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Autor: Filippi, Maria Letizia / Moscariello, Andrea / Hunziker, Johannes
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Stable isotopes in Lake Geneva carbonate sediments and molluscs: Review and new data

MARIA LETIZIA FILIPPI¹, ANDREA MOSCARIELLO² & JOHANNES HUNZIKER¹

Key words: Stable isotopes, lake, carbonate, molluscs, Late-Glacial, Holocene, Western Switzerland

ABSTRACT

New isotopic results on bulk carbonate and mollusc (gastropods and bivalves) samples from Lake Geneva (Switzerland), spanning the period from the Oldest Dryas to the present day, are compared with pre-existing stable isotope data. According to preliminary calibration of modern samples, Lake Geneva endogenic calcite precipitates at or near oxygen isotopic equilibrium with ambient water, confirming the potential of this large lake to record paleoenvironmental and paleoclimatic changes. The onset of endogenic calcite precipitation at the beginning of the Allerød biozone is clearly indicated by the oxygen isotopic signature of bulk carbonate. A large change in $\delta^{13}\text{C}$ values occurs during the Preboreal. This carbon shift is likely to be due to a change in bioproductivity and/or to a "catchment effect", the contribution of biogenic CO_2 from the catchment area to the dissolved inorganic carbon reservoir of the lake water becoming significant only during the Preboreal.

Gastropods are confirmed as valuable for studies of changes in paleotemperature and in paleowater isotopic composition, despite the presence of a vital effect.

Mineralogical evidence indicates an increased detrital influence upon sedimentation since the Subboreal time period. On the other hand, stable isotope measurements of Subatlantic carbonate sediments show values comparable to those of pure endogenic calcite and of gastropods (taking into account the vital effect). This apparent disagreement still remains difficult to explain.

RESUME

Des nouvelles données isotopiques sur la roche totale et les mollusques (gastéropodes et bivalves) du Léman (Suisse), concernant la période comprise entre le Tardi-Glaciaire et aujourd'hui, ont été comparées avec les données contenues dans la littérature. Sur la base d'une calibration préliminaire sur des échantillons actuels, la calcite endogène du Léman semble précipiter à, ou proche de, l'équilibre isotopique (oxygène) avec l'eau du lac. Ceci met en évidence les potentialités de ce grand lac d'enregistrer les changements paléoenvironnementaux et paléoclimatiques. Le début de la précipitation de la calcite endogène à partir de l'Allerød est clairement indiqué par le signal isotopique de l'oxygène de la roche totale. Un grand changement dans les valeurs du $\delta^{13}\text{C}$ se vérifie pendant le Preboreal. Cette variation est probablement due à un changement de bio-productivité et/ou à un «effet du bassin hydrographique», la contribution de la CO_2 biogénique de la part du bassin au réservoir du carbonate dissous dans l'eau du lac devenant important seulement pendant le Preboreal.

Les gastéropodes sont confirmés être utiles pour les études de la paléotempérature et de la composition isotopique de l'eau, bien que il y ait un effet vital.

Les évidences minéralogiques indiquent une augmentation de l'influence détritique sur la sédimentation à partir du Subboreal. D'autre côté, des mesures isotopiques préliminaires sur des sédiments carbonatés subatlantiques ont des valeurs comparables à celles de la calcite endogène pure et des gastéropodes (en considérant l'effet vital). Cet apparent contraste reste difficile à expliquer.

Introduction

Small lakes are statistically more studied than large lakes by stable isotope geochemists. The reason is probably that small lakes are easier to access and easily monitored. Furthermore, they are characterised by rapid responses to environmental changes induced by a restricted number of variables. Large waterbodies such as Lake Neuchâtel, Lake Geneva, Lake Constance (Bodensee), Lake Zürich, Lake Lugano, Lake Maggiore, Lake of the Four Forest Cantons (Vierwaldstätter See)

have been difficult to study from the isotopic point of view due to multiple carbonate sources, if compared with studies of small basins (Gerzensee, Lobsigensee, Faulenseemoos, Aegelsee, Amsoldingersee and many others) (Eicher 1979, for a review), with abundant chalk (Seekreide). Recent studies are changing this lack of data (Niessen 1987; Lister 1988a; Lister 1988b; Niessen & Kelts 1989; Chondrogianni 1992; Schwalb 1992; Schwalb et al. 1994).

¹ Institut de Minéralogie et Pétrographie, BFSH2, Université de Lausanne CH-1015 Lausanne

² Section des Sciences de la Terre, Université de Genève, CH-1211 Genève 4

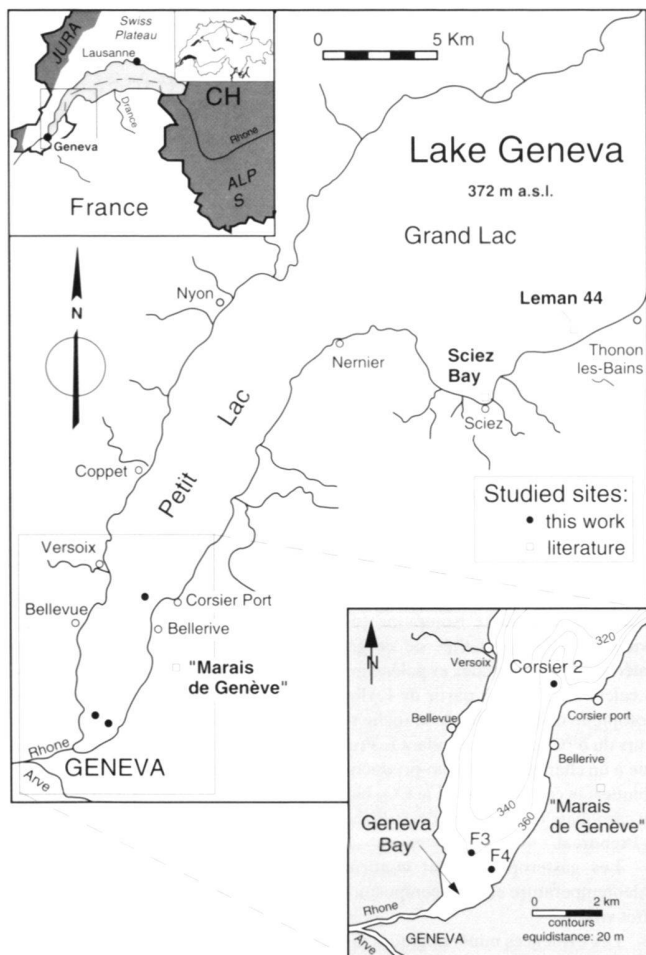


Fig. 1. Geographical setting of the studied area and location of the studied sites in the Geneva Bay: F3, F4, Corsier 2 cores (black circles). Open squares indicate sites investigated in the literature: Leman 44, by Serruya & Vergnaud-Grazzini (1966); "Marais de Genève", by Blanc et al. (1977); Sciez Bay, by Chaix et al. (1982).

Among these large Swiss lakes, Lake Geneva has a curious story. Following a pioneering isotopic study (Serruya & Vergnaud-Grazzini 1966; Fontes & Gonfiantini 1970; Blanc et al. 1977), little has been done since. An international commission was created for the protection of lake water quality against pollution (Commission International pour la Protection des Eaux du Léman, CIPEL) in 1957. The CIPEL commission publishes each year a report on Lake Geneva health state, measuring physico-chemical parameters, floral and faunal indicators, polluting substances, etc. Unfortunately, no stable isotopic analyses are included in this otherwise fairly extensive data base.

Within the Swiss National Science Foundation Project PNR 31 we ran isotopic analyses on Lake Geneva calcareous sediments to study its isotopic response to past environmental changes. This study is still in progress. In this paper we com-

Table 1. Some Physical Parameters for Lake Geneva

	Lake Geneva	„Grand Lac“	„Petit Lac“
Mean geographical site	46°27' lat. N 6°32' long. E of Greenwich		
Elevation above sealevel (mSL)	372	372	372
Surface area (SA) km ²	582.4	503	79
Volume (V) km ³	89	86	3
Discharge outflow (D) m ³ /s	240		
Rhone inflow m ³ /s	178		
Dranse inflow m ³ /s	18.8		
Residence time yrs	11.9		
Maximum depth m	310	310	76
Average depth m	153	172	41
Epilimnion summer temperature °C	20.2	20.2	
Hypolimnion summer temperature °C	5.2	5.8	

pare our preliminary results with older studies, emphasising the potential of this large lake for paleoenvironmental reconstruction.

Lake Geneva and stable isotopes: the state of art

Lake Geneva (Léman for Francophones) (Fig. 1) is the largest lake in Western Europe. It occupies a flat-bottom basin, excavated in Molassic deposits between the Alpine arc and the Jura chain. It is divided into two geographic units, the "Grand Lac" (Big Lake) and the "Petit Lac" (Small Lake), either side of the "barre de Promenthoux" (Nernier-Promenthoux). Principal parameters of the lake are given in Table 1.

The first and pioneering isotopic work on Lake Geneva was by Serruya & Vergnaud-Grazzini (1966). It represents one of the first applications of stable isotopes to lacustrine sediments. Serruya & Vergnaud-Grazzini presented a sedimentological, mineralogical, chronological and isotopic study of a 4.5 m long core (Leman 44), taken to the West of Thonon-le-Bains, spanning the Dryas (Oldest?) to Boreal pollen zones. They recorded high carbon and oxygen isotope values in the lower part of the core, interpreted as influenced by detrital input. To verify this hypothesis, they measured the isotopic value of marine limestone outcropping in the catchment area near Thonon. These correspond fairly well to the mean isotopic values of the bottom core. The negative trend in the upper core was explained, with respect to oxygen isotopes, by the onset of endogenic calcite precipitation and increased temper-

ature, and for carbon, by a major influence of organic CO₂ due to vegetation development within the lake (Serruya & Vergnaud-Grazzini 1966). Later, Fontes & Gonfiantini (1970) studied the isotopic composition of the atmospheric water vapour over Lake Geneva to estimate the climatic zone of influence of the lake on the atmosphere. They determined the lake water isotopic composition (mean $\delta^{18}\text{O}$ -12.31‰, mean δD -87.2‰) for the first time. Blanc et al. (1977) analysed ^{18}O and ^{13}C from shells and lacustrine chalk from Holocene marshes near Geneva, dated to circa 11,000 BP by the ^{14}C method. Palynological data and isotope records as climatological indicators led them to propose a mean water temperature equal or less than 11°C at the time of carbonate formation (Younger Dryas-Preboreal interval). In her Ph. D. thesis, Lemeille (1980) performed a few isotopic analyses on lake water ($\delta^{18}\text{O}$ -12.27‰) and on the $\delta^{13}\text{C}$ value of both dissolved inorganic carbon (DIC, $\delta^{13}\text{C}$ -7.43‰) and a living gastropod (*Limnea*, $\delta^{13}\text{C}$ -7.21‰). The recent isotopic studies on Lake Geneva end with the work of Chaix et al. (1982). These authors studied the isotopic composition of malacological fauna from Lake Geneva and other lakes of the Northern Pre-Alps. They also monitored the water and DIC isotopic composition (mean $\delta^{13}\text{C}$ -7.25‰). Their results emphasise the large contribution of biogenic carbon dioxide in the shell construction.

Material and methods

Isotopic analyses were carried out on the Late-glacial and Holocene sediments, forming the uppermost 5–8 m of Petit Lac sediments (Serruya 1969; Vernet & Parent 1970; Reynaud 1982; Moscariello 1996). Cores F3 and F4, located in the Geneva Bay (Fig. 1), were cored simply by the weight of the drill string of a rotary corer (diameter 180 mm) during geotechnical investigations carried out on behalf of the Canton of Geneva. Core F3 (8 m) is located in the middle of the Bay at 13.7 m water depth, whereas core F4 (6 m) is close to the eastern shore at 10.3 m water depth. Core Corsier 2 (4.4 m), located at 16.5 m water depth about 700 m off-shore from the eastern coast (Fig. 1), was cored with a 6 m pneumatic fixed piston corer of 8 cm in diameter (Mackereth 1958), using coring facilities of the Institute F.-A. Forel (University of Geneva).

Cores lined with plastic jackets and stored in a cold room were cut in halves and sampled for sedimentological (i.e. microfacies, grain-size), mineralogical and palynological investigations. Analytical procedures and detailed results are described elsewhere (Moscariello 1996). In order to analyse bulk carbonate isotopic composition, the following samples of whole sediment were collected ($\approx 2 \text{ cm}^3$):

core F3: 23 samples between 4 and 8 m, covering the Older Dryas-Older Atlantic biozones

core F4: 40 samples between 0 and 6 m, covering the Boreal biozone

core Corsier 2: 4 samples (upper 60 cm), covering the Sub-boreal-Subatlantic biozones.

Carbonate crust on a cobble collected at 3 m water depth in the Geneva Bay (Fig. 1) was also measured. Specimens of the gastropods *Valvata piscinialis* and *Bithynia tentaculata* were picked from core Corsier 2 between 0 and 60 cm. Two specimens of modern bivalve *Anodonta cygnea* (nacreous shell) were collected on the lake shore near Vidy (Lausanne) to check the modern isotopic composition.

Carbonate mineralogy of molluscs (calcite/aragonite) was determined by infrared absorption spectroscopy. Analyses were performed with a Perkin-Elmer, FT-IR (Fourier Transform Infrared type) Paragon 1000 spectrometer (Institute of Mineralogy, University of Lausanne).

For stable isotopic analysis, 10–20 mg samples of bulk carbonate were reacted with 100% phosphoric acid, following the standard procedure of McCrea (1950). The same procedure was applied to the analyses of gastropods and modern bivalves. Gastropod species *Valvata piscinialis* and *Bithynia tentaculata* were picked out from the wet sediment fraction > 0.6 mm, cleaned ultrasonically (10–30 seconds), dipped in 5% sodium hypochlorite solution for less than 15 h to remove organic matter, carefully washed four times with distilled water and dried at 80°C for 4 h (Charef & Sheppard 1984). Material treated in this way was checked for contamination with a binocular microscope and crushed to small size. A fractionation factor of 1.00931 at 50°C was used for the reaction between calcite and phosphoric acid (Swart et al. 1991). The same value was used for the aragonitic samples (molluscs), because there are no significant differences for calcite and aragonite, as was verified by Tarutani et al. (1969). All isotopic ratios were determined using a Finnigan MAT 251 multi-collector mass spectrometer (Institute of Mineralogy, University of Lausanne). Results are reported in the standard per mil (‰) notation relative to the PDB international standard (Craig 1957):

$$\delta \text{‰} = (\text{R}_{\text{sample}} - \text{R}_{\text{standard}} / \text{R}_{\text{standard}}) * 1000$$

where R is the ratio ($^{13}\text{C}/^{12}\text{C}$) or ($^{18}\text{O}/^{16}\text{O}$).

Note on the analysed carbonate material

There are three main sources of carbonate sedimentation in fresh water lakes: detrital input, organic production and inorganic precipitation (Kelts & Hsü 1978). The latter can be induced both by biogenic and physical factors. The bulk carbonate analysed in our core is primarily composed of epilimnetic calcite, with minor amount of bioclasts and detrital minerals. The precipitation of epilimnetic calcite is triggered by biogenic factors during CO₂ assimilation by Macrophyta (shallow water) and Microphyta (open water) (Kelts & Hsü 1978). The influence of bioclasts and detrital minerals on the isotopic results is generally negligible, because of their small amount as evidenced by SEM analyses (Moscariello 1996).

Lacustrine crusts are, as defined by Schneider (1977) and by Schneider et al. (1983), “biogenic growth structures which in addition incorporate trapped detritus and inorganically precipitated calcite”. In our case, however, the biogenic structures

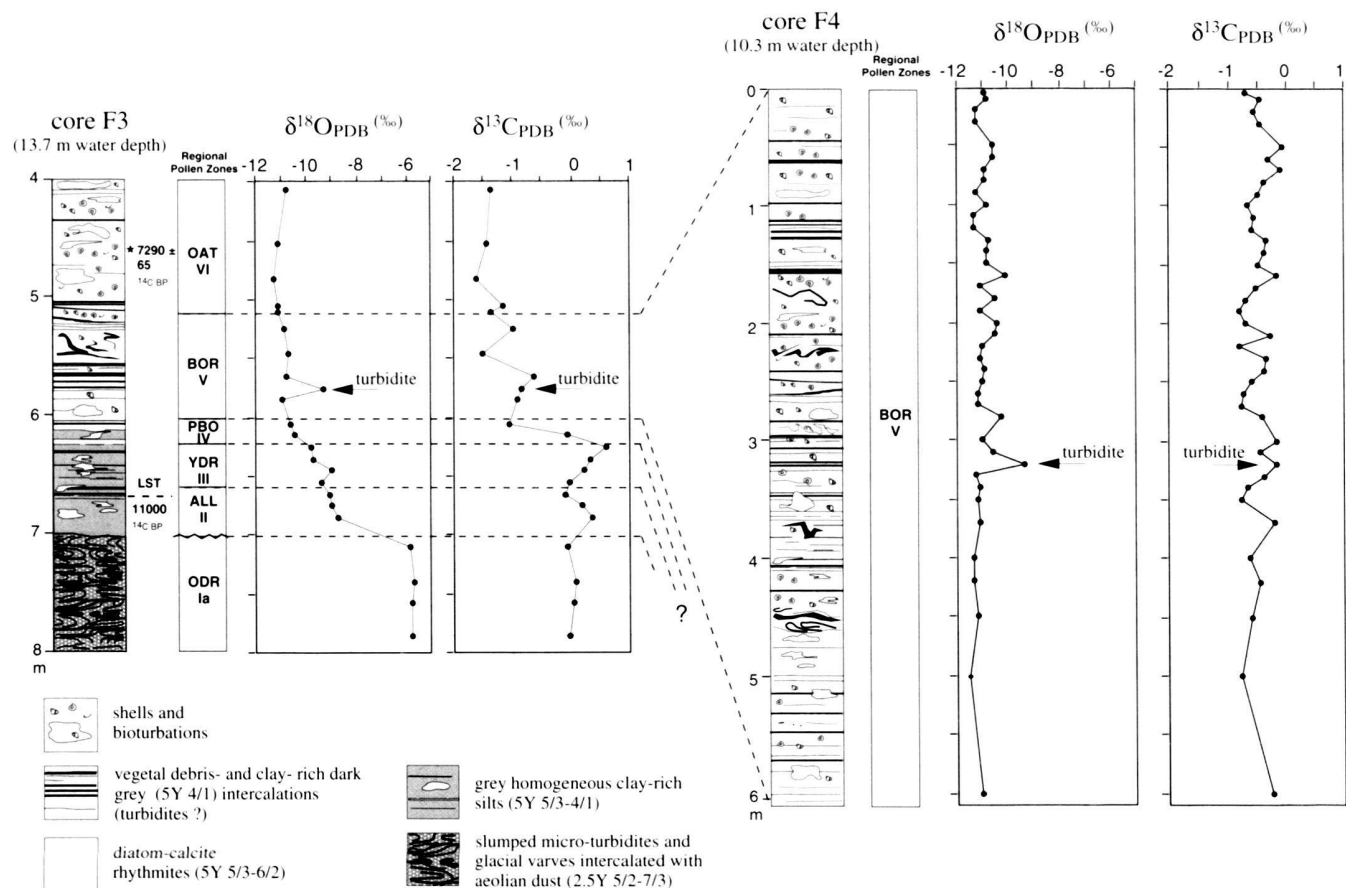


Fig. 2. Stratigraphy and bulk carbonate isotope curves (oxygen and carbon) of cores F3 and F4. LST= Laacher See Tephra, ash layer dated 11,000 BP by radiocarbon (Bogaard & Schmincke 1985). OAT = Older Atlantic; BOR = Boreal; PBO = Preboreal; YDR = Younger Dryas; ALL = Allerød; ODR = Oldest Dryas. Color codes in the sediment description legend are after Munsell (1954). Arrows indicate samples -5.75 m (F3) and -3.20 m (F4), corresponding to dark, clay-rich levels (turbidites?) which have not been considered for mean calculations (see text). Chronostratigraphy is defined by Local Pollen Zones which are correlated with Regional Pollen Zones after Ammann (1989) (Moscariello et al., in press, and A.M. Schneider in Moscariello 1996).

are poorly preserved, and trapped detritus and inorganically precipitated calcite predominate. These crusts are typically restricted to the shallow water environments within the photic zone.

Gastropods and bivalves analysed come from different depths: *B. tentaculata* and *V. piscinalis* specimens were separated from the uppermost Corsier 2 core sediment (16.5 m of water depth), whereas Anodonta samples were collected on the lake shore. Gastropods isotopic composition was analysed for comparison with the bulk carbonate isotopic composition, to have a detrital free signal. Bivalves and carbonate crust isotopic results were used to check the oxygen isotopic equilibrium of calcite precipitation at present day.

The Late-Glacial and Holocene sedimentological framework

The sedimentological features and chronological framework of core F3 (Fig. 2) have already been discussed in Moscariello et al. (in press) and Moscariello (1996). The sedimentary interval

investigated for stable isotope analysis (Oldest Dryas – Older Atlantic, $\approx 14,000$ –6,000 yr. BP uncalibrated ^{14}C ages) is characterised by three important lithological changes, corresponding to significant variations in lacustrine paleoenvironment. During the Oldest Dryas, sedimentation was dominated by detrital supply and was characterised by the accumulation of glacial varves intercalated with micro-laminated distal turbidites and aeolian dust. The latter are rich in detrital calcite and phyllosilicates, whereas on the whole Oldest Dryas sediments contain more quartz and feldspar than Allerød sediments. Mineralogical content of different biozones is summarised in Table 2. The Allerød biozone directly overlies the Oldest Dryas biozone, the Bølling biozone being probably removed by a slump shortly after deposition. An important reduction in detrital supply occurred in the Allerød period: only settling of clay-rich silts occurred, forming homogeneous, structureless deposits. Estimated sedimentation rate passes from 1–1.2 mm/yr for the Oldest Dryas to drastically lower values, reaching 0.3 mm/yr in the Allerød biozone. Meanwhile, the progres-

Table 2. Average whole sediment composition of core F3 (0–8 m) and Corsier 2 (C 2, 0–4.4 m). Values in %.

	calcite		pyrite		dolomite + ankerite		quartz		K-feldspar		plagioclase		phyllo-silicates		ID	
biozones	F3	C2	F3	C2	F3	C2	F3	C2	F3	C2	F3	C2	F3	C2	F3	C2
Subatlantic	61.7	65.7	0.6	0.9	0.3	0.3	11.9	7.7	0.4	0.6	4.9	1.7	8.4	11.5	11.7	11.5
2 σ	20.5	10.0	0.6	0.4	0.7	0.6	18.5	4.5	2.5	1.4	13.0	1.3	5.2	4.8	7.9	8.0
Subboreal	72.2	66.8	0.9	1.1	0.1	0.6	6.7	7.9	0.2	0.6	1.5	2.2	10.4	13.6	8.0	7.2
2 σ	8.2	11.9	0.5	0.4	0.6	0.8	1.6	4.0	0.7	0.9	0.6	1.4	4.7	4.5	9.2	12.8
Atlantic	72.1	69.3	0.8	0.8	0.3	0.8	5.9	6.6	0.4	0.2	1.7	1.8	10.4	10.4	8.4	10.1
2 σ	16.0	5.7	0.6	0.4	0.7	0.5	3.3	2.2	0.9	0.8	2.4	1.3	4.2	2.3	12.4	7.2
Boreal	66.5		0.8		0.6		6.1		0.3		1.3		13.5		10.9	
2 σ	20.2		1.0		0.9		4.0		0.7		1.0		9.6		17.1	
Pre Boreal	52.1		1.0		1.6		9.8		0.5		2.3		16.0		16.8	
2 σ	31.5		0.5		1.7		6.1		1.4		2.1		6.2		22.3	
Younger Dryas	35.4		1.2		1.7		13.0		0.7		3.0		18.6		26.4	
2 σ	13.7		0.7		0.8		4.2		1.0		1.9		5.0		11.0	
Bølling/Allerød	44.2		0.6		2.0		13.8		0.8		2.6		18.9		17.1	
2 σ	10.3		0.3		0.6		7.0		1.2		2.6		9.1		17.6	
Oldest Dryas	35.5		0.0		3.4		19.0		0.7		2.7		15.7		23.0	
2 σ	17.2		0.0		2.5		9.2		1.1		3.3		6.5		7.6	

ID (non identified minerals) correspond to the clay and heavy mineral fraction of the sediment.

Number of samples analysed: 80 for F3, 44 for Corsier 2.

sive climatic warming that occurred through the Bølling and Allerød periods, triggered the onset of endogenic calcite precipitation. Contrasting climatic conditions during the Younger Dryas were characterised by increased detrital supply (clay minerals) strongly diluting endogenic calcite sedimentation. Since the beginning of the Preboreal, in response to climate-induced changes in limnic conditions (increased water temperature, organism colonisation) and environmental modification in the catchment area (vegetation development, decreased soil erosion and detrital supply), calcite production recovered. Finely laminated calcite-diatom rhythmites (Kelts & Hsü 1978) are formed by seasonal calcite precipitation, which characterises up to 80% of the bulk sediment (Moscariello 1996). However, settling processes were occasionally disturbed by high energy sedimentation phases, especially during the Boreal time period. Turbidity currents and lake-level fluctuations (probably during a general lowering phase of the lake-level) provoked resedimentation of littoral deposits. Slumps were also frequent at that time. During the Boreal time period, the uppermost 6 m of core F4 accumulated. The same biozone is only 0.87 m thick in core F3, probably as a consequence of the greater distance from the shore.

Scattered mineralogical analyses throughout the Boreal biozone of core F4 indicate a comparable sediment composition with the corresponding biozone of core F3. These data are consistent with sedimentological observations (Fig. 2).

The sediments of the whole core Corsier 2 (4.4 m) repre-

sent the chronological interval from the Older Atlantic to the present day, as inferred from the pollen record (A.M. Schneider, pers. comm., 1995). Their sedimentological features are substantially different from those of core F3. Corsier 2 sediments consist of homogeneous structureless, grey, clay-rich silts (mean grain-size between 8 and 10 μ m) containing scattered shells that, toward the top, form concentrated beds 3–4 cm thick. Primary sedimentary structures formed by calcite-diatom rhythmites are preserved in places, but have generally been obliterated by widespread bioturbation and degassing cavities. Sediments mainly comprise calcite (mean 68%). Nevertheless, SEM observations reveal that endogenic crystals are strongly diluted by fine silt-sized detrital minerals. In particular, the amount of dolomite, phyllosilicates and clay minerals (Table 2) is slightly higher than in coeval Geneva Bay sediments. This abundance of detrital minerals is probably a result of the proximity of the core site to the inflow of local tributaries (Fig. 1) which, during seasonal flood discharges, generate fine-grained distal plumes, rich in detrital material collected from the neighbouring calcareous uplands (Jura, Chablais) and their glacial cover.

Detrital mineral content in core Corsier 2 sediments increases upwards. A similar trend was also described for core F3 (Moscariello 1996) and related to increased soil erosion caused by deforestation on the catchment (as suggested by pollen data) joined with increased wave-induced littoral reworking.

As a whole the differing composition between cores F3 and F4 and core Corsier 2 is due to a stronger dilution of detrital minerals as the distance from the main tributary mouths increases. Such a difference is better emphasised by the sediments of the “Grand Lac” (Sauvage 1967; Serruya 1969), where the allogenic component is clearly predominant over the endogenic one that form together with other carbonates the 20–50% of the bulk (Serruya & Vergnaud-Grazzini 1966). This fact has been clearly demonstrated for superficial deposits throughout the lake (Jaquet et al. 1983).

New isotopic data

The isotopic trend of core F3 (Fig. 2) has been presented and discussed elsewhere (Filippi 1996; Moscariello 1996); isotopic data are listed in Table 3. There is a distinct negative trend in oxygen isotopic composition from the core bottom toward the top. The bottom samples (Oldest Dryas) have the highest $\delta^{18}\text{O}$ values (-5.7‰). From 7 to 6 m (Allerød-Preboreal) $\delta^{18}\text{O}$ values change from -8.7‰ to -10.6‰ . The $^{18}\text{O}/^{16}\text{O}$ ratio stays more or less constant around -10.95‰ during both the Boreal and Older Atlantic, except for a dark clay-rich layer (sample -5.75 m, -9.3‰). The trend of the carbon isotope curve is characterised by an abrupt negative shift of 1.6‰ between 6.25 and 6 m (Preboreal). The mean $\delta^{13}\text{C}$ value under 6.25 m is $+0.15\text{‰}$, while above 6 m it is -1.2‰ .

Fig. 2 shows a comparison between isotopic values of the F3 and F4 cores (Tab. 4). F4 sediments (Boreal biozone) are

Table 3. F3 isotopic results (bulk carbonate).

Depth (cm)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{PDB}}$ (‰)
406	-1.38	-10.77
452	-1.44	-11.11
482	-1.62	-11.27
505	-1.16	-11.07
510	-1.38	-11.09
525	-0.99	-10.84
545	-1.51	-10.70
565	-0.61	-10.80
575	-0.84	-9.32
585	-0.89	-10.90
605	-1.03	-10.59
615	-0.05	-10.44
625	0.60	-9.78
635	0.34	-9.70
645	0.23	-8.92
655	-0.02	-9.35
665	-0.08	-9.01
675	0.18	-8.97
685	0.36	-8.73
710	-0.06	-5.81
740	0.09	-5.63
758	0.04	-5.71
786	-0.02	-5.71

Table 4. F4 isotopic results (bulk carbonate).

Depth (cm)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{PDB}}$ (‰)
5	-0.72	-10.91
10	-0.47	-10.88
20	-0.56	-11.27
30	-0.45	-11.23
50	-0.06	-10.59
60	-0.31	-10.62
70	-0.12	-10.93
80	-0.41	-10.93
90	-0.51	-11.28
100	-0.66	-10.87
110	-0.57	-11.36
120	-0.59	-11.35
130	-0.36	-10.79
140	-0.38	-10.84
150	-0.50	-10.80
160	-0.18	-10.13
170	-0.55	-11.10
180	-0.71	-10.55
190	-0.82	-11.05
200	-0.71	-10.47
210	-0.30	-10.50
220	-0.80	-11.02
230	-0.37	-11.11
240	-0.39	-10.91
250	-0.61	-10.99
260	-0.76	-11.21
270	-0.78	-11.13
280	-0.44	-10.26
300	-0.17	-11.03
310	-0.48	-10.62
320	-0.17	-9.40
330	-0.40	-11.22
340	-0.66	-11.10
350	-0.79	-11.18
370	-0.20	-11.06
400	-0.63	-11.33
420	-0.46	-11.35
450	-0.62	-11.19
500	-0.79	-11.48
600	-0.24	-11.03

characterised by variable isotopic composition, ranging between -11.5 and -10.1‰ for oxygen and from -0.8 and -0.1‰ for carbon, corresponding to many clay-rich intercalations and high sedimentation rate. F4 mean values of -11‰ for $\delta^{18}\text{O}$ and of -0.5 for $\delta^{13}\text{C}$ correspond fairly well to the coeval F3 mean values ($\delta^{18}\text{O} = -10.5\text{‰}$ and $\delta^{13}\text{C} = -0.97\text{‰}$). Sample -3.20 m is not considered in the mean calculation because it corresponds to a restricted dark level, similarly to sample -5.75 m in F3 core (turbidites?).

In Figure 3 isotopic data from F3 and F4 are plotted together with a few stable isotope analyses performed on more recent material (data are listed in Table 5). All molluscs analysed grow a pure aragonite shell. In the Corsier 2 core (uppermost 60 cm, Subboreal-Subatlantic biozones), samples of both bulk carbonate and gastropods were analysed. Experiments on

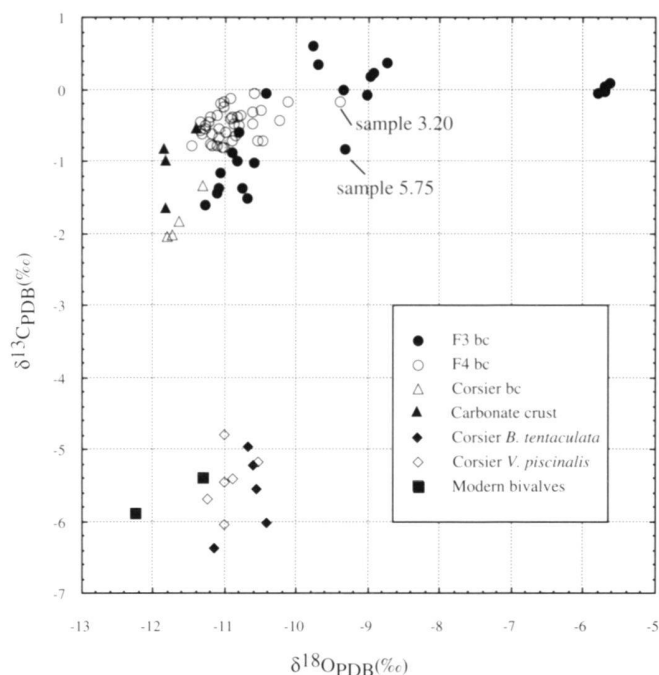


Fig. 3. Isotopic ratios of all samples measured in this work. bc = bulk carbonate; *B. tentaculata* and *V. piscinalis* are gastropod species. Samples 5.75 (F3) and 3.20 (F4) correspond to dark layers, probably turbidites. F3, F4, Corsier cores, and encrustation are from the "Petit Lac" (Geneva Bay side); modern bivalves are collected on the Vidy beach (near Lausanne). As general remark, molluscs $\delta^{13}\text{C}$ values are definitely more negative than those of bulk carbonate (see discussion in the text).

the variability of isotopic composition between different monospecific individual gastropods from the same stratigraphic level confirmed that variations of ± 0.5 ‰ in isotope ratios from gastropods (*B. tentaculata* and *V. piscinalis*) are not significant. Mean isotope ratios of Corsier bulk carbonate are slightly more negative than Older Atlantic F3 ratios, both for oxygen and for carbon. Corsier $\delta^{18}\text{O}$ values of whole rock (-11.55 ‰) and gastropods (-10.85 ‰) are quite similar, but not for carbon isotopes. There is a 3 to 4‰ difference between gastropods and bulk carbonate $\delta^{13}\text{C}$ values, the former being lower than the latter. In the same way, the oxygen isotopic composition of modern bivalves (*Anodonta cygnea*) collected on the lake shore (mean $\delta^{18}\text{O}$ -11.8 ‰), and of modern carbonate crust (over a cobble from a depth of 3 m, mean $\delta^{18}\text{O}$ -11.72 ‰) is perfectly comparable, whereas $\delta^{13}\text{C}$ values are definitely different (mean $\delta^{13}\text{C}$ -5.65 ‰ for *A. cygnea*, and -1.01 ‰ for carbonate crust). The $\delta^{13}\text{C}$ of the carbonate crust varies from -1.65 to -0.54 ‰. This wide range is probably linked to the microbial origin of carbonate or its close relation with algal filaments, which is also observed for ooid sand formation (Moscardello 1997).

Table 5. Late Holocene and recent samples isotopic results.

Location	Sample	Depth (cm)	$\delta^{13}\text{C}_{\text{PDB}}$ (‰)	$\delta^{18}\text{O}_{\text{PDB}}$ (‰)
Corsier	bulk carbonate	1-2	-1.35	-11.31
Corsier	bulk carbonate*	1-2	-1.36	-11.29
Corsier	bulk carbonate	15	-1.84	-11.63
Corsier	bulk carbonate	33	-2.05	-11.80
Corsier	bulk carbonate	60	-2.02	-11.73
Corsier	<i>B. tentaculata</i> (2)	1-2	-6.39	-11.13
Corsier	<i>B. tentaculata</i> (2)	15	-6.04	-10.41
Corsier	<i>B. tentaculata</i>	33	-5.23	-10.59
Corsier	<i>B. tentaculata</i> (2)	60	-5.56	-10.56
Corsier	<i>B. tentaculata</i> (1)	60	-4.97	-10.68
Corsier	<i>V. piscinalis</i>	1-2	-4.80	-10.99
Corsier	<i>V. piscinalis</i>	15	-6.07	-10.99
Corsier	<i>V. piscinalis</i>	33	-5.44	-10.95
Corsier	<i>V. piscinalis</i> (1)	60	-5.70	-11.24
Corsier	<i>V. piscinalis</i>	60	-5.18	-10.53
Petit Lac	carbonate crust 1	0	-1.65	-11.83
Petit Lac	carbonate crust 2	0	-1.00	-11.81
Petit Lac	carbonate crust 3	0	-0.83	-11.85
Petit Lac	carbonate crust 4	0	-0.54	-11.41
Lausanne shore	<i>A. cygnea</i> (big)	0	-5.39	-11.30
Lausanne shore	<i>A. cygnea</i> (small)	0	-5.90	-12.25

* sample cleaned by hand picking

(n) number of organism analysed; when not specified all organism found in the level where analysed

Comparison with pre-existing isotopic data

All the isotopic data published on Lake Geneva carbonates are plotted in Figure 4, together with the mean isotopic composition of local marine limestone measured by Serruya and Vergnaud-Grazzini (1966), added for comparison. As is clearly shown in Figure 4, there is a group of bulk carbonate values, corresponding to the lower parts of core F3 and of Lemman 44 core (Serruya & Vergnaud-Grazzini 1966), lying very near to the detrital isotopic composition. This agreement of isotopic values indicates the predominance of detrital input into the sediment during the Late-glacial time. Bulk carbonate isotopic composition evolves then towards lower values (ca -2 ‰) both for oxygen and carbon. The exception to this trend is represented by Younger Dryas/Preboreal data of Blanc et al. (1977), with lower $\delta^{13}\text{C}$ and higher $\delta^{18}\text{O}$ values with respect to the general data set. Molluscs analysed by these authors clearly shift in $^{13}\text{C}/^{12}\text{C}$ ratio if compared with bulk carbonate (around 4–5‰ difference), while oxygen isotope compositions stay quasi-stable, or become slightly higher. Similarly, $\delta^{13}\text{C}$ values of recent and modern molluscs are at least 3‰ lower than $\delta^{13}\text{C}$ values of synchronous bulk carbonate, whereas $^{18}\text{O}/^{16}\text{O}$ ratios of biogenic and inorganic carbonate are comparable. The analyses on modern molluscs by Chaix et al. (1982) are character-

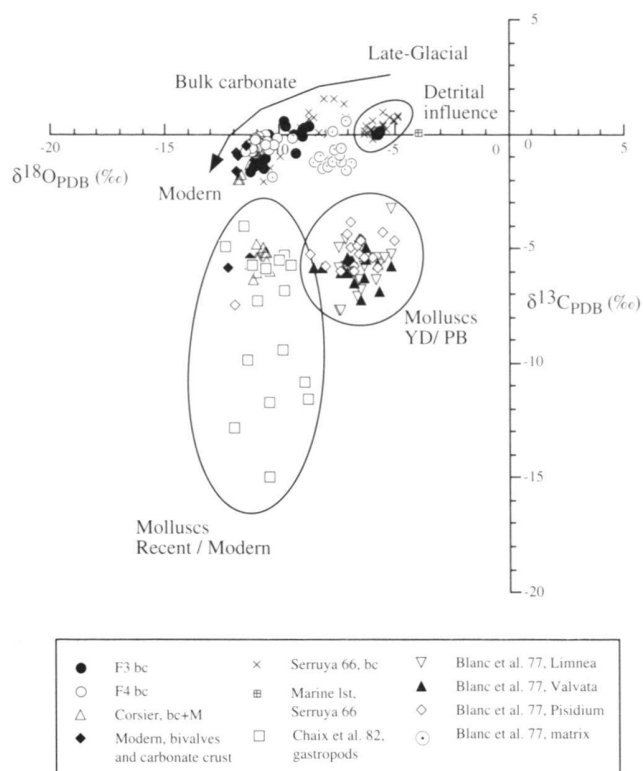


Fig. 4. Isotopic results of all published data on lacustrine carbonate of Lake Geneva. The isotopic composition of marine limestone (square with cross inside), measured by Serruya and Vergnaud-Grazzini (1966), is given for comparison. bc = bulk carbonate; Ist = limestone; YD = Younger Dryas; PB = Preboreal. *Limnea*, *Valvata* and *Pisidium* are mollusc species; matrix indicates inorganic carbonate. Data are taken from Serruya & Vergnaud-Grazzini (1966), Blanc et al. (1977), Chaix et al. (1982) and this work (F3, F4, Corsier cores, and modern samples).

used by widely scattered $\delta^{13}\text{C}$ values, which they explain with a large contribution of biogenic CO_2 , whereas $^{18}\text{O}/^{16}\text{O}$ ratios are similar to our measurements.

The gastropod isotopic puzzle

Benthic-organisms secreting a carbonate shell are generally well suited for isotopic studies. In contrast to bulk carbonate, they offer the advantage of being free of the influence of detrital input. In lacustrine systems, ostracodes and gastropods are favoured organisms for isotopic studies because of their abundance in lake sediments. In conformity with their life conditions, they carry very precise information on paleoenvironment (temperature, productivity, water isotopic composition).

As the fundamental assumption is that carbonate shells are precipitated in isotopic equilibrium with parent water, a usual step is to calibrate the system, i.e. to verify the assumption with modern data. For ostracode calibration, we refer to the work of Heaton et al. (1995), Lister (1988a; 1988b; 1989), Lister et al. (1991), Palacios-Fest et al. (1994) and von Grafenstein et al. (1992). The relationships between gastropods and stable isotopes was studied by French authors during the 1980s (Lemeille et al. 1983), following the example of Keith et al. (1964), Stuiver (1970) and Fritz & Poplawski (1974). In the earlier studies, gastropods were assumed to precipitate their shell at equilibrium. However, Lemeille's (1980) experiment on gastropods grown in a laboratory under controlled conditions demonstrated a strong "metabolic" component in the isotopic composition of *Planorbis* and *Limnea* shells, in addition to the temperature effect. There is an almost 2‰ difference in $\delta^{18}\text{O}$ value between these two species, grown up in the same water. Such a vital effect is stronger than any possible fractionation due to the presence of aragonite in the shell (α aragonite-calcite = 0.6‰ for oxygen) (Tarutani et al. 1969). Therefore, absolute temperatures calculated from the isotopic composition of gastropods are unrealistic if not calculated using a species-calibrated temperature equation. On the contrary, the estimation of a relative temperature change is still meaningful, even if hydrological factors must also be taken into account. Unfortunately, temperature and hydrological effects on the isotopic composition of gastropods are not as easy to differentiate as in the case of ostracode isotopic composition. Benthic ostracodes can be found in deep water, where annual temperature variations are negligible, whereas the majority of gastropods prefer shallow photic water environments where daily and seasonal temperature variations are important. The isotopic composition of benthic ostracodes is influenced almost exclusively by parent water $\delta^{18}\text{O}$ value, while the gastropod isotopic ratios reflect both temperature effect and water isotopic composition. The carbon isotopic fractionation between aragonite and calcite ($\epsilon_{\text{ar-cl}}$) is $1.7 \pm 0.4\text{‰}$ and is independent of temperature from 10° to 40°C (Romanek et al. 1992). Differences between bulk carbonate and gastropod isotopic results are thus partially reduced by the aragonitic composition of the shell, and they would be of 5 to 6‰ if corrected for the aragonite-calcite fractionation factor. Carbon isotope in gastropods may widely vary according to depth, temperature and biomass (Chaix et al. 1982). Lemeille (1980) demonstrated that there is a good correlation between the carbon isotopic composition of the DIC and of gastropods. She concluded that gastropods precipitate carbonate near the carbon isotopic equilibrium with the DIC, and can, therefore, bring information on DIC sources. Furthermore, Chaix et al. (1982) pointed out that $\delta^{13}\text{C}$ in carbonate depends essentially on the nature and abundance of biomass, becoming a possible indicator of productivity. Following these authors, the carbon isotopic composition of gastropod shells is largely influenced by biogenic CO_2 (mean $\delta^{13}\text{C} = -26\text{‰}$), which would explain the more negative $\delta^{13}\text{C}$ with respect to the coeval bulk carbonate $\delta^{13}\text{C}$ (difference of more than 4‰).

Temperature and paleotemperature

Calculations using O'Neil's revised equation (Friedman & O'Neil 1977),

$$1000 \ln \alpha_{\text{calcite-water}} = 2.78 (10^6/T^2) - 2.89$$

assuming isotopic equilibrium with local water ($\delta^{18}\text{O}_{\text{SMOW}} = -12.3\text{‰}$) (Fontes & Gonfiantini 1970; Lemeille 1980), give calcite precipitation temperatures of 12–13°C for modern and recent carbonate samples (carbonate crust on cobble and Corsier bulk carbonate). Molluscs range between 11–12° and 16°C for Corsier gastropods and modern bivalves, respectively. These values fit well with the measured lake water mean temperature of the “Petit Lac” in the spring (11°)–summer (17°) period (CIPEL 1994), confirming that carbonate precipitation occurs at or near oxygen isotopic equilibrium. Boreal and Older Atlantic carbonate isotopic composition suggest temperatures slightly lower and/or lake water $\delta^{18}\text{O}$ values slightly higher than today's. This difference could be attributed to a change in paleoclimate (colder temperature and/or different rain source than today's), or to a lowering in the lake level (higher lake water $\delta^{18}\text{O}$ values) as documented by several authors (see Moscardiello 1996, for a review); unfortunately, there are no specific data to prefer one hypothesis to the other. An input of meltwater within the lake could also have played a role in lowering the temperature, but then lake water $\delta^{18}\text{O}$ values should have been lowered as well, which is not the case.

Paleotemperature calculations inferred from the Lemeille equation (Lemeille 1980; Lemeille et al. 1983)

$$t^{\circ}\text{C} \approx 23.2 - 4.19 (\delta^{18}\text{O}_c - \delta^{18}\text{O}_w)$$

give temperature values 7°C higher than the values estimated with O'Neil's equation. Our data set leave us with an uncertainty: whether the calcite (or aragonite) of the samples was precipitated in July–August ($\approx 22^{\circ}\text{C}$) (CIPEL 1994) or in May–June (12–14°C) (CIPEL 1994). In either case, calculated temperatures are still reasonable and the difference between modern and Boreal–Older Atlantic samples is unchanged. In contrast, using the equation proposed by Blanc et al. (1977) gives unrealistic results (negative temperature?) for our modern samples. Similarly, the O'Neil and Lemeille equations give unreasonable temperatures for Blanc et al. samples. Since both these equations seem to fit modern data, we consider the Blanc equation not to be applicable to our data set. To explain the odd temperatures obtained with O'Neil or Lemeille equations on Blanc et al. data we suggest the lake water isotopic composition to be locally higher (-8‰ ?) than in the whole lake, due to shallow water and different microenvironmental conditions (marsh?, isolated lagoon?). This hypothesis is supported by sedimentological data (Blanc et al. 1977) that indicate the presence of lacustrine chalk primarily composed of debris of Characeae (typical of shallow water), overlain by a peat layer after the Preboreal. It seems, therefore, reasonable to expect evaporation (higher $\delta^{18}\text{O}$ values) and vegetation overgrowth to be more important in the locality where Blanc

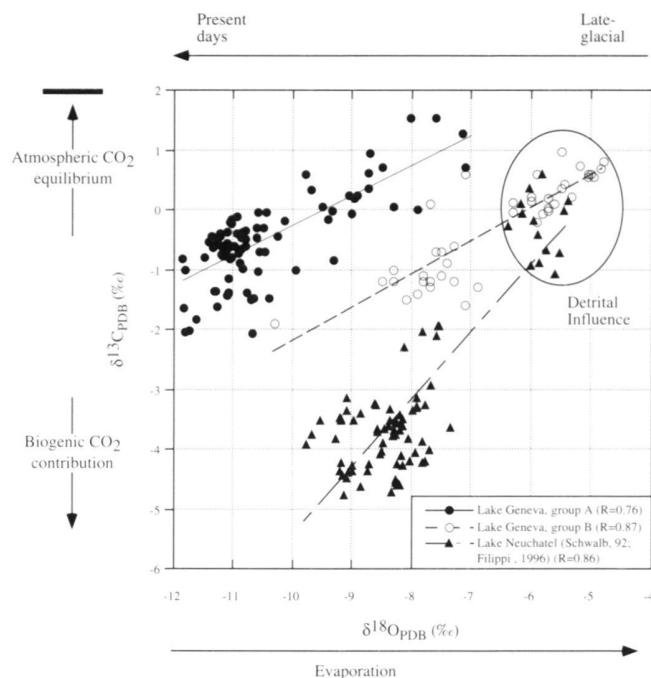


Fig. 5. Comparison between bulk carbonate isotopic composition of Lake Geneva (Serruya & Vergnaud-Grazzini 1966; Blanc et al. 1977, and this work) and of Lake Neuchâtel (Schwalb 1992; Filippi 1996). Group A is formed by: Leman 44 (Serruya & Vergnaud-Grazzini 1966) from 3 to 130 cm, F3 (from 406 to 685 cm), F4, Corsier 2, modern samples (this work). Group B is formed by: Leman 44 (Serruya & Vergnaud-Grazzini 1966) from 140 to 441 cm, F3 (from 700 to 786 cm), and Blanc et al. (1977) data. Arrows indicate time evolution and predominant mechanism governing the isotopic ratios and their effects. Black flattened rectangle indicates $\delta^{13}\text{C}$ calcite value at equilibrium condition with atmospheric CO_2 ($+2\text{‰}$ at 20°C) (Romanek et al. 1992).

et al. collected their samples than in the other sites studied. Moreover, Blanc et al. $\delta^{13}\text{C}$ values are lower than that of the other authors, confirming a major contribution of biogenic CO_2 during carbonate precipitation.

$\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ correlation in bulk carbonate

As shown in the $\delta^{18}\text{O}/\delta^{13}\text{C}$ cross plot (Fig. 5), in Lake Geneva there are two groups of carbonate with highly covariant trends. Upper F3, F4, Corsier 2, and modern samples together with Boreal Serruya data form group A, while the lower part of F3 and of Serruya core together with Blanc et al. data make up group B. We compared these trends with the bulk carbonate isotopic composition of a Late-glacial to Holocene core from Lake Neuchâtel (Schwalb 1992; Filippi 1996) (Fig. 5). Lake Neuchâtel is a large hard-water lake in the Jura zone (Switzerland). Its data display a good $\delta^{18}\text{O}$ – $\delta^{13}\text{C}$ correlation ($R=0.86$), and even if the plot shows two distinct areas where points concentrate, values evolve on the same regression line. Good cor-

relation between carbon and oxygen isotopic composition is generally characteristic of hydrologically closed lakes, with high rate of evaporation, as clearly demonstrated by Talbot (1990). Lake Geneva and Lake Neuchâtel are considered hydrologically open and evaporation is negligible, so that factors other than these should play a role to explain the covariant trend. Detrital influence on the isotopic signal represents a starting point for both lakes (overlapping zone in Fig. 5), confirming the predominance of detritus in the Late-glacial sediments. The covariant trends are, therefore, at least in the Late-glacial, mixing lines. Then, Lake Neuchâtel isotopic ratios jump towards lower values for both carbon and oxygen isotopes, similar to group B values of Lake Geneva and to $\delta^{18}\text{O}$ values of group A. Such evidence would indicate a decrease of the detrital input, a possible input of meltwater (lower $\delta^{18}\text{O}$ values) and an increased productivity within the lake (lower $\delta^{13}\text{C}$ values). These three possibilities, more than excluding one the others, play together an interactive role. On the contrary, $\delta^{13}\text{C}$ values of Lake Geneva group A stay stable or rise slightly and then gently decrease during and after the Preboreal. The substantial difference between the two lakes is the carbon isotope evolution: modern $\delta^{13}\text{C}$ values in Lake Neuchâtel bulk carbonate are around $-4/-5\text{‰}$ (Filippi 1996), in contrast to the -2‰ of Lake Geneva. Why does this difference exist, and why are the isotopic data of Lake Geneva divided into two groups? To answer this question we need to remind that lacustrine carbonate $\delta^{13}\text{C}$ values depend primarily on the $\delta^{13}\text{C}$ value of dissolved inorganic carbon (DIC). To simplify, when DIC is in equilibrium with atmospheric CO_2 ($\delta^{13}\text{C} = -7.8\text{‰}$) (Friedli et al. 1986), $^{13}\text{C}/^{12}\text{C}$ ratio in carbonates should be around $+2\text{‰}$ at a water temperature of 20°C (Romanek et al. 1992). If the influence of biogenic CO_2 (mean $\delta^{13}\text{C} = -26\text{‰}$) is strong, the $^{13}\text{C}/^{12}\text{C}$ ratio in carbonates can be very low. It seems, therefore, that the recycled biogenic CO_2 contribution is larger in Lake Neuchâtel than in Lake Geneva. In addition, the large surface area and the longer residence time in Lake Geneva (11.9 yr., compared with ≈ 8.3 yr. of Lake Neuchâtel) favour aqueous CO_2 -atmospheric CO_2 exchange, leading to near-equilibrium condition ($\delta^{13}\text{C}$ calcite near $+2\text{‰}$). We explain the slow decreasing of Lake Geneva $\delta^{13}\text{C}$ values ($\approx 1\text{‰}$) at the end of the Late-glacial to be linked to the geographic characteristics of the catchment area. The mean altitude of Lake Geneva hydrological basin is higher than that of Lake Neuchâtel and the area is much larger. Glaciers were an important feature in Lake Geneva catchment area during Late-glacial (Moscariello et al. in press), and vegetational cover and soils probably took longer to develop than in the Lake Neuchâtel catchment area. Palynological data from Lake Geneva cores (Moscariello et al. in press) indicate a switch from unforested glacial to dense interglacial forested landscape since the Bølling/Allerød time period, and a readvance of dense forests with the immigration of mesophilous taxa (*Corylus*, *Quercus*, *Tilia* and *Ulmus*) during the Preboreal. Only at that time the contribution of biogenic- CO_2 to the DIC composition of Lake Geneva water would have become significant.

The only exception is the marsh zone near Geneva, where Blanc et al. performed their analyses. This zone was far from the main inflows (Fig. 1), and probably shallower, warmer and more vegetated than the rest of the lake, which would explain the lower $\delta^{13}\text{C}$ values and, therefore, the presence of group B. Conversely, the core Lemman 44 studied by Serruya & Vergnaud-Grazzini (1966) seems to be influenced by detrital input for a longer time (up to the lower Boreal) than the F3 core, which is likely due to the closeness of the Dranse inflow to the core site (Fig. 1).

Conclusions

Lake Geneva endogenic carbonate seems to precipitate at or near oxygen isotopic equilibrium with ambient water, according to temperature calculations for modern samples. Further studies on sediment traps are necessary to confirm our preliminary data. The Late-glacial/Holocene isotopic signal on bulk carbonate documents the decrease of detrital input and the onset of endogenic calcite precipitation at the beginning of the Allerød biozone. $\delta^{13}\text{C}$ values decrease drastically during the Preboreal (tentatively correlated to upper Boreal in the Lemman 44 core). This variation is likely to be due to a change in productivity (Moscariello et al. in press) and/or to a "catchment effect" (i.e. geographic characteristics), the catchment taking a certain time to develop vegetation and soils. The contribution of biogenic- CO_2 to the DIC composition of lake water became significant during the Preboreal. Until this period, the aqueous-atmospheric CO_2 exchange and the influence of dissolved detrital carbonate determined the DIC isotopic composition, except for particular and restricted microenvironments like the marsh studied by Blanc et al. (1977). This "catchment effect" would be small or negligible in smaller hydrological basins with lower mean altitude, as demonstrated by the comparison with Lake Neuchâtel.

Gastropods provide a detrital free isotopic signal, useful to compare with the bulk carbonate isotopic ratio for studies on change in paleotemperature and in paleowater isotopic composition, despite the presence of a vital effect (Lemeille 1980). Unfortunately, material found in the core F3 was neither sufficient (sterile levels) nor qualitatively adequate (no monospecific samples over the studied period) for stable isotope analyses. Benthic ostracodes from core F3 are at present under study in order to eliminate the detrital influence problem and, thus, to reconstruct the Late-glacial / early-Holocene paleohydrological history of Lake Geneva.

Mineralogical evidence indicate an increased detrital influence on sedimentation since the Subboreal time period. On the other hand, preliminary stable isotope measurements of uppermost Corsier 2 sediments (Subboreal/Subatlantic time period) testify negligible detrital components, as demonstrated by the comparison with the carbonate crust and gastropods isotopic values, assumed to reflect a pure endogenic signal. This apparent disagreement still remains puzzling to explain.

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