruppia* seeds		–13	7280 ± 60	7195 ± 75	[7867–7899] (0.04) [7924–8177] (0.96)	8018	[7872–8130]

$^a\delta^{13}C$ data were obtained using AMS and are not for paleodietary or ecological analysis. Associated uncertainty is larger than 2‰.

Table 2 ^{14}C dates on SP.1 samples. Sample and laboratory references, in raw ^{14}C ages. The difference with charcoal ^{14}C dating (atmospheric reference) provides the reservoir age for *Ruppia* seeds and charophyte oospores.

					Unmodeled data				
Sample nr	Lab code	Facies	Depth (m)	Material	C mass (µg)	$\delta^{13}C^a$ (‰)	^{14}C age (yr BP)	Calibrated range (2σ) (probability) (cal yr BP)	Estimated reservoir age (yr BP)
SP1-1	SacA 21777	Laminated dolomitic marl	2.63	Charcoal	1000	–14	5465 ± 30	[6208–6254] (0.42) [6257–6307] (0.58)	—
SP1-2	SacA 21778			*Ruppia* seeds	1100	–18	5550 ± 30	—	85 ± 42
SP1-3	SacA 21779			Charophyte oospores	1000	–12	5475 ± 30	—	10 ± 42

$^a\delta^{13}C$ data were obtained using AMS and are not for paleodietary or ecological analysis. Associated uncertainty is larger than 2‰.

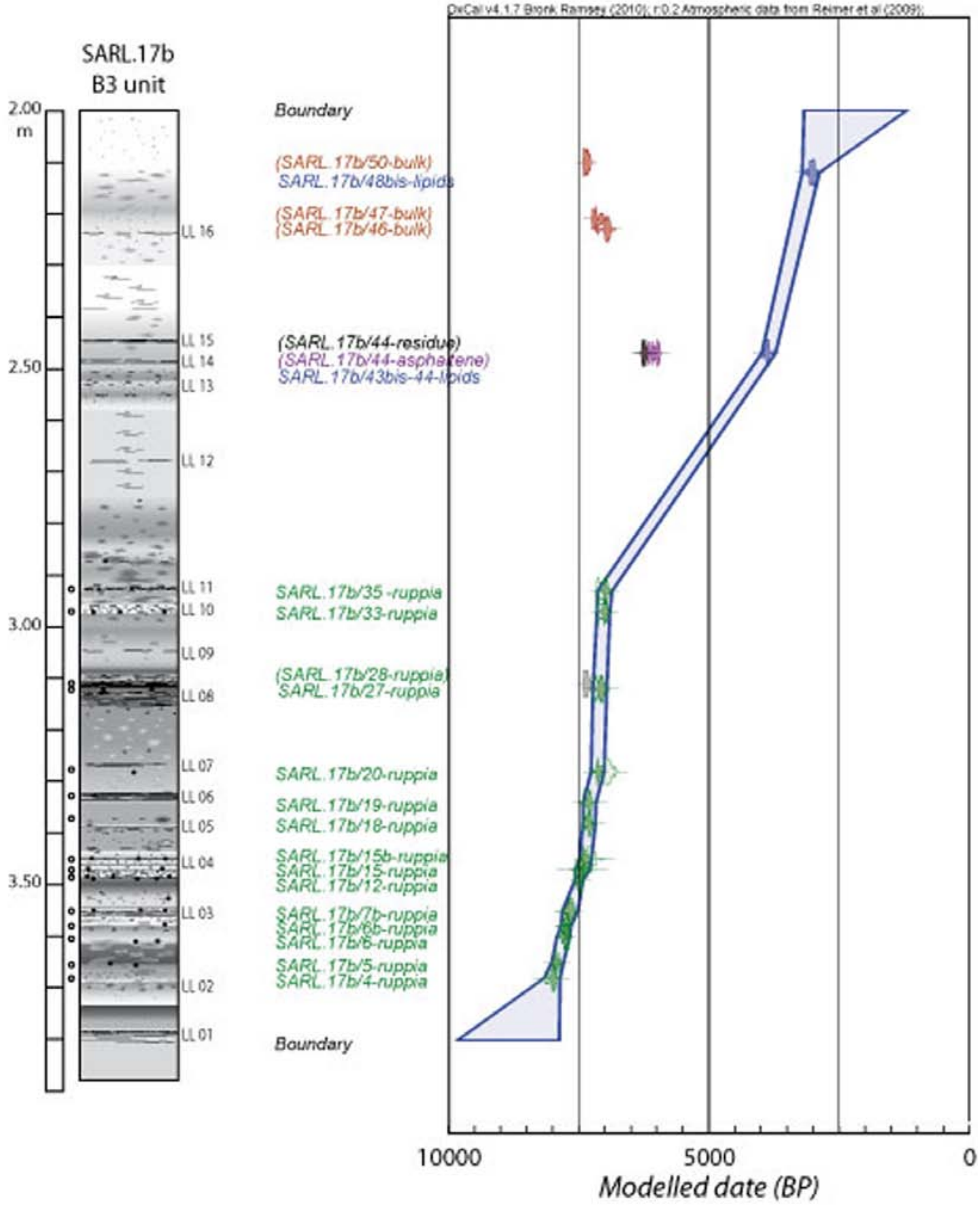

Figure 3 Age-depth relationships for core SARL.17b. Depth is shown in meters below present-day soil surface and the *x* axis is in OxCal modeled yr BP (see text). Lithology as for Figure 2. Laminae are listed as LL 01 to LL 16; centimetric white layers with small black spots and lines are composed of microbial dolomite with *Ruppia* seeds. Light circles: sampled *Ruppia* seeds. Modeled age: prior (light) and a posteriori (dark) age probability distribution for ^{14}C dates are shown for *Ruppia* seeds (reservoir age corrected, green), bulk organic matter (brown), lipids (blue), asphaltene (purple), and residue (black). The outlier SARL.17b/28 *Ruppia* ^{14}C age is shown in gray. The sample name in parentheses is for a sample whose ^{14}C age is excluded in the age-depth model. The OxCal model is shown in the blue-shaded zone. Two boundaries are fixed at the core top and bottom to close the model but do not impact the model definition.

Macroremains

Macroscopic observation and lithostratigraphy (laminated sediments) indicate that seeds of wigeongrass (*Ruppia*) are not reworked. The geochronological succession is consistent and only 1 slight inversion is observed (SARL.17b/28). However, as already stated, *Ruppia* uses DIC as a source of photosynthetic carbon. Aging as a result of the hardwater effect is therefore very likely. This effect was assessed by using a combination of terrestrial and aquatic ^{14}C dating in the lateral pit SP1 (Figure 2) and the results were then applied on the raw ^{14}C dates.

The dates obtained on the 3 macroremains from the same sample from pit SP 1 are given in Table 2 and are as follows: charcoal: 5465 ± 30 yr BP; *Ruppia* seeds: 5550 ± 30 yr BP; charophyte oogonia: 5475 ± 30 yr BP. The charcoal age differs from that of wigeongrass by only ~85 yr. This value (85 ± 42 yr BP) may be used to correct the reservoir effect of the dates obtained on *Ruppia* seeds. As an approximation, it is assumed relatively constant over time corresponding to the accumulation of sediments of the core, although it may have changed slightly over time (Geyh et al. 1998, 1999). The relative similarity between the datings of charcoal and charophyte oogonia should be emphasized. Charophytes, which use both atmospheric and DIC carbon as a source of photosynthetic carbon, show consistently less ^{14}C offset. This further indicates that the reservoir effect plays a negligible role in the ^{14}C composition of charophyte fructifications and therefore that charophyte oogonia (*C.* cf. *canescens*) can be used can be used in ^{14}C dating. It should be noted that as the lake has been dry for the last 2 centuries, dating was not possible on the present-day DIC nor on aquatic plants.

Lipids

For the ages obtained on lipid extracts (Table 1, Figure 3), the sample SARL.17b/44 (2.47 m) provides an age of 3570 ± 30 yr BP for the deasphalted lipid fraction, whereas the asphaltene fraction gives 5265 ± 35 yr BP and the residue fraction gives 5435 ± 45 yr BP. The lipid fraction of the sample SARL.17b/48b at 2.12 m provides an age of 2880 ± 30 yr BP. Thus, the deasphalted lipid fraction shows significantly younger ages than those measured either on bulk OM or on asphaltenes and residues. These ages are nevertheless coherent, with lipids extracted from sample SARL.17b/48b being younger than those extracted from sample SARL.17b/44.

The difference in ^{14}C dates between the asphaltene (and residue) and the deasphalted lipid fraction (~1700 to 2000 ^{14}C yr) implies that organic compounds that differ in origin and in age comprise these fractions. The age difference between deasphalted lipids and asphaltenes in sample SARL.17/44 is ~2000 ^{14}C yr (Table 1), i.e. slightly less than the difference between the age of the lipid fraction in sample SARL.17b/48bis and that of bulk OM of the 2 closest samples (SARL.17b/47 and SARL.17b/50), which is ~2500 ^{14}C yr. The aging of the asphaltene and residue fractions may be attributed to the contribution of old carbon derived either from soils or from the geological substratum. Thus, and although there is no current knowledge/evidence for the aging of asphaltenes when compared to deasphalted lipids, our results suggest that removing asphaltenes from a lipid extract makes it possible to access a significantly younger carbon fraction than that of the total lipid extract and of the bulk OM. ^{14}C dating performed on individual molecules of which the source organism is constrained remains, when feasible, the most efficient means of avoiding using fossil organic matter (i.e. Eglinton et al. 1997).

Age Model

Macroremains of terrestrial plants remain the most reliable material to establish a ^{14}C chronology of a lacustrine or palustrine record (Hatté and Jull 2007). However, if they are not available, alternative materials should be sought. Macroremains from aquatic or floating plants can be used with relative confidence if there is no geologically old carbonate in the lake catchment or the reservoir age can be established. In the latter case, reservoir age has also to reasonably be assumed not to have significantly changed over the time of sequence deposition. Climatic and geomorphological variations have to be taken into consideration. The use of bulk OM should remain the least preferred option since it contains carbon of undetermined sources and ages. This is the problem we faced for the upper part of the sequence studied here. In the absence of any reliable macroremains, the analysis of the lipid fraction mostly composed of molecular biomarkers of vascular higher plants appears an efficient alternative. The Sarliève chronology was thus completed by using ^{14}C results obtained on these lipid fractions.

The age-depth model is built on ^{14}C dating of *Ruppia* seeds and lipids using the OxCal program, designed for the analysis of chronological information (Bronk Ramsey 2008, 2009) based on (1) calibrated intervals obtained by IntCal09 calibration (Reimer et al. 2009) on reservoir-age-corrected *Ruppia* and on lipid ^{14}C datings; (2) stratigraphical information (i.e. succession order); and (3) Bayesian statistics. OxCal can be used to model the *a posteriori* modeled age distribution for all samples and to establish the most likely age-depth model. OxCal can also be used to identify likely outliers within a dating series. This is the case for SARL.17b/28 sample in the Sarliève series, which appears too old and falls outside all possible age-depth models (A = 0.9 for this point in the P_Sequence context). When this datum is removed, OxCal provides the *a posteriori* age distribution (Table 1) and age-depth model presented in Figure 3 (chosen option: P_Sequence that returns A_{model} = 105.3 and A_{overall} = 105.8).

The coherency of the age model applying the reservoir age we defined on only 1 couple of dates corroborates our assumption of constant reservoir age along the sequence. The model clearly shows a constant rapid accumulation from 3.7 to 2.9 m with accumulation of 80 cm in ~1100 yr, followed by a drastic slowdown or a hiatus leading to a missing part until 2.5 m, and then a rapid accumulation rate from 2.5 to 2.1 m, with 40 cm in ~860 yr.

Paleoenvironmental Implications

The newly acquired age-depth model specifies the top of the *Ruppia* seed-rich laminites (close to 2.75 m on SARL.17b) as ~6250 cal BP, and the top of the laminite interval as about 3000 cal BP instead of 5300 estimated BP (Fourmont et al. 2009; Macaire et al. 2010). Considering that dates based on OM bulk were too old by at least 1000 yr, Fourmont et al. (2009) excluded these data and preferred to define their age model by correlation with the palynological framework.

Trément et al. (2007) estimated the *Fagus* diffusion observed in another Sarliève core, SARL 2b, as 6390 ± 50 yr BP (i.e. [7247–7426 yr cal BP]) based on bulk OM dating (Figure 4), but the authors considered this data as obviously too old compared to the data from the other sites in the French Massif Central, which were estimated as 5800–5400 yr BP. Correlations between SARL.17b and SARL.2b (Figure 4) enable this event to be placed at 2.50 m depth in SARL.17b, close to 4000 yr cal BP according to the present age-depth model. The Atlantic-Subboreal chronozone transition, based on the *Fagus* proliferation, indicated as 5770 ± 70 yr BP (i.e. 6411–6727 yr cal BP) according to the same authors, also judged as too old by ~1000 yr, is close to 3100 yr BP (~3300 cal BP, at ~2.25 m taking correlations into account) according to the new model. This event also appears to be much more recent than the dates indicated for other sites in the French Eastern Massif Central near Sarliève, namely 4840 yr BP (~5500 yr cal BP) (Argant and Cubizolle 2005).

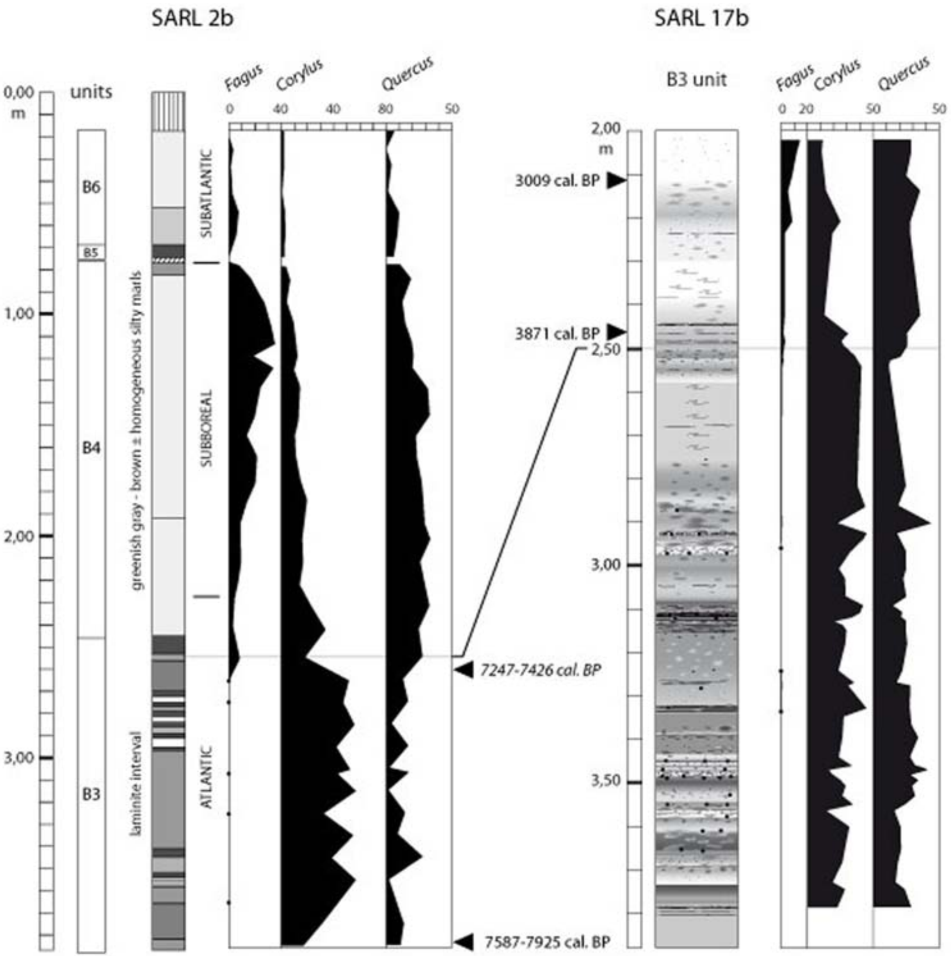

Figure 4 Correlations between SARL 17b and SARL 2b (Trément et al. 2007). Sedimentary units according to Fourmont et al. (2009) and Macaire et al. (2010). Distribution of *Fagus*, *Corylus*, and *Quercus* pollen. Age indicated for 3.84 m in SARL 2b was obtained on *Ruppia* seed (and so it must be corrected for the reservoir effect as estimated in the present work); however, the age for 2.60 m was obtained on bulk OM and must be dismissed. The diffusion of *Fagus* dated by Trément et al. (2007) in SARL 2b is synchronous with a decrease in *Corylus* and an increase in *Quercus*. A similar pattern is observed in SARL 17b, for which the dating is substantially more recent.

Three possible explanations for these differences can be suggested: (i) the type of material used to date these previous series; (ii) more probably, the obvious diachronism of the vegetation evolution depending on the altitude of the sites studied, and their climatic conditions—as noted by Trément et al. (2007), all the sites previously studied and used as reference for palynology are located between 975 and 1400 m asl whereas the altitude of the Sarliève basin is only 345 m asl, and this area is characterized today by much drier conditions than in the nearby massifs (Kessler and Chambraud 1986); and (iii) a potential differing impact of human activities between the different sites.

The change in sedimentation rate that occurs above 2.90 m in SARL.17b could be explained in 2 ways. First, the geometry of the lacustrine fill extends far laterally on the basin margin so that even an increase in sedimented volume, as calculated by Macaire et al. (2010), could in fact result in a smaller height of deposits and thus in a decrease in the vertical sedimentation rate. Second, the climatic evolution is characterized by an increase in moisture as indicated by palynology (Trément et al. 2007) and sedimentology (Bréhéret et al. 2008). This led to a rise in lake level and the opening of the lacustrine system by the outlet. As a result, the suspended matter was then exported, thus depriving the lake of this supply.

CONCLUSION

By combining several ^{14}C approaches—evaluating the freshwater reservoir effect, dating of macrofossils and lipids extracted from sediments (excluding asphaltenes that were shown to be aged)—the chronological framework of the Neolithic paleoenvironment around the Sarliève paleolake has been refined. This study provides the first reliable dates to characterize the end of the lake restriction, and the advent of the *Fagus* proliferation in the Sarliève area (3300 cal BP), which is much more recent than the beginning of the Subboreal chronozone known in the French Massif Central (5500 cal BP). The decrease in the sedimentation rate evidenced around 6250 cal BP is attributable to a rise in lake level and the concomitant export of suspended matter by opening of the outlet.

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