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Paleoenvironmental evolution of the Pliocene Villarroya Lake, northern Spain, from stable isotopes and trace-element geochemistry of ostracods and molluscs

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Abstract Stable isotopes and trace-element content of calcite ostracod valves and aragonite mollusc shells from the Pliocene lacustrine succession of Villarroya allow depicting the geochemical record of environmental changes and to compare our data to the paleoenvironmental reconstruction obtained from other proxies. The lower sequences (A and B) are

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characterized by relatively high isotopic and Me/Ca values in the biogenic carbonates. The recorded large variations of $\delta^{18}O$ in these carbonates mainly reflect variations in the $\delta^{18}O_w$ due to precipitation–evaporation processes and, to a lesser extent, variations in temperature of calcification. The $\delta^{13}C$ data inform about changes in DIC although they are probably biased by the vital effects of the studied taxa. Minor and trace element contents in ostracod (Mg/Ca, Sr/Ca) and mollusc shells (Sr/Ca) are mainly linked to the Me/Ca of the lake water (Me/Ca$_w$), and to a lesser extent to temperature and to uptake kinetic effects. Several possible mechanisms may make the Me/Ca$_w$ to vary: long periods of Ca-carbonate (calcite, aragonite) deposition after charophyte development, and different inputs for Ca and Mg to the lake due to changes in drainage area configurations through time, including the changes in saline inputs (Na-Cl type) to the lake. The stable isotopes and the calculated Sr/Ca$_w$ and Mg/Ca$_w$ from sequence C display lower values than those from sequences A and B. The isotopic values from biogenic carbonates of unit C indicate isotopically diluted waters in a hydrologically open lacustrine environment. Distinct $\delta^{13}C$ and $\delta^{18}O$ plots for molluscs from unit C reflect the different biotopes and metabolism type. For several intervals of the Villarroya succession there is no direct relationships among: (i) salinity changes inferred from invertebrate paleoecology, (ii) paleoenvironmental slices based on isotopic signatures and Me/Ca$_w$ calculations (from biogenic carbonate

geochemistry) and (iii) climate in the hinterland deduced from pollen data. Lakes where geochemical behaviour is constrained by sporadic saline inputs and/or relative depletion in Ca due to long periods of Ca-carbonate precipitation or biomineralization, like the Pliocene Villarroya lake was, do not show clear correlation patterns between geochemical signals and climate proxies. In these lakes only major environmental trends display unambiguous geochemical signatures, and only some main shifts in the geochemical signature profiles may be correlated with significant global and/or regional environmental changes that have been reported from other paleoenvironmental records.

Introduction

During the Pliocene the climate changed from a greenhouse climate with higher temperature (T) and precipitation (P) than the present to a system in which progressively higher amplitude and frequency oscillations in P and T occurred until reaching Pleistocene climatic conditions (glacial-interglacial fluctuations). The last relatively warm period deduced from marine data took place at ∼3 Ma (Crowley 1996; Lourens et al. 1996), and was characterized by mean global surface temperatures that may have been ∼3°C warmer than the present (Raymo et al. 1996; Bartoli et al. 2005). The Mid-Pliocene warmth was followed by substantial cooling, linked to a major change in amplitude and frequency of climate variations which is reflected in most climatic proxies (cf. Sancetta and Silvestri 1986; Raymo et al. 1989; Bartoli et al. 2005, 2006). However, despite the importance of the changing climate scenario there is little pluridisciplinary research on Pliocene lacustrine sequences in Europe (e.g. Albianelli et al. 1997; Willis et al. 1999; Ghinassi et al. 2004).

Lacustrine sequences are reported as highly sensitive archives of global and local climate changes. In particular, biogenic carbonates from lacustrine deposits can provide paleoenvironmental information, which is recorded in their chemical and isotopic composition. In the present paper, the geochemical

methods of paleoenvironmental analyses are applied to ostracod and mollusc carbonates from a Pliocene lacustrine sequence of the Villarroya Basin to provide additional elements to the paleolimnological approach based up to now on the sedimentology, the palynology and the paleoecology of ostracods and molluscs (Anadón et al. 2002a; Martín-Rubio et al. 2006). In addition, the paleolimnological record of environmental changes in the biogenic carbonates will be compared with the paleoenvironmental interpretations from other proxies. In our case, we have analyzed the calcitic ostracod valves of several Candonidae species and the aragonitic shells of several mollusc taxa: three gastropod and one bivalve species. All these taxa were selected for geochemical analyses because of their good preservation and their relative abundance throughout most of the section.

Geological setting

General

The Pliocene Villarroya Basin (La Rioja, northern Spain), is located in the NE part of the Sierra de Cameros, NW Iberian Chain, close to the overthrust contact of this chain on the marginal alluvial facies of the Tertiary Ebro Basin (Fig. 1). The Pliocene Villarroya basin-fill deposits, formed by lacustrine
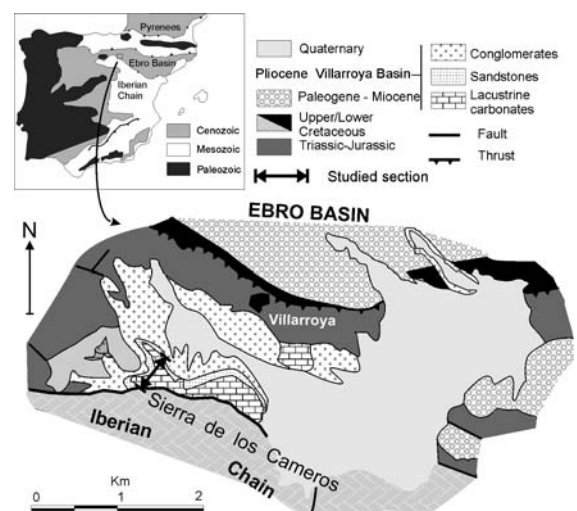
Fig. 1 Geological setting of the Villarroya Basin (from Muñoz et al. (2002) and Anadón et al. (2002a), modified)

and alluvial sediments up to 100 m thick, crop out in a small, elongated area, 6 km long by 2 km wide.

The Sierra de Cameros in the area surrounding the Villarroya Basin consists of a thick Mesozoic sequence formed of marine Jurassic limestones, 300–800 m thick, and a thick succession of non-marine Upper Jurassic to Lower Cretaceous (Weald) deposits up to 8,000 m thick, that include sandstones, shales and lacustrine limestones (Tischer 1966; Guiraud and Seguret 1985; Mas et al. 1993). The Paleogene alluvial facies of the Ebro Basin margin close to the Villarroya Basin consist of a thick succession of red and brown sandstones and mudstones which is overlain by conglomerates with interbedded red sandstones and mudstones, over 700 m thick (Muñoz-Jiménez 1992).

The Villarroya basin-fill sequence is formed of a basal interval of alluvial sediments, 12 m thick, which is overlain by lacustrine deposits, up to 30 m thick (Fig. 2), that in turn are overlain by red alluvial deposits, over 60 m thick. The general stratigraphy of the basin-fill deposits has been described by Brinkmann (1957a, b), Muñoz-Jiménez (1992), Muñoz et al. (1992) and Anadón et al. (2002a).

An important Late Pliocene large-mammal fauna has been recovered from a mammal site located in the alluvial deposits of the upper part of the basin fill sequence (Carvajal 1928; Villalta 1952). Nevertheless, the more precise adscription to the Upper Pliocene mammal zones has been controversial (Pueyo Morer et al. 1996, 1997; Alberdi and Azanza 1997; Laplana et al. 1999; Agustí and Oms 2001). The last data on the magnetostratigraphy of the basin indicate that the Gilbert Chron is not represented and the complete basin-fill section represents most of Gauss and Matuyama chrons (Pueyo et al. 2005, and their unpublished data).

The lacustrine deposits: paleoenvironmental indicators

The best outcrops of the lacustrine deposits are located in the NW part of the basin, where a 30 m thick succession is well exposed close to the road to Cornago (Figs. 1, 2). In previous works (Rodríguez-Lázaro et al. 1997; Anadón et al. 2002a) we have differentiated three sequences in these lacustrine deposits (A–C, Fig. 2). Sequences A and B consist each of a lower unit formed by laminated carbonate lutites and silty packstones (A_1 and B_1) that are overlain by laminated packstones and carbonate varves (units A_2 and B_2). Sequence C consists of bioturbated carbonate lutites.

The *thin bedded to laminated lutites and silty packstones* (units A_1 and B_1) are formed by mixtures of detrital biogenic carbonates with minor amounts of terrigenous carbonate and siliciclastic silt-sized grains and clay minerals. The biogenic carbonates usually consist of shells or shell fragments from ostracods and gastropods and charophyte encrustation debris. These facies correspond to profundal fine-grained, detrital lacustrine deposits with noticeable to predominant biogenic component. The lack of bioturbation and preservation of lamination both point to anoxic or suboxic lacustrine bottom in the profundal zones. Terrigenous sands and gravels are interbedded with the laminated lutites and silty packstones and may be interpreted as sublacustrine dilute mass flow deposits. The laminated sands probably correspond to tractive subaqueous flows.

Thin bedded to laminated biogenic carbonates and *varves* constitute well-defined units (A_2 and B_2) in the lacustrine deposits. These are formed by accumulations of biogenic silty and sand-sized carbonates with minor siliciclastic components. The most frequent biogenic components are charophyte stem incrustations, with minor amounts of ostracod and gastropod shells and charophyte oogonia. However, some gastropodal coquina beds also occur. These facies correspond to profundal basinal lacustrine deposits with predominant biogenic clastic deposition under anoxic or suboxic bottom conditions, as deduced from the excellent preservation of lamination and lack of bioturbation. The presence of interbedded slumped horizons in some varved intervals records unstable toe-of-slope proximity. The couple of laminae in varves corresponds to annual deposits and spectral analysis on the thickness of the couplets, and on the thickness of each lamina indicate decadal to centennial cyclicities (Muñoz-Jiménez and Sánchez-Valverde 1997; Muñoz et al. 1999, 2002; Utrilla et al. 1999, and our unpublished data). The sequential arrangement of A and B sequences suggests cyclical changes in the depositional features (in at least two different scales). Each sequence (A or B) includes a first phase when sedimentation is mostly dominated by fine extrabasinal detrital inputs followed by a second phase in which carbonate
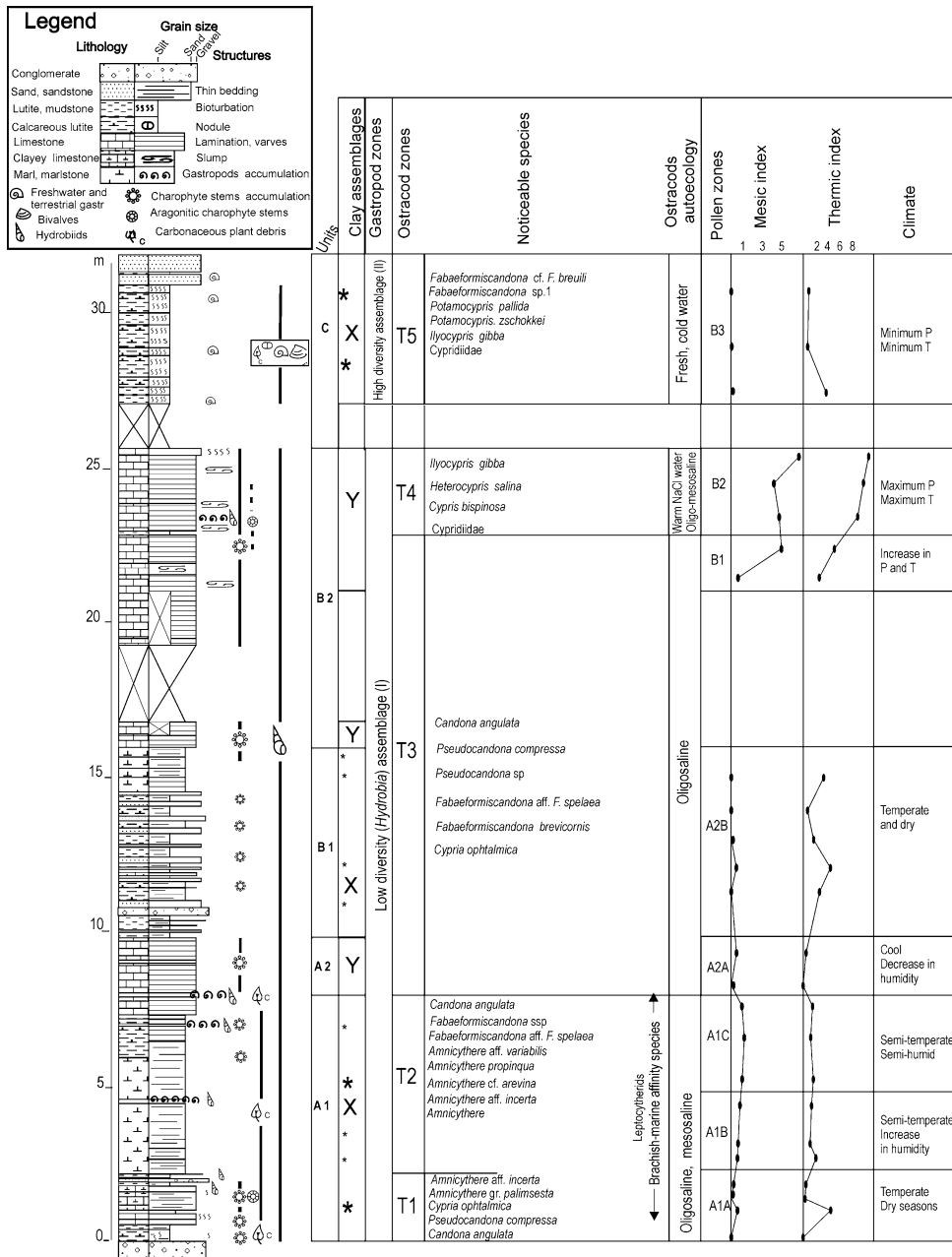
Fig. 2 Stratigraphy and paleoenvironmental data from the Villarroya main section after Anadón et al. (2002a) and Martín-Rubio et al. (2006). Asterisk (*) denotes noticeable amounts of chlorite and kaolinite which correspond to conspicuous inputs from the northern basin margin. The relative size of the symbol indicates the importance of the input. The mesic index is defined by the total percentage of mesic trees. The thermic index is defined by the total percentage of the sum of mesic taxa + evergreen *Quercus* + *Olea Phyllerea* + *Arbutus* + Myrtaceae + *Cistus* (See details in Anadón et al. 2002a). In the climate column, T = temperature, P = precipitations. Ostracod and mollusc content from Martín-Rubio et al. (2006) and Rodriguez-Lázaro et al. (1997) respectively

production in charophyte meadows and its cyclical accumulation (varve-like, minor scale) in basinal zones dominated.

Massive, bioturbated mudstones are located in the uppermost part of the regressive, lake-fill succession (sequence C). Mudstones usually are grey in colour,

with vertical mottling and bioturbation traces. This interval corresponds to a littoral, shallow lacustrine to palustrine environment.

There is a close relationship between sedimentology, bulk mineralogy and the composition of the clays (Anadón et al. 2002a). The terrigenous, exogenic-dominated units A_1, B_1 and C are characterized by clay assemblage X (illite, paragonite, palygorskite, kaolinite, chlorite, smectite and interstratified clays) (Fig. 2). The varve-dominated biogenic carbonate units, A_2 and B_2 are characterized by clay assemblage Y (in which smectite and interstratified clays are almost absent). Smectite and interstratified clays probably formed in soils under suitable conditions, whereas high amounts of kaolinite and chlorite in some discrete beds are interpreted as considerable inputs from the N and NW basin margin. Fluctuations in clay minerals along the studied succession not only depend on climate, but also on paleogeography and tectonics.

A total of 24 mollusc taxa have been recorded in the studied section. Two main assemblages can be differentiated on the basis of the diversity and species composition (Rodriguez-Lázaro et al. 1997; Anadón et al. 2002a). The low diversity assemblage I is mainly formed by *Hydrobia* aff. *slavonica* (Brusina), which characterizes most levels from sequences A and B. A streaking feature is the absence of pulmonates in these sequences, which suggests their origin in a profundal lacustrine setting. The high-diversity assemblage II, which corresponds to sequence C, is formed by: 5 aquatic gastropods, one bivalve, and 14 terrestrial gastropods. The aquatic species comprise two prosobranchs, three pulmonates and, at least one bivalve species (*Pisidium* sp.). The terrestrial pulmonates comprise hygrophilous taxa, which are predominant, mesophilous species and some taxa of xerophilous affinity. This assemblage indicates a fresh water, palustrine or shallow, marginal lacustrine environment.

About 31 species of ostracods have been collected from the studied section. Their taxonomy and ecology are described elsewhere (Martín-Rubio 2003; Rodrí-guez-Lázaro and Martín-Rubio 2005; Gliozzi et al. 2005; Martín-Rubio et al. 2006). The complete, revised list of ostracod taxa is provided by Martín-Rubio et al. (2006), which differentiate five intervals (T1–T5) on the basis of the ostracod assemblages (Fig. 2). Interval T1 is characterized by the presence of leptocytherids, except for the most basal levels. The presence of these taxa suggests an increase in salinity, from oligosaline to oligo-mesosaline waters. In T2, some oligosaline species from T1 disappear, suggesting an increase in salinity. T3 is characterized by lack of leptocytherids and re-appearance of some taxa from T1, all suggesting lowering in salinity. Ostracods from T4 indicate an increase in temperature and salinity in the lake water. T5 ostracods indicate a major faunal change and point to a freshwater, cold shallow lacustrine–palustrine environment.

Eight pollen zones (PZs), which record marked climate changes, have been differentiated in the lacustrine deposits (Fig. 2; Anadón et al. 2002a). The lower part of the lacustrine sequence (PZs A1A to A2A) may be correlated with the beginning of Mediterranean winters (relative cooling) of about 3.5–3.6 Ma (Suc et al. 1995). The upper part of sequence B (PZs A2B to B2) reveals an increase in warm and moist conditions to vegetation similar to the present Mediterranean mid altitude forests. On the basis of the age range of paleomagnetics this warm phase may be correlated with the warmth of 3.1–3.0 Ma (Anadón et al. 2002a), also recorded in several pollen spectra from Western Europe (Rousseau et al. 1992, 1995; Suc et al. 1995). The climate change recorded in sequence C (PZ B3) correlates with the subsequent cooling after the Mid-Pliocene warmth.

Materials

Geochemical analyses were performed on 89 samples of biogenic carbonates. The samples were collected from about 1 cm-thick sediment slices from the studied section and comprise calcitic ostracod valves of four Candonidae species and aragonitic shells of several mollusc taxa: three gastropod and one bivalve species. All these taxa were selected because of their good preservation and relative abundance throughout some intervals of the section.

Ostracods

The analyzed ostracod valves belong to species of the family Candonidae. They correspond to the following taxa described in Martín-Rubio et al. (2006): *Fabae-formiscandona* sp. 2, which is common in sequences A to lower B2; *Pseudocandona compressa* (Koch), which is common in the lower A1 sequence;

Fabaeformiscandona aff. *F. spelaea* (Klie), which is frequent in sequences A and B, and *Fabaeformiscandona* cf. *F. breuili* (Paris), present in sequence C.

Molluscs

The analyzed mollusc shells correspond, for the mollusc assemblage I (sequences A and B) to the aquatic prosobranch gastropod *Hydrobia* aff. *H. slavonica* (Hydrobiidae). For the mollusc assemblage II (sequence C), taking into account the higher diversity and varying habitats, the samples include shells of the aquatic prosobranch gastropod *Pseudamnicola*? sp. (Hydrobiidae), the infaunal bivalve *Pisidium* sp., and the terrestrial pulmonate *Carychium schlickumi* Strauch.

Methods

Stable isotopes and trace and minor element contents in ostracod carbonate were obtained from well-preserved valves of each ostracod sample. The valves were separated and carefully cleaned with ethanol and distilled water, using a fine brush. Only valves in pristine conditions have been analyzed in order to avoid effects of diagenesis on the trace element and isotope data (Keatings et al. 2000a). Each analysis was performed on 4–14 ostracod adult valves. For each mollusc sample, 1–3 aragonitic shells were individually cleaned in 96% ethanol and distilled water using a fine brush. The cleaned shells were crushed and carefully powdered to avoid mineralogical transformations.

For stable isotope analyses ($\delta^{13}C$, $\delta^{18}O$), the multi-valve samples from ostracods and the powder samples from mollusc shells were reacted with anhydrous phosphoric acid at $78 \pm 2°C$ in a Finnigan "Kiel" extraction system coupled directly to the inlet of a Finnigan MAT 251 triple collector isotope ratio mass spectrometer (Stable Isotope Laboratory, University of Michigan, USA). Data are reported in $\delta‰$ notation relative to PDB standard. Precision is maintained at better than 0.1‰ on both $\delta^{13}C$ and $\delta^{18}O$. To perform minor and trace element analyses, ostracod multi-valve samples and powder samples from molluscs were dissolved in 5 ml of dilute ultrapure HNO_3 acid (2%). The solution was analyzed for Ca (317.933 nm), Mg (279.553 nm) and Sr (421.552 nm) using an Inductively Coupled Plasma Optic Mass Spectrometry (ICP-OES Thermo Jarrell Ash) at the Serveis Científic-Tècnics (Universitat de Barcelona, Spain). The limits

of detection were 0.025 ppm for Ca, 5 ppb for Mg, and 5 ppb for Sr. All analyses were run against multi-element standards prepared from Johnson Matthey[TM] stock solutions. The mean precision of the analyses was: 0.54% for Ca, 2.74% for Mg and 0.65% for Sr.

Results

Stable isotopes ($\delta^{13}C$ and $\delta^{18}O$) of biogenic carbonates

Ostracod calcitic valves display a wide range of stable isotope values: $\delta^{13}C$ range from −9.29‰ to
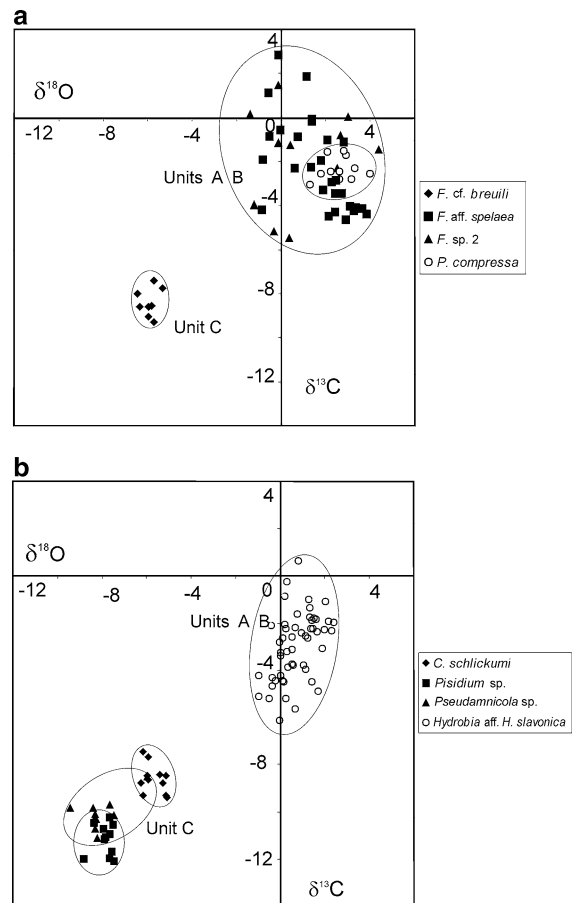
Fig. 3 Stable isotopic composition ($\delta^{13}C$, $\delta^{18}O$; PDB notation) of ostracod (**a**) and mollusc (**b**) carbonates. In order to allow the comparison of the isotopic values of calcite (ostracod valves) and aragonite (mollusc shells), $\delta^{18}O$ and $\delta^{13}C$ values of aragonite have been corrected by substracting 0.6‰ and 1.7‰ respectively to the laboratory data. (cf. Tarutani et al. 1969; Romanek et al. 1992)

2.87‰; δ^{18}O range from −6.44‰ to 4.40‰ (Table ESM 0-1 electronic supplementary material, Fig. 3a). Two main groups appear in the δ^{13}C, δ^{18}O plot (Fig 3a). One main group is formed by isotopic signatures from sequences A and B (δ^{13}C between −5.48‰ and 2.87‰; δ^{18}O between −1.43‰ and 4.40‰). Particularly *Fabaeformiscandona* aff. *F. spelaea* displays δ^{13}C values between −4.62‰ and 2.87‰ and δ^{18}O values between −0.85‰ and 3.82‰. *Fabaeformiscandona* sp. 2 displays δ^{13}C values between −5.48 ‰ and 1.46‰ and δ^{18}O values between −1.43‰ and 4.40‰. *Pseudocandona compressa*, which have been collected in a one-m thick interval in A1, display a distinctive, relatively close packing: δ^{13}C values between −3.03‰ and −1.51‰ and δ^{18}O values between 1.28‰ and 4.00‰. The second main group corresponds to *Fabaeformiscandona* cf. *F. breuili* from sequence C, which displays significant lower mean isotopic signatures and more homogeneous values than those reported above (δ^{13}C between −9.29‰ and −7.39‰; δ^{18}O between −6.44 ‰ and −5.32‰).

For aragonite mollusc shells, δ^{13}C ranges from −10.40‰ to 2.35‰, δ^{18}O ranges from −8.85‰ to 2.98‰ (Table ESM-0-1; Fig. 3b). In order to allow the comparison of the plots for isotopic values of calcite (ostracod valves) and aragonite (gastropod shells), δ^{18}O and δ^{13}C and values of aragonite plotted in Fig. 3b have been corrected by subtracting 0.6‰ and 1.7‰ respectively from the laboratory data for the effect of polymorphism (and Mg substitution of Ca) on isotope fractionation between calcium carbonate and water (cf. Tarutani et al. 1969; Romanek et al. 1992). Similarly to ostracods, two main groups of mollusc samples may be differentiated on the basis of the isotopic signature. One group, formed by *Hydrobia* values (mollusc assemblage I, sequences A and B), comprises the higher δ^{13}C and δ^{18}O signatures: δ^{13}C values are comprised between −4.44‰ and 2.35‰; δ^{18}O ranges from −0.37‰ to 2.98‰ (Fig. 3b). The second main group, which corresponds to mollusc assemblage II, sequence C, includes consistent isotopic signatures both for δ^{13}C and δ^{18}O (δ^{13}C between −10.40‰ and −5.74‰; δ^{18}O between −8.85‰ and −4.46‰) which represent δ^{13}C and δ^{18}O signatures lower than those from assemblage I. In this overall pattern of assemblage II a distinct plot, with the relatively higher values δ^{13}C and δ^{18}O isotopic signatures, is formed by isotopic

compositions from *Carychium schlickumi*, the terrestrial gastropod, whereas the prosobranch *Pseudamnicola* and the bivalve *Pisidium* display different, closer distributions.

There is a correspondence between the main groups of distributions of the isotopic values from ostracods and molluscs (Fig. 3a, b), which in addition display similar ranges of values. This indicates a similar isotopic record of the main environmental features of each sequence for the corresponding ostracod and mollusc assemblages.
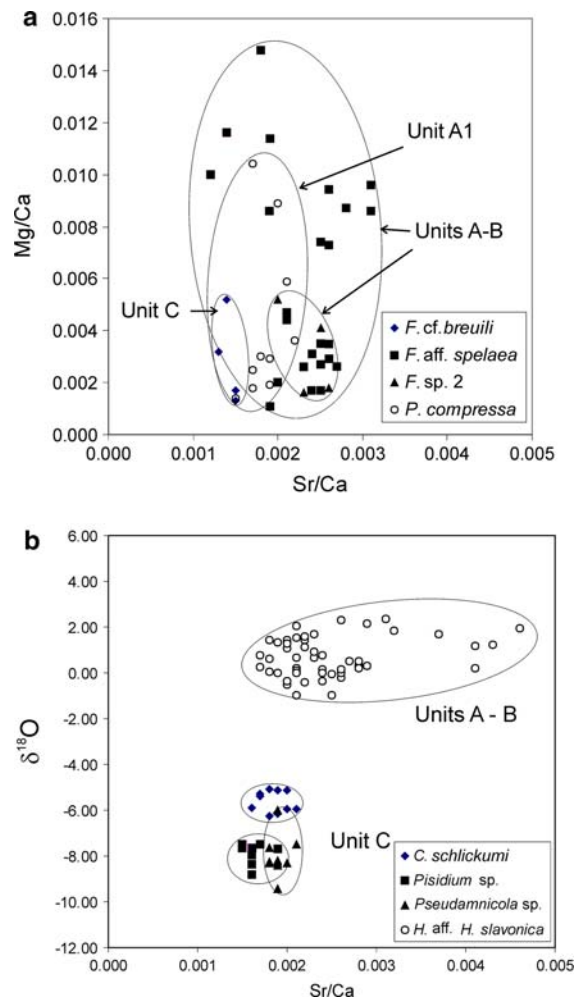
Fig. 4 (**a**) Trace element ratio distributions (Mg/Ca versus Sr/Ca molar ratios) from ostracod valves. (**b**) Sr/Ca molar ratio versus δ^{18}O in aragonite mollusc shells. Applied corrections as in Fig. 3

Mg/Ca and Sr/Ca in biogenic carbonates

For ostracod calcite valves, the Sr and Mg content expressed as Sr/Ca and Mg/Ca molar ratios are listed in Table ESM-0-1 and plotted in Fig. 4a. The Sr/Ca values range from 0.0013 to 0.0031, the Mg/Ca values range from 0.0010 to 0.0148. The overall larger range of Mg/Ca values in comparison to the Sr/Ca range is also shown by the distributions of each taxa (Fig. 4a). For carbonate from mollusc shells (aragonite), the Sr contents expressed as Sr/Ca ratios are listed in Table ESM-0-1. The Sr/Ca values range from 0.0016 to 0.0046. Samples may be grouped in two different sets. Samples from hydrobids (sequences A and B) display a large range of Sr/Ca values. The second main set includes shells from diverse taxa in sequence C, which displays narrow ranges of Sr/Ca values. The Sr/Ca–δ^{18}O diagram (Fig. 4b) shows that the diverse mollusc samples from sequence C display individual concentrated plots, while *Hydrobia* from sequences A and B display a scattered plot, with a wide range of Sr/Ca values.

Geochemistry: discussion

Stable isotopes

Stable isotope background

The paleoenvironmental interpretation of stable isotope data from biogenic carbonates and other lake sediment archives has been recently reviewed by Schwalb (2003), Leng and Marshall (2004) and Leng et al. (2006). The main features related with our work are summarized as follows.

The δ^{18}O of ostracod calcite is a function of the isotopic composition and temperature of the water where the ostracod moults, whereas the δ^{13}C in first order reflects the isotopic composition of the dissolved inorganic carbon (DIC) in water (von Grafenstein et al. 1999). Von Grafenstein et al. (1992) first suggested that isotope differences among valves from several coexistent species might reflect vital effects. Recently, Xia et al. (1997a), von Grafenstein et al. (1999), and Dettman et al. (2005) found vital effects or systematic offsets of the ostracod carbonate from an inorganic calcite precipitated in isotopic equilibrium with ambient δ^{18}O and temperature. Keatings

et al. (2002b) suggest that the δ^{18}O signatures in ostracod valves are related to the pH of calcite formation and the calcite–water ^{18}O/^{16}O fractionation may be species and stage specific, and related to the rate of valve calcification. The δ^{13}C values of ostracod valves are mainly controlled by δ^{13}C of the DIC, but it seems to be biased by microhabitat effects and vital offsets (von Grafenstein et al. 1999).

Oxygen isotope composition in aquatic mollusc carbonate reflects the δ^{18}O of the lake water during the growth season, as suggested by several authors (i.e. Fritz and Poplawski 1974; Chaix et al. 1982; Dettman et al. 2005). Moreover, Fritz and Poplawski (1974) emphasize that DIC and not the food source controls the δ^{13}C for gastropods and bivalves from fresh-water lakes. However, Fastovsky et al. (1993) point out that some freshwater molluscs appear to secrete shells in equilibrium whereas others do not. In addition, offsets in the isotope composition between diverse species from the same water body have been reported. In some cases, these differences are related to different ecological requirements (i.e. Krantz et al. 1987). There is a general agreement that if the offset tends to be consistent between species, trends in intra-species values may be used for inferring environmental changes (Tevesz et al. 1997).

Concerning land snails (terrestrial pulmonates) Heller and Magaritz (1983) emphasize that C, O and Ca in shells are derived from the water that the snails absorb through their skin or drink from the upper layers of the soil. Lécolle (1985) reports that δ^{18}O contents of shells are linked to the δ^{18}O values of precipitations and correlate with the annual mean temperature. Goodfriend and Magaritz (1987) point out that the basic pattern of shell carbonate oxygen isotope variation is set by the ^{18}O content of the environmental water. Zanchetta et al. (2005) add to these factors the importance of the atmospheric water vapour, dew and evaporation. However, which environmental water (rain water, water vapour or dew) has the predominant influence is no clear, although in most regions the isotopic composition of atmospheric water vapour (or dew) is a direct function of rain and perhaps also temperature (Goodfriend et al. 1989; Goodfriend 1992). On the other hand, the diverse values of δ^{13}C for terrestrial shell carbonate may be explained on the basis of the relative contribution of metabolic CO_2 (organic carbon in the diet, released as respiratory CO_2), ingested carbonates, and the degree

of exchange with atmospheric CO_2 (Goodfriend 1992). Balakrishnan et al. (2005) interpret the diverse values of $\delta^{13}C$ in land snail shells as linked to the predominant photosynthetic pathways (C_3, C_4) in the local plant communities.

Stable isotopes ($\delta^{13}C$ and $\delta^{18}O$) of biogenic carbonates from Villarroya

Ostracods in the lacustrine sequence from Villarroya show noticeable variations in $\delta^{13}C$ and $\delta^{18}O$ (Figs. 3, 5). We may assume, according to von Grafenstein et al. (1999) that the vital offsets for the diverse *Fabaeformiscandona* species should be very similar and therefore they may constitute an overall consistent *Fabaeformiscandona* isotopic record. The relatively wide range and high isotopic values for *Fabaeformiscandona* in sequences A and B suggest noticeable changes in the isotopic-concentration of the waters where they lived and they represent the isotopic record of a closed lake (cf. Talbot 1990).

There is an overlap of the isotopic values from *P. compressa* (collected from a thin interval in A1) and those from *Fabaeformiscandona* sp. 2 and *F.* aff. *spelaea* from A and B1 units (Fig. 3a). The values from *P. compressa*, which display a relatively small scattering ($\delta^{13}C$ between −3.03‰ and −1.51‰, and $\delta^{18}O$ between 1.28‰ and 4.00‰; Table ESM-0-1, Fig. 3a) suggest relatively low spreading of summer water-isotopic values and temperatures in the recorded interval, taking into account that adult valves of *P. compressa* form in summer (Meisch 2000).

Fabaeformiscandona cf. *breuili* valves in unit C display lower mean isotopic signatures and more homogeneous values than those of ostracods from sequences A and B. The isotopic values of ostracods from unit C, which may be related to isotopically diluted waters, are interpreted as corresponding to record meteoric signatures (cf. Holmes and Chivas 2002; Schwalb 2003) and therefore correspond to a hydrologically open lacustrine environment. In fact, the meteoric waters in the region today display $\delta^{18}O_{SMOW}$ isotopic signatures around −7‰ (Plata 1994) and $\delta^{18}O$ in Quaternary tufa deposits from the central Ebro Basin is around −7‰ (Arenas et al. 2000). Andrews (2006) provides isotopic values for recent riverine tufas from Spain around −7‰ $\delta^{18}O$ and −6‰ $\delta^{13}C$. Therefore, poorly evaporated meteoric waters would produce isotopic values for

carbonates similar to those from biogenic carbonates from sequence C.

For molluscs, the $\delta^{13}C$–$\delta^{18}O$ plots from *Hydrobia* in sequences A and B correspond to the higher isotopic values (Fig. 3b). The plots of the other mollusc taxa, from sequence C, are closely arranged with low $\delta^{13}C$ and $\delta^{18}O$ values. In prosobranch gastropods, like *Hydrobia* and *Pseudamnicola* are, $\delta^{13}C$ mainly reflects the isotopic composition of DIC, while $\delta^{18}O_{shell}$ signatures record the $\delta^{18}O$ composition of the lake water and temperature. The relatively enriched $\delta^{18}O$ and $\delta^{13}C$ overall values from *Hydrobia* are indicative of long residence time during a major phase of intense evaporation, although the range in $\delta^{18}O$ values (about 3.5‰) suggests noticeable variations in the water balance, in accordance with the $\delta^{18}O$ data from ostracods. The high $\delta^{13}C$ values of *Hydrobia* point to a relatively high exchange with atmospheric CO_2 and/or noticeable loss of depleted CO_2 in the DIC pool of the lake by other mechanisms (i.e. high productivity episodes). Variations in $\delta^{13}C$ values may be linked to diverse rate of CO_2 exchange with the atmosphere and/or productivity changes.

Some vertical changes in isotopic signatures from *Hydrobia* must be noted (Fig. 5): both, $\delta^{13}C$ and $\delta^{18}O$ mean isotopic signatures of *Hydrobia* from the lower part of the section (m 1–8; unit A1) are slightly higher than those from the upper part of the section (m 21–25; upper B2 unit), similarly to the ostracod data. This could reflect that the waters in the lower interval were more evolved (longer residence time) than in the upper interval. However, the overall lowering in $\delta^{18}O$ in *Hydrobia* within the upper B2 unit should correspond to an increase in water temperature in accordance with the increase in thermic index from pollen data (B1 and B2 pollen zones).

The molluscs from unit C, exhibit $\delta^{13}C$ and $\delta^{18}O$ values lower than those from the *Hydrobia* assemblage of units A and B. These low isotopic values should reflect shorter residence time, much less evolved waters, and therefore, noticeable meteoric imprints in comparison with those recorded in units A and B. In the overall pattern of signatures of molluscs from unit C a distinct plot, with the relatively higher $\delta^{13}C$ and $\delta^{18}O$ isotopic signatures, corresponds to *C. schlickumi*, the pulmonate terrestrial gastropod, whereas the prosobranch gastropod *Pseudamnicola* and the bivalve *Pisidium* display lower signatures that
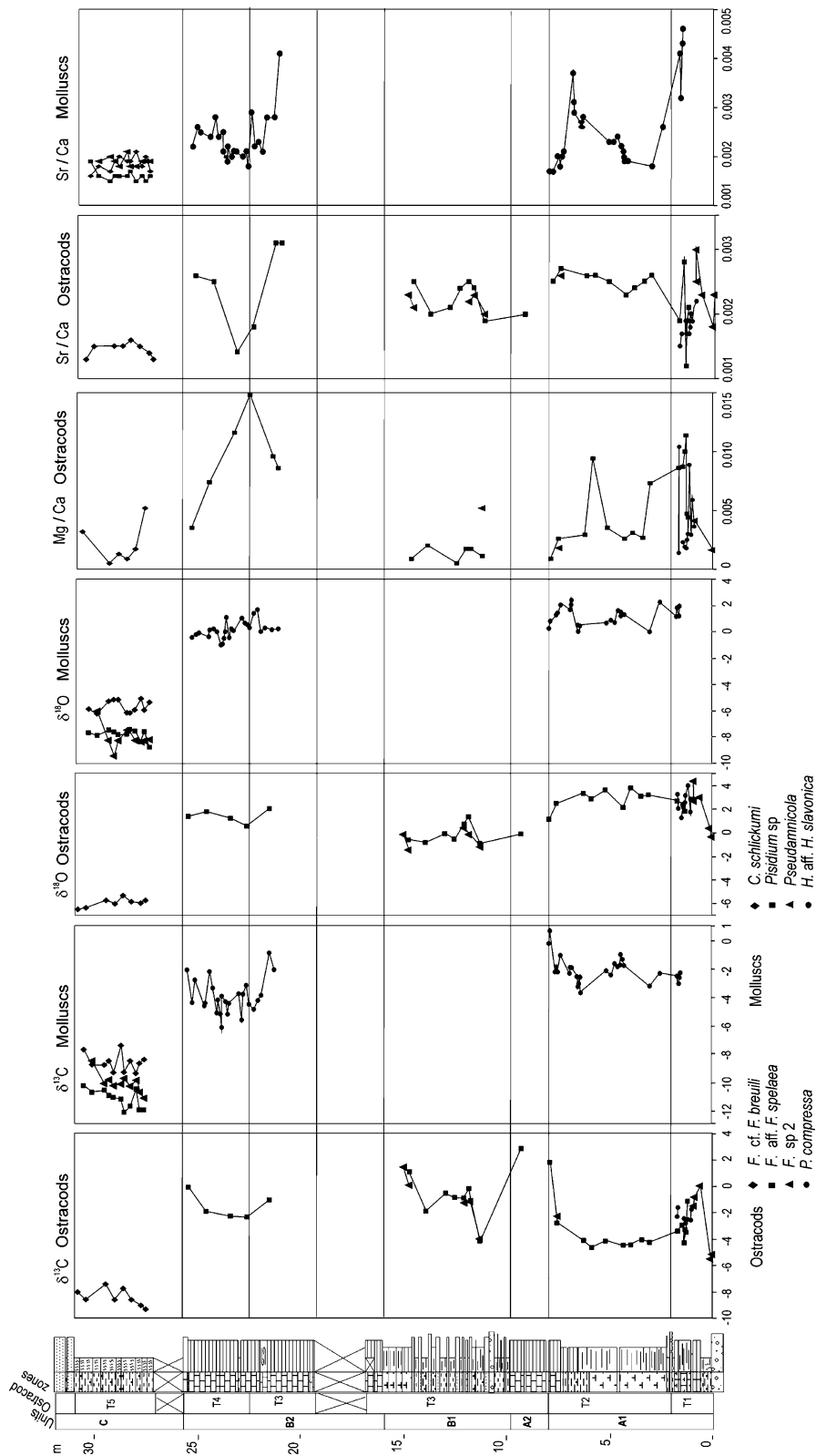
Fig. 5 Vertical distribution of $\delta^{13}C$, $\delta^{18}O$ (PDB notation) and Mg/Ca and Sr/Ca (molar ratios) for ostracod valves and mollusc shells from the Villarroya section. Legend for log as in Fig. 2. Applied corrections as in Fig. 3

are overlapped (Fig. 3b). The small, although consistent, offsets in $\delta^{13}C$ between *Pseudamnicola* and *Pisidium* are interpreted to record differences between DIC in the lake water and in the interstitial waters below the sediment-water interface. The infaunal bivalve *Pisidium* incorporates relatively higher amounts of depleted ^{12}C than the epifaunal prosobranch *Pseudamnicola*. This depleted ^{12}C derives from a high proportion of light CO_2 from OM decay in the sediment porewaters, whereas the aquatic prosobranch *Pseudamnicola* better records the C signature of the DIC in the water column of the lake. This is in agreement with the observations from Krantz et al. (1987) which report consistent differences in isotopic signatures between infaunal and epifaunal molluscs (1–1.5‰ $\delta^{13}C$ lower in the infaunal shells). However, $\delta^{18}O$ values for *Pseudamnicola* and *Pisidium* are very similar, with no significant offsets.

The $\delta^{18}O$ values from the terrestrial snail *C. schlickumi* record some relative enrichment when compared with the aquatic molluscs from the assemblage. Indeed, the $\delta^{18}O$ values from *C. schlickumi* may reflect the record of some evaporation of rain water or dew and uptake from soil water (cf. Zanchetta et al. 2005; Balakrishnan et al. 2005). The relatively high $\delta^{13}C$ values from *C. schlickumi* probably reflect a mixture of C3 and C4 plant diet together with ingested carbonates (cf. Balakrishnan et al. 2005).

Minor and trace elements

Minor and trace elements (Mg, Sr) background

Since the early works by Chivas et al. (1983), which for the first time demonstrated quantitatively the relationships between trace element contents in lacustrine ostracods and water chemistry and temperature, many papers have focused on geochemical studies of ostracod shells for paleoenvironmental reconstruction. Chivas et al. (1985) introduced the partition coefficient (Kd) approach of the minor and trace metal elements (Me, expressed in molar ratios against Ca) between the ostracod shell (Me/Ca) and the water: $Kd(Me) = (Me/Ca)_{calcite}/(Me/Ca)_{water}$. Since then, the use of the trace element approach based on ostracods has been applied to reconstruct hydrochemical features, like paleothermometry and

paleohydrochemistry, in different paleoenvironments (see summaries in De Deckker and Forester 1988; Palacios-Fest et al. 1994; Holmes 1996; Wansard 1999; Holmes and Chivas 2002; Anadón et al. 2002b). A number of works in non-marine ostracods have shown the variation of KdMe in relation with water temperature variations, especially for Mg (Chivas et al. 1985, 1986a, b; Engstrom and Nelson 1991; Xia et al. 1997b; see a summary in Holmes and Chivas 2002). Moreover Wansard et al. (1998) and De Deckker et al. (1999) have shown that this initial consideration may be complicated by variations of Me/Ca_w i.e. KdMe may show strong variations depending on Me/Ca_w; this is especially noticeable for Mg (Wansard et al. 1998; De Deckker et al. 1999; Holmes and Chivas 2002) similarly to that shown by inorganic calcites, although in this case for higher ranges of Mg/Ca_w (Mucci and Morse 1983). Holmes and Chivas (2002) have summarized the complexities of the use of partitioning coefficients and have added other concerns, as the taxonomic uncertainty for some species. They have concluded that although members of the same genus or closely-related genera have similar KdMe, this is not constant for a given genus and it may be affected by a range of environmental factors (i.e. Me/Ca_w, salinity, temperature and other water features) each one influencing in a different way.

The mollusc carbonate mechanisms of trace element uptake are mainly related to the shell mineralogy, the concentration of the elements in the water where the mollusc grow and several physiological factors (Lorens and Bender 1980). The Sr and Mg uptake in non-marine mollusc shells has been studied by a number of authors, and in some cases the KdSr has been provided for specific freshwater taxa (i.e. Faure et al. 1967, Buchard and Fritz 1978; Müller 1978; Renard 1985; Rosenthal and Katz 1989). Several factors such as salinity, temperature and growth rate may modify the partitioning coefficient between the water and the mollusc shell carbonate (Rosenthal and Katz 1989). Although variable from one taxa to other, in some cases the partitioning coefficients, like KdSr of aragonitic freshwater molluscs, are unaffected by variations in T and growth rate (i.e. Buchardt and Fritz 1978). The Mg uptake in carbonates is energetically favoured in the rhombohedral structure of calcite, whereas larger cations such as Sr are favoured in the orthorhombic structure

of aragonite. Moreover, Rosenthal and Katz (1989) indicate that Mg/Ca of aragonitic mollusc shells cannot be used for environmental studies because the strong mineralogical control on Mg in the shell-forming extrapallial fluid would mask any environmental signature. This is also complicated by the fact that a certain fraction of Mg is not bound to the aragonite lattice and it may be preferentially leached during early diagenesis. Therefore, only Sr/Ca values from aragonite mollusc shells have been used for calculations of Sr/Ca ratios from lake waters.

Mg/Ca and Sr/Ca in biogenic carbonates from Villarroya and in lake waters

Ostracods. *Fabaeformiscandona* species display a wide range of Me/Ca values along the studied section: Mg/Ca 0.0011–0.0148; Sr/Ca 0.0012–0.0031 (Table ESM-0-1, Fig. 4a). Only samples from B1 unit (11.3–13.96 m) and C unit display narrow ranges of Sr/Ca$_{ostr}$ and Mg/Ca$_{ostr}$ (Fig. 5). In general, the lower values for Mg/Ca$_{ostr}$ correspond to B1, a unit, which is characterized by relatively low carbonate content. The highest Mg/Ca$_{ostr}$ values are attained in lower A1 and in upper B2 units, which correspond to carbonate-rich intervals.

Pseudocandona compressa from unit A1 displays a wide scattering in Mg/Ca (0.0014–0.0104) and into a lesser extent in Sr/Ca (0.0015–0.0022), which is in contrast with the relative low scattering in stable isotopes. Taking into account that in this species the adults form its carapaces in summer (Meisch 2000) the relatively narrow range of $\delta^{18}O$ values in comparison to the wide Mg/Ca range suggests that the changes in $\delta^{18}O$ and T were less important than the changes in Mg/Ca$_w$ (and into a lesser extent in Sr/Ca$_w$). The wide range in Me/Ca$_w$ recorded in this spring-summer ostracod species probably are linked to the noticeable and variable summer carbonate deposition from charophyte meadows.

Partition coefficients in some *Candona* species depend on the Mg/Ca of the waters where they calcify (Xia et al. 1997b; Wansard et al. 1998; Holmes and Chivas 2002). Although there is no published data on the partition coefficients in *Fabaeformiscandona* we have used, for paleohydrochemical estimations for lake waters based on ostracods, the KdMe in *Candona rawsoni* Tressler, which may be considered as related taxa. A KdMg value for

C. rawsoni in waters of moderate Mg/Ca$_w$ has been selected (KdMg = 0.0044 ± 0.0015, for Mg/Ca$_w$ ∼2.7 and Sr/Ca$_w$ 0.0040; Xia et al. 1997b; Holmes and Chivas 2002) taking into account that a moderate Mg/Ca$_w$ in the Pliocene Villaroya Lake may be assumed. In fact, the abundant aragonite charophyte calcifications in the Villarroya lacustrine deposits point to waters with Mg/Ca$_w$ > 0.6 in which the charophyte-rich sequences were formed (cf. Anadón et al. 2002a, c). Moreover, a KdMg < 0.01 should correspond for *Candona* spp. that grew in a water with Mg/Ca > 0.6 (cf. Fig. 5 in Wansard et al. 1998). In this way, the calculated Mg/Ca$_w$ range for the Pliocene Villarroya Lake waters is 0.220–5.172 (Table 1). This relative wide range is also consistent with a lacustrine environment where noticeable charophyte meadows developed in some episodes leading to a high production of Ca-carbonate (Anadón et al. 2002a). These episodes resulted in higher Mg/Ca$_w$ values because of Ca depletion in water in comparison to the stages when the charophyte meadows did not form. This feature explains the relatively high Mg/Ca$_w$ values (0.593–5.172) calculated from the carbonate-rich B2 sequence (samples VR 774–VR 795), while calculations on samples from clayey intervals provide Mg/Ca$_w$ values between 0.186 and 0.586 (unit B1; samples VR 96–VR 115).

Sr/Ca ratios in ostracod valves, especially for *Candona*, are mainly related to Sr/Ca$_w$, and into a certain degree to Mg/Ca$_w$, with low dependence on temperature variations (cf. Wansard et al. 1998). KdSr for a single species display changes at very high Mg/Ca$_w$ values (i.e. Mg/Ca$_w$ ∼36; Xia et al. 1997b; Holmes and Chivas 2002). Therefore, for a lacustrine sequence that formed in lake waters with relative low to moderate Mg/Ca$_w$ (i.e. Mg/Ca$_w$ ∼3, cf. Xia et al. 1997b), changes in Sr/Ca$_{ostr}$ in candonids should correspond to changes in Sr/Ca$_w$. For Villarroya Pliocene waters, the inferred Mg/Ca$_w$ range suggests that this ratio probably did not influence the KdSr in *Fabaeformiscandona*, and Sr/Ca$_{ostr}$ variations mainly reflect changes in Sr/Ca$_w$. The past Sr/Ca$_w$ ranges in Villarroya have been calculated here by using the KdSr = 0.312 ± 0.028 obtained for adult *C. rawsoni* in water with Mg/Ca around 2.7 (Holmes and Chivas 2002 calculated from Xia et al. 1997b). The obtained Sr/Ca$_w$ for Villarroya ranges from 0.0030 to 0.0085. This range corresponds to values which are frequent

Table 1 Reconstruction of past Mg/Ca and Sr/Ca ratios in lake waters

Unit			Ostracod calcite							Shell aragonite			
	m	Sample	Ostracod species	Mg/Ca	Sr/Ca	Mg/Ca$_w$ range[a]		Sr/Ca$_w$ range[b]		Mollusc taxa	Sr/Ca	Sr/Ca$_w$ range[c]	
C	29.06	VR 508	*F.* cf. *F. breuili*	0.0013	0.0015	0.220	0.448	0.0044	0.0053	*Pseudamnicola*	0.0018	0.0046	0.0067
	28.24	VR 505	*F.* cf. *F. breuili*	0.0017	0.0015	0.288	0.586	0.0044	0.0053	*Pseudamnicola*	0.0018	0.0046	0.0067
	27.78	VR 503	*F.* cf. *F. breuili*	0.0052	0.0014	0.881	1.793	0.0041	0.0049	*Pseudamnicola*	0.0019	0.0048	0.0071
B2	25.47	VR 800	*F.* aff. *F. spelaea*	0.0035	0.0026	0.593	1.207	0.0076	0.0092	*Hydrobia*	0.0022	0.0056	0.0082
	24.61	VR 795	*F.* aff. *F. spelaea*	0.0074	0.0025	1.254	2.552	0.0074	0.0088	*Hydrobia*	0.0024	0.0061	0.0089
	23.42	VR 785	*F.* aff. *F. spelaea*	0.0116	0.0014	1.966	4.000	0.0041	0.0049	*Hydrobia*	0.0021	0.0053	0.0078
	22.64	VR 780	*F.* aff. *F. spelaea*	0.015	0.0018	2.542	5.172	0.0053	0.0063	*Hydrobia*	0.0029	0.0074	0.0108
	21.53	VR 775	*F.* aff. *F. spelaea*	0.0096	0.0031	1.627	3.310	0.0091	0.0109	*Hydrobia*	0.0028	0.0071	0.0104
	21.25	VR 774	*F.* aff. *F. spelaea*	0.0086	0.0031	1.458	2.966	0.0091	0.0109	*Hydrobia*	0.0041	0.0104	0.0152
B1	14.77	VR 115	*F.* aff. *F. spelaea*	ND	0.0025			0.0074	0.0088				
	13.96	VR 106	*F.* aff. *F. spelaea*	0.002	0.002	0.339	0.690	0.0059	0.0070				
	13	VR 102	*F.* aff. *F. spelaea*	ND	0.0021			0.0062	0.0074				
	12.53	VR 101	*F.* aff. *F. spelaea*	ND	0.0024			0.0071	0.0085				
	12.08	VR 100	*F.* aff. *F. spelaea*	0.0016	0.0025	0.271	0.552	0.0074	0.0088				
	11.84	VR 98	*F.* aff. *F. spelaea*	0.0017	0.0024	0.288	0.586	0.0071	0.0085				
	11.3	VR 96	*F.* aff. *F. spelaea*	0.0011	0.0019	0.186	0.379	0.0056	0.0067				
A2	9.31	VR 91	*F.* aff. *F. spelaea*	ND	0.002			0.0059	0.0070				
A1	7.94	VR 81	*F.* aff. *F. spelaea*	ND	0.0025			0.0074	0.0088	*Hydrobia*	0.0017	0.0043	0.0063
	7.57	VR 77	*F.* aff. *F. spelaea*	0.0026	0.0027	0.441	0.897	0.0079	0.0095	*Hydrobia*	0.002	0.0051	0.0074
	6.3	VR 66	*F.* aff. *F. spelaea*	0.0029	0.0026	0.492	1.000	0.0076	0.0092				
	5.9	VR 65.	*F.* aff. *F. spelaea*	0.0094	0.0026	1.593	3.241	0.0076	0.0092				
	5.2	VR 63	*F.* aff. *F. spelaea*	0.0035	0.0025	0.593	1.207	0.0074	0.0088	*Hydrobia*	0.0023	0.0059	0.0086
	4.34	VR 55	*F.* aff. *F. spelaea*	0.0026	0.0023	0.441	0.897	0.0068	0.0081	*Hydrobia*	0.0019	0.0048	0.0071
	3.96	VR 52	*F.* aff. *F. spelaea*	0.0031	0.0024	0.525	1.069	0.0071	0.0085				
	3.46	VR 49	*F.* aff. *F. spelaea*	0.0027	0.0025	0.458	0.931	0.0074	0.0088				
	3.1	VR 46	*F.* aff. *F. spelaea*	0.0073	0.0026	1.237	2.517	0.0076	0.0092	*Hydrobia*	0.0018	0.0046	0.0067
	1.71	VR 29	*F.* aff. *F. spelaea*	0.0086	0.0019	1.458	2.966	0.0056	0.0067	*Hydrobia*	0.0032	0.0081	0.0119
	1.5	VR 25	*F.* aff. *F. spelaea*	0.0087	0.0028	1.475	3.000	0.0082	0.0099				
	1.4	VR 23	*F.* aff. *F. spelaea*	0.01	0.0012	1.695	3.448	0.0035	0.0042				
	1.35	VR 22	*F.* aff. *F. spelaea*	0.0114	0.0019	1.932	3.931	0.0056	0.0067				
	1.3	VR 20	*F.* aff. *F. spelaea*	0.0047	0.0021	0.797	1.621	0.0062	0.0074				
	1.23	VR 18	*F.* aff. *F. spelaea*	0.0044	0.0021	0.746	1.517	0.0062	0.0074				
	0.05	VR 1	*F.* sp. 2	0.0016	0.0023	0.271	0.552	0.0068	0.0081				

Pliocene Villarroya Basin. Complete data from ostracods. Summary data from molluscs (only data from those samples coincident with ostracod samples have been included)

[a] Mg/Ca range for water calculated from KdMg for *Candona rawsoni* 0.0044 ± 0.0015

[b] Sr/Ca range for water calculated from KdSr for *Candona rawsoni* 0.312 ± 0.028

[c] Sr/Ca range for water calculated from KdSr for *B. tentaculata* 0.331 ± 0.062

KdMg and KdSr ranges for *C. rawsoni* from Holmes and Chivas (2002) after Xia et al. (1997b), for relatively low Mg/Ca$_w$ (Mg/Ca ~2.7)

KdSr for *B. tentaculata* = 0.331 ± 0.062 obtained by the authors from Lake Arreo along 2 year monthly sampling. Mg/Ca$_w$ range 0.305–0.490

in non-marine waters (Renard 1985; Anadón et al. 2002d). Changes in Sr/Ca$_w$ recorded in the Villarroya succession were controlled by the charophyte meadows development, similarly to Mg/Ca$_w$, and the saline inputs to the lake (see below).

Molluscs. For paleohydrochemical reconstructions we have selected the hydrobids (*Hydrobia* aff. *slavonica* and *Pseudamnicola* sp.) because of its abundance along the studied section. There is no published data on the partition coefficients for hydrobids, therefore, we have used KdSr$_{arag}$ = 0.331 ± 0.062 determined for shells of another prosobranch gastropod (*Bithynia tentaculata* Linné) from modern waters in Lake Arreo (northern Spain) by the present authors (Anadón et al., unpublished; see Table 1). We use this KdSr because it has been obtained from a larger number of samples than the data from Müller (1978) who determined the KdSr for several limnic gastropods (*Lymnaea, Planorbis, Bithynia* and *Valvata*), which average 0.252, ranging from 0.185 to 0.350. The obtained ranges of Sr/Ca$_w$ values for the Pliocene Villarroya lake using KdSr$_{arag}$ = 0.331 ± 0.062 are very similar to those obtained from Sr/Ca in calcitic ostracod shells (see Table 1).

Comparison of the geochemical records from hydrobids and ostracods must take into account the different life cycle and shell-growth pattern for each kind of organism. *Hydrobia* aff. *slavonica*, is a prosobranch gastropod with a life period of 1–3 years, like most hydrobids, although growth mainly occurs during the first year of life (cf. Fetter and Graham 1962). Therefore a complete *Hydrobia* shell records the variations in temperature, chemistry and isotopic signatures of water along 1 year around. This is in contrast with the geochemical record from ostracods, where the two valves from each adult carapace form in short time intervals i.e. hours to few days (Turpen and Angell 1971). On the other hand, adult moulting time is particular for each taxa (i.e. *P compressa* adult carapaces form in spring and summer while *F. breuili* is probably a permanent form; Meisch 2000). Therefore the geochemical record of a multi-shell sample has a different significance in each case, i.e. mean of 1-year around geochemical records in the case of *Hydrobia* samples and mean of several one-day to week-records in the case of ostracod samples. For ostracod species that attain the adult stage along the year we may assume that the geochemical record is a proxy of mean annual conditions while for ostracod

species that attain the adult stage in spring-summer only (like *P. compressa* does) the geochemical record corresponds to a mean of such time intervals.

Other calculations on Sr/Ca$_w$ may be obtained from the bivalve *Pisidium* (sequence C; Table ESM-0–2) using the KdSr = 0.378 (range 0.228–0.563) provided by Müller (1978) for this genus. The Sr/Ca$_w$ calculated from *Pisidium* is 0.0028–0.0070, a wide range which overlap the Sr/Ca$_w$ range (0.0046–0.0071) obtained from hydrobids. On the other hand, the Sr/Ca ratios in the terrestrial pulmonate *Carychium*, are very similar to those displayed by the other molluscs (*Pisidium, Pseudamnicola*) in sequence C. The origin of the Sr and Ca in the shell of this snail is probably linked to soil water absorption and littoral sediment ingestion. This may explain the similar geochemical features (stable isotopes and Sr content) of *Carychium* and of the companion aquatic mollusc shells, and the difference between signatures from this assemblage and that of *H.* aff. *slavonica* (i.e. Fig. 4b).
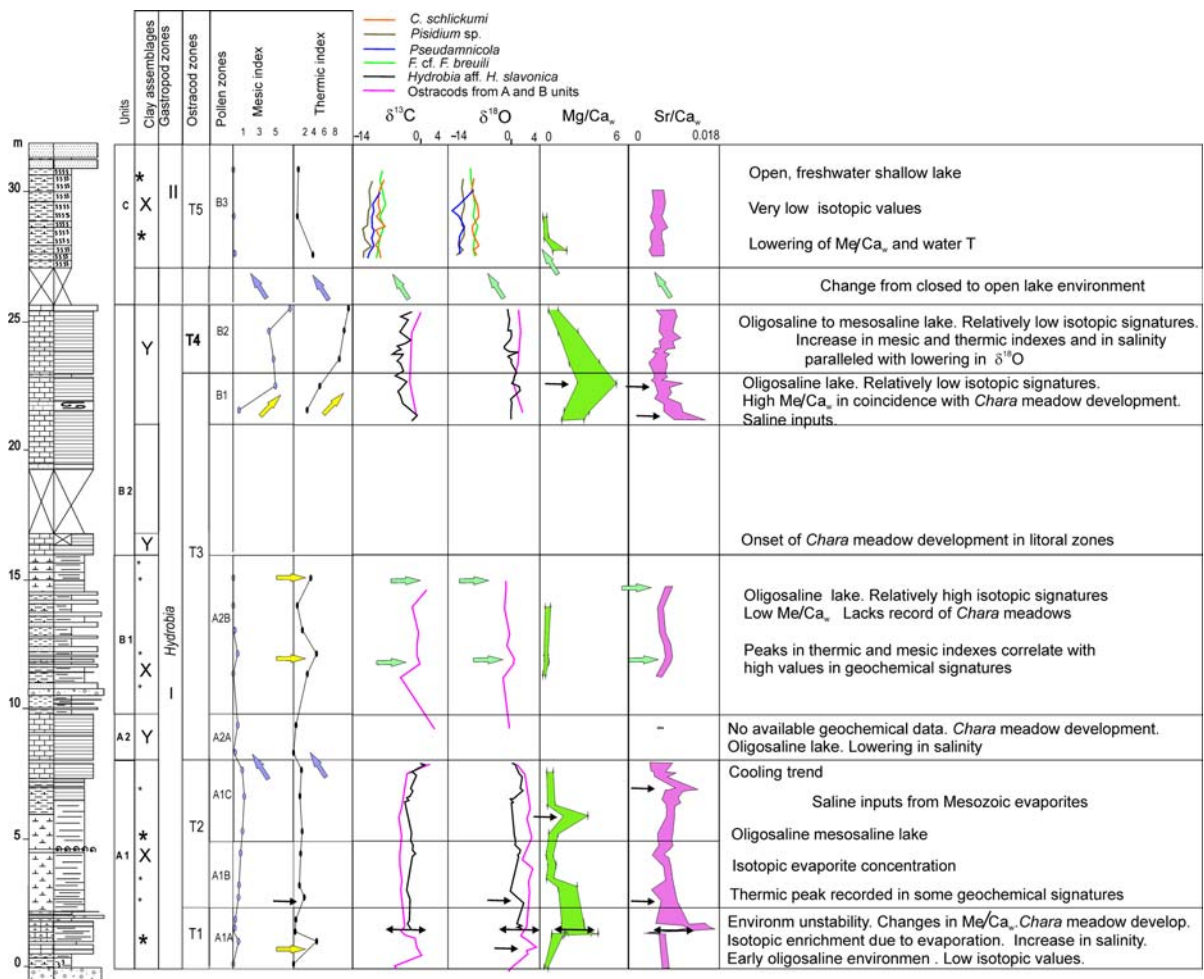
Paleoenvironmental evolution

The geochemical record of the Villarroya Pliocene lacustrine sequence which is based on stable isotopes and trace-element contents of ostracod valves and mollusc shells, has been combined with other environmental proxies (from sedimentological, mineralogical and paleoecological data) to perform a paleoenvironmental evolution (Fig. 6) which is described in the framework of the main sequences from Anadón et al. (2002a).

Sequence A

This sequence consists of a lower siliciclastic-dominated unit (A1) and an upper carbonate dominated unit (A2).

Unit A1

This unit (0–7.9 m) consists of thin bedded to laminated carbonate lutites and silty packstones. Thin bedded laminated bioclastic packstones also occur. This unit is characterized by clay assemblage X (with smectite and interstratified clays). Unit A1 corresponds to the ostracod intervals T1 and T2 (Martín-Rubio et al. 2006) which are

Fig. 6 Synthetic paleohydrological and paleohydrochemical features recorded in the Pliocene lacustrine sequence of Villarroya, in comparison with paleoenvironmental data from

Anadón et al. (2002a). Ranges for Mg/Ca and Sr/Ca in waters have been calculated from data in Table 1. Legend for log as in Fig. 2. Applied corrections as in Fig. 3

mainly characterized by the presence of leptocytherids (several species of genus *Amnicythere*) together with ilyocyprids and candonids except the lowermost two samples that do not contain leptocytherids. These basal ostracod samples, in comparison to overlying samples, display relatively low isotopic values, around −5.3‰ δ^{13}C and 0‰ δ^{18}O, and low Me/Ca ratios (Table ESM-0-1). They correspond to the establishment of the lacustrine environment.

The appearance of leptocytherids in lower T1 suggests an increase in salinity from oligosaline to mesosaline water (Na-Cl affinity). A coeval overall increase in δ^{18}O suggests an increase in evaporitic concentration linked to the increase in salinity in

lower T1 (Table ESM-0-1). The rest of T1 zone shows higher, but oscillating δ^{13}C and δ^{18}O values in ostracod valves (Figs. 5, 6) that may be interpreted as reflecting changes in the evaporation–precipitation balance which is in agreement with the temperate climate with dry seasons deduced from pollen data. The recorded changes in Me/Ca in waters may be explained by the relative and variable depletion of Ca in the waters linked to the noticeable $CaCO_3$ charophyte deposition also recorded in the lithologic log.

At 2.1 m (T1–T2 transition) some oligosaline (or low mesosaline) ostracod species from zone T1 disappear: *Cyclocypris taubachensis* Diebel and

Pietrzeniuk, *P. compressa* and *Cypria ophtalmica* (Jurine), suggesting an undetermined change in salinity to T2. This change also corresponds to a slight increase in $\delta^{18}O$ from T1 to T2, also in accordance with the presumed temperature increase deduced from the pollen data. T2 formed under semi-temperate and sub-humid conditions, with a thermic peak that correlates with high $\delta^{18}O$ in *Hydrobia*.

The rest of this unit, which corresponds to a semi-temperate and semi-humid climate, displays quite homogeneous geochemical values with isolated peaks in Me/Ca_w (Fig. 6), which may correspond to sporadic development of charophyte meadows (Mg/Ca) or saline inputs (Sr/Ca). Salinity in the lake waters probably derived mostly from saline inputs from Mesozoic evaporites (cf. Anadón et al. 2002a).

In general, the $\delta^{13}C$ and $\delta^{18}O$ values from ostracods and *Hydrobia* in unit A1 exhibit poorly defined covariant trends that are interpreted as resulting from E/P processes in closed lacustrine environments (cf. Talbot 1990).

Unit A2

Unit A2 (7.9–9.9 m) mainly consists of organogenic laminated carbonate deposits and is characterized by clay assemblage Y (without smectite and interstratified clays) and very low values of thermic and mesic indexes resulting from a cooler climate and decrease in humidity with regard to A1. The base of this unit is featured by the disappearance of the warm-water leptocytherid ostracods (T2–T3 transition), which correlates with a decrease in the thermic index, and the presence of oligosaline taxa (decrease in salinity in comparison with unit A1).

Sequence B

This sequence also consists of a lower siliciclastic-dominated unit (B1) and an upper carbonate dominated unit (B2).

Unit B1

Unit B1 (9.9–16.3 m) is made up of siliciclastic laminated mudstones and clays with interbedded carbonate mudstones. This unit is characterized by clay assemblage X (with smectite and interstratified clays). The unit B1 still corresponds to the zone T3,

with oligosaline ostracods. The $\delta^{18}O$ from ostracod and mollusc shells (and the calculated Sr/Ca_w and Mg/Ca_w ranges) exhibit lower overall values than those from upper A1 unit. The $\delta^{13}C$ values display moderate oscillations in B1. Moderate offsets in $\delta^{18}O$ and in Sr/Ca_{ostr} at middle B1 (11.84 m) may be interpreted as recording a maximum in evaporation because it matches with peaks in the thermic and mesic indexes from pollen data (Anadón et al. 2002a).

Unit B2

This unit (16.3–25.5 m) consists mainly in biogenic laminated carbonates and varves and is characterized by clay assemblage Y (without smectite and interstratified). The lower part of the sampled interval (mid-upper B2 unit) corresponds to the high T3 zone, with oligosaline ostracods. The overlying beds belong to zone T4, which is characterized by oligosaline to mesosaline ostracods (Martín-Rubio et al. 2006). The $\delta^{18}O$ values from *Hydrobia* display a narrow range of values and they show a slight decrease from the base to the upper part of this unit. Ostracod valves display lower $\delta^{13}C$ and slight higher $\delta^{18}O$ values than those from lower T3 zone. Sr/Ca_w, Mg/Ca_w and $\delta^{13}C$ in mid B2 unit exhibit the highest values from the lacustrine sequence (Fig. 5; Table 1), in coincidence with the saline episode deduced from ostracod autoecology, and a noticeable charophyte carbonate deposition. In upper B2, the high deduced Mg/Ca_w and salinity correlates with an overall slight decrease in $\delta^{18}O$ values from *Hydrobia*, which would indicate an increase in water temperature. All these features also correspond to high values in climatic (thermic and mesic) indexes (Fig. 6) which may be related to the Mid Pliocene global warmth (Anadón et al. 2002a).

Sequence C

Sequence C (27.5–31.3 m) is characterized by grey massive, bioturbated mudstones, clay assemblage X (with smectite and interstratified), and low mesic and thermic indexes from pollen data pointing to a cool and dry climate. This clay-rich palustrine sequence records major noticeable faunistic, climatic and environmental changes when compared with the underlying sequences (cf. Muñoz et al. 1992; Anadón

et al. 2002a). The ostracod association is characterized by *F.* cf. *breuili* and other freshwater species, whereas the mollusc association displays a wide spectrum of freshwater and minor terrestrial taxa.

The geochemistry of the biogenic carbonates also reflects differences between sequence C and the underlying lacustrine deposits. The biogenic carbonates are characterized by noticeable low $\delta^{13}C$ and $\delta^{18}O$ values, when compared with data from the lower intervals. These values indicate isotopically diluted waters and correspond to meteoric signatures.

The transition from B to C sequence corresponds to the change from a closed, oligo- to meso-saline environment to an open, freshwater environment with a paludal, well-vegetated fringe, as indicated by the paleoecology of ostracods and molluscs and the geochemical signatures: the stable isotopes and the calculated Sr/Ca_w and Mg/Ca_w from sequence C display lower values than those from sequences A and B, mainly reflecting the values from the incoming waters to the lake.

Concluding remarks

Stable isotopes and trace-element content of biogenic carbonates (calcite valves from Candonidae ostracods and aragonite shells from four mollusc species) from the Pliocene lacustrine sequence of Villarroya allow us to illustrate the geochemical record of environmental changes of this lake and to compare our data to the paleoenvironmental reconstruction obtained from other proxies (cf. Anadón et al. 2002a).

The sequences A and B are characterized by relatively high isotopic signatures and Me/Ca values in the biogenic carbonates. The recorded large oscillations of $\delta^{18}O$ in biogenic carbonates reflect variations in the $\delta^{18}O_w$ (due to precipitation-evaporation processes) and, into a lesser degree, variations in temperature of calcification. The $\delta^{13}C$ data inform about variations in DIC although they are probably biased by the vital effects of the studied taxa. Minor and trace element contents in ostracod (Mg/Ca, Sr/Ca) and mollusc shells (Sr/Ca) are mainly linked to the Me/Ca of the lake water, and into a lesser extent to temperature and to uptake kinetic effects. Some changes to high ranges in the calculated Mg/Ca_w ratios (and other minor Sr/Ca_w peaks) are linked to changes in the sedimentation style, from detrital

clastic to biogenic, being the latter dominated by charophyte carbonate deposition (Fig. 6) with subsequent Ca depletion in the lake water. The Sr/Ca_w for the Pliocene Villarroya lake calculated from the ostracod calcite valves and from the aragonite mollusc shells display very similar ranges for each sampled layer. Several possible mechanisms may make the Me/Ca in lake water to change: long periods of Ca-carbonate (calcite, aragonite) biomineralization and different inputs of solutes to the lake through time which may be due to a change in drainage area configurations. Taking into account the abundance of aragonite charophyte incrustations, some Sr depletion episodes in the waters must be regarded (i.e. upper B2 unit).

During some episodes recorded in sequences A and B, apart from evaporative concentration, saline inputs (mainly of Na-Cl type) have influenced the solute composition of the lake waters: presence of leptocytherids along A1 and of *Heterocypris salina* (Brady) in upper B2. Moreover, saline inputs of Na-Cl (and Sr) may be invoked because of the presence of extant saline thermal springs in the area (Auqué et al. 1988; Coloma et al. 1996). In fact, during the Tertiary, saline inputs to the Ebro Basin marginal environments close to the Villarroya Basin have been also documented (Coloma et al. 1995, 1996, 1997). In some cases, solute inputs may have increased the lake salinity without significant changes in the isotopic composition of the lake waters. This is the reason why, for several intervals of the Villarroya succession, there is no obvious correlation among: (i) salinity changes deduced from invertebrate paleoecology, (ii) paleoenvironmental slices based on isotopic signatures and Me/Ca_w calculations (from biogenic carbonate geochemistry) and (iii) climate in the hinterland derived from pollen data. In turn, the charophyte meadows development probably was influenced by climate and by tectonics (control on the platform development). However, some main shifts in the geochemical signature profiles may be correlated with significant global and/or regional environmental changes that have been reported from other paleoenvironmental records (Fig. 6). Lakes where geochemical behaviour is constrained by sporadic saline inputs and/or relative depletion in Ca due to long periods of Ca-carbonate precipitation or biomineralization, do not show clear correlation patterns between geochemical signals and climate

proxies. In these lakes only major environmental trends (due to major paleoenvironmental changes) display clear geochemical records.

The transition from B to C sequence corresponds to the change from a closed, oligo- to meso-saline environment to an open, freshwater environment with a paludal, well-vegetated fringe, as indicated by the ecology of the invertebrate fossils and the geochemical signatures: the stable isotopes and the calculated Sr/Ca$_w$ and Mg/Ca$_w$ from sequence C display lower values than those from sequences A and B. The isotopic values from biogenic carbonates of unit C indicate isotopically diluted waters and correspond to meteoric signatures (hydrologically open lacustrine environment). In addition, the δ^{13}C and δ^{18}O plots for molluscs from unit C reflect the diverse biotopes and the variety of metabolisms which are especially highlighted in the δ^{13}C signatures.

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