Sedimentology (2000) **47**, 1135–1156

Quaternary palaeohydrological evolution of a playa lake: Salada Mediana, central Ebro Basin, Spain

BLAS L. VALERO-GARCÉS*, ANTONIO DELGADO-HUERTAS†, ANA NAVAS‡, JAVIER MACHÍN‡, PENÉLOPE GONZÁLEZ-SAMPÉRIZ* and KERRY KELTS§
**Instituto Pirenaico de Ecología CSIC, Apdo 202, 50080 Zaragoza, Spain*
(E-mail: blas@ipe.csic.es; pgonzal@posta.unizar.es)
†Estacion Experimental del Zaidin CSIC, Prof. Albareda 18008 Granada, Spain
‡Estación Experimental de Aula Dei, CSIC, Apdo 202, 50080 Zaragoza, Spain
§Limnological Research Center, U of MN, 220 Pillsbury Hall, Minneapolis MN-55455, USA

ABSTRACT

Sedimentary features, mineralogy, bulk geochemical composition, stable isotope analyses and pollen data from sediment cores were used to reconstruct the Late Quaternary depositional evolution of the Salada Mediana playa lake (central Ebro Basin, northeastern Spain). The 150-cm-long sediment core sequence is composed of gypsum- and dolomite-rich muds (Lower and Middle sections) and black, laminated, calcite-bearing sediments (Upper section). The Salada Mediana formed as a karstic depression in the Miocene gypsum substratum during the Late Pleistocene. The Lower section was deposited in a sulphate–carbonate saline lake that ended with a period of desiccation and basin floor deflation. Subsequent deposition (Middle section) took place in a playa-lake system. Two cycles of lower water table and expanded saline mud flats occurred. The Holocene sequence is missing, probably as a result of aeolian erosion. Sedimentation resumed only a few centuries ago, and saline pan environments dominated until modern times. The Salada Mediana facies succession was mainly governed by fluctuations in the hydrological balance, brine composition, and salinity; however, aeolian processes (detrital input and deflation) and recycling of previously precipitated salts also played a significant role.

Keywords Geochemistry, Iberia, Quaternary, saline lakes, stable isotope.

INTRODUCTION

A semiarid climate and the presence of extensive endorheic areas have favoured the development of numerous small saline lakes in Spain. The majority of them are grouped in four areas: the central Ebro Basin, the northern Castille, La Mancha and the Guadalquivir basin (Comín & Alonso, 1988; Pueyo-Mur & De la Peña, 1991). Most of the lakes are shallow and ephemeral, and were formed by karstic or aeolian processes on Tertiary evaporitic units. Their chemistry, strongly influenced by the substrate, is dominantly sodium chloride or magnesium sulphate. During the past decades, considerable limnological, sedimentological and geochemical work has been carried out on some modern Spanish lake basins (see Pueyo-Mur & De la Peña, 1991 for more references), such as La Mancha (De la Peña & Marfil, 1986; Ordoñez *et al.*, 1994), the central Ebro Basin (Pueyo-Mur, 1979; Davis, 1994; Auqué *et al.*, 1995; García-Vera, 1996; Sánchez-Navarro *et al.*, 1998), Gallocanta, the largest saline lake in Spain (Comín *et al.*, 1990), and Salines (Giralt *et al.*, 1999).

Knowledge of the sedimentology and hydrogeology of seasonal playa-lake systems has greatly improved in recent years with studies in arid regions of Canada (northern Great Plains and British Columbia) and Australia (see references in

Smoot & Lowenstein, 1991 and Renaut & Last, 1994). In the Iberian Peninsula, however, modern depositional environments and processes have been described for only a small number of lakes, and even fewer have been cored and their sedimentary sequences analysed in detail (e.g. Gallocanta, Salines, some of the Ebro Basin). The reduced thickness of sediment accumulated in these basins, the presence of numerous sedimentary hiati, and the complexity of evaporite deposition and early diagenetic processes have discouraged the study of these lacustrine basins as palaeoenvironmental and palaeoclimate records. However, the sediments accumulated in groundwater-fed, discharge playas that experience large fluctuations in water level, chemical composition, and salinity are potentially sensitive indicators of changes in the hydrologic budget (Rosen, 1994). Integrated studies, including sedimentology, mineralogy and geochemistry, are needed to understand the depositional dynamics of these playa lakes, and to provide models to interpret their palaeorecords. Saline lacustrine deposits have helped to reconstruct Quaternary palaeoclimates worldwide (Renaut & Last, 1994), but the potential of the Spanish saline lake records has only recently been acknowledged (Davis, 1994; Giralt *et al.*, 1999). The sediments of playa lakes provide the best, and in some cases only, record of past environmental conditions in these semi-arid regions. The purpose of this paper is to discuss the modern hydrology and sedimentology, and the Quaternary palaeodepositional evolution of one of these Spanish playa lakes, Salada Mediana, located in a closed-drainage area in the central Ebro Basin, Iberian Peninsula.

METHODS

A 150-cm-long core was collected with a modified 5-cm diameter Livingstone corer in the centre of the playa lake in August 1996. The sediment core was split, photographed, described and sampled every centimetre for organic matter and carbonate content (sample size was about 2 g), and every 5 cm for other analyses (sample size was about 5 g). In all cases, sample thickness was 1 cm. Although care was taken to sample only the mud matrix and not to include large evaporite crystals (mostly gypsum), small micro crystals could not be excluded and some were probably sampled together with the mud matrix. Facies were identified based on colour, lithology and sedimentary structures. Organic matter content was determined by loss-on-ignition analyses at 450 °C, and carbonate contents were measured with a calcimeter. Whole sediment mineralogy was characterized using a Siemens D-500 diffractometer; relative amounts (high, medium and low) of minerals were determined using peak intensity. The magnesium and calcium content of dolomites and calcites were calculated from the position of the main peaks (Goldsmith *et al.*, 1961). The absence of iron in the dolomites was inferred using the lattice spacing of d_{004} (Goldsmith & Graf, 1958a; Runnells, 1970; Al-Hashimi & Hemingway, 1974). Five core samples (at 3, 16, 50, 100 and 150 cm depth) were selected to evaluate the dolomite superstructure reflections; silicon was used as an internal standard. The degree of ordering of the dolomite samples was calculated from the relative peak heights of the d_{015} and d_{110} reflections (Goldsmith & Graf, 1958a,b). Clay minerals were identified on oriented samples (<2 μm), dried at room temperature, and treated with ethylene-glycol. Carbon and sulphur elemental analyses were performed with a Perkin-Elmer 260 Analyser. A JSM-6400 scanning microscope with EDAX facilities was used for SEM observations. Bulk sediment samples (0·5 g) were digested with a heated mixture of HCl and HNO_3 (3:1 ratio), filtered, and analysed for major (Ca, Mg), minor (Al, Sr, Na, Fe, Mn) and trace element (B and Li) composition with a JY 98 inductively coupled plasma spectrometer. Potassium content was measured with a Perkin Elmer/Coleman 51-Ca photometer. Samples of about 2 cm thick intervals and 25 g weight were selected every 10 cm for pollen analyses. Pollen was extracted in 18 samples by chemical attack and flotation on Thoulet solution. Pollen counts ranged from 180 to 868 grains per sample.

Oxygen and carbon isotopic compositions were measured on bulk-sediment samples according to standard procedures (McCrea, 1950) and the isotopic values reported in the conventional delta notation relative to the PDB standard. Most samples were composed of only one dolomite phase (stoichiometric, well-ordered, non-ferroan dolomite). For samples with a mixed calcite (low magnesium and high magnesium phases) and dolomite mineralogy, a double extraction at 25 and 50 °C was performed (Al-Aasm *et al.*, 1990). Acid fractionation factors used were 1·01044 at 25 °C for the calcite (Kim & O'Neil, 1997) and 1·01065 at 50 °C for the dolomite (Rosenbaum & Sheppard, 1986). This separation technique should be valid for the Salada Mediana sediments because only one dolomite phase is present. The

$\delta^{13}C$ values of organic matter were measured after carbonate removal with HCl 1:1. Isotopic compositions of modern sediments, cyanobacterial mats and halophytic plants were also analysed. Water samples from the lake, the nearby Ginel river, a cistern used for cattle, and rainfall were collected during the winter and spring of 1997 and their $\delta^{18}O$, δD, and major cation and anion compositions were measured. Analytical precision was better than 0·1‰ for $\delta^{18}O$ and $\delta^{13}C$ in carbonates, organic matter and water, and better than 2‰ for δD in water.

GEOGRAPHICAL AND GEOLOGICAL SETTING

The saline lakes in the Ebro Basin

The Ebro Basin is a large depression surrounded by the Pyrenees to the north, the Iberian Range to the southeast, and the Catalan Ranges to the east. It is mostly filled with Tertiary continental deposits (Quirantes, 1978; Pérez *et al.*, 1989; Salvany *et al.*, 1994). In the Salada Mediana area, gypsum and marls of the Mediana Gypsum Unit (Zaragoza Formation, Miocene) overlie marls and clays of the Codo Member (Longares Formation, Miocene; Fig. 1). The Mediana Gypsum Unit was deposited in a saline lake – saline mud flat complex, related to distal areas of large alluvial fans originating in the Iberian Range during the Lower Miocene (Upper Agenian–Middle Aragonian; Pérez *et al.*, 1989).

The central Ebro Basin is the most northerly area of truly semiarid climate in Europe. The climate is Mediterranean with a strong continental influence, and is characterized by very hot summers, cold, dry winters, and low rainfall (300–350 mm year^{-1}). The high insolation and evapotranspiration (1000–1500 mm year^{-1}), and the prevalence of strong, dry, NW winds also contribute to a water deficit through the year, especially during the summer. Rainfall is irregularly distributed, although spring and fall precipitation accounts for >70% of the total annual rainfall.

Lake depressions in the central Ebro Basin commonly occur in groups, particularly in the central plateau of Los Monegros, located north of the Ebro river (Fig. 1), where about 100 have been described (16 of them flooded every year; Pueyo-Mur & De la Peña, 1991). There are some topographical depressions near Salada Mediana, but none of them are ever flooded. Most saline pans in the central Ebro basin have brines of

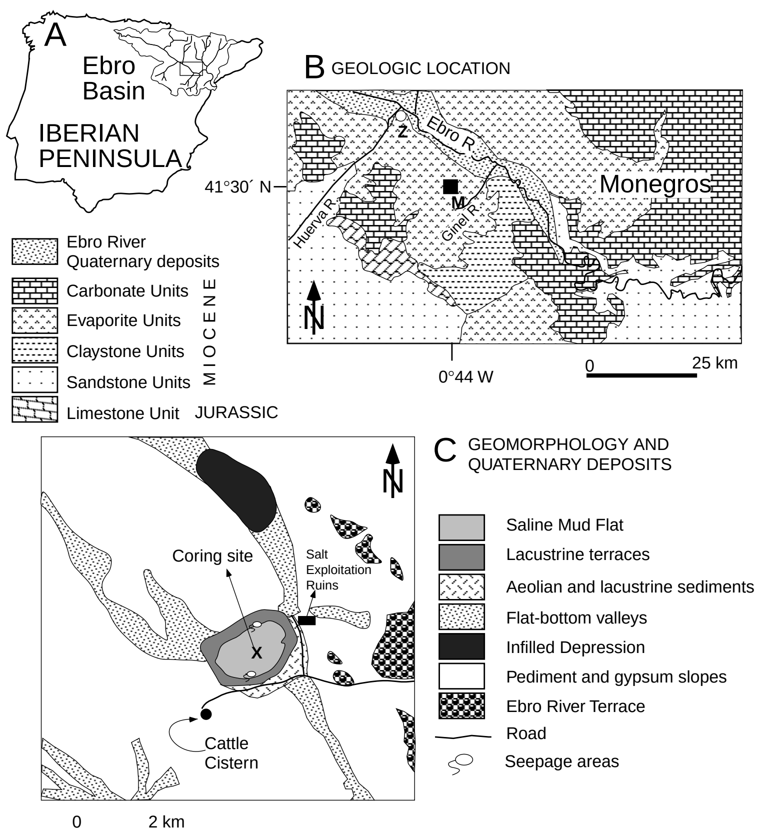

Fig. 1. (A) Location of the Salada Mediana in the Central Ebro basin, Iberian Peninsula. (B) The playa lake is located south of Zaragoza (Z), close to the village of Mediana (M) and lies on the Miocene Evaporite unit. (C) Map showing the Quaternary deposits surrounding the lake and location of the coring site.

(Cl^-)–($SO_4^=$)–(Na^+)–(Mg^{2+}) type, which undergo strong seasonal oscillations in concentration because of groundwater input, evaporation and progressive salt precipitation. Several playa lakes were used during historical times as a source of salts. The genesis of the depressions has been related to dissolution of the Tertiary evaporite substrate, preferential water circulation through faults, differential erosion and surface deflation (Quirantes, 1978; Pueyo-Mur, 1979; Soriano, 1990; Pueyo-Mur & De la Peña, 1991; Benito *et al.*, 1998; Sánchez-Navarro *et al.*, 1998).

The Modern Salada Mediana

Geomorphology and sub-environments

The 'Salada Mediana' playa lake (latitude: 41°30′ 10′ N, longitude: 0°44′ W, 350 m a.s.l.) is a small (main axis about 325 m × 500 m; 14 ha surface), seasonal (maximum water depth, $Z_{max} = 50$–0 cm) playa lake, located 20 km southeast of Zaragoza, on the Mediana Gypsum Unit (Miocene; Fig. 1B and 2A). The lake lies in a depression developed on an extensive pediment. Quaternary sediments in the watershed correspond to the remains of Ebro river terraces and the aeolian–alluvial infill of flat-bottomed valleys composed of gypsarenites and gypsites. Gypsisols develop over the alluvial valleys, Sollonchaks around the Salada Mediana, and Cambisols over the pediment (Navas & Machín, 1997). The watershed of the Salada Mediana itself is small and has been altered by farming during the last decades. Currently, the Salada Mediana has no surface inlets or outlets. However, several small, relict, non-functional creeks enter the depression from the north and one of them connects with the Ginel river valley to the south (Soriano, 1990). Small rounded areas within these valleys may correspond to prior depressions filled with sediments or to alluvial karstic sinkholes (Fig. 1C). The precise age of this drainage system is unknown. The lake and the drainage system could have originated during the Lower and Middle Pleistocene, a period of increased evaporite solution, responsible for the formation of many depressions in the central Ebro valley (Benito *et al.*, 1998). However, most of the depressions in the Mediana area formed after pediment-terrace complex 3 (Soriano, 1990) dated as Upper Pleistocene by the presence of *Elephas meridionales* (van Zuidam, 1980). The development of some of these depressions could have been synchronous with the relict drainage system, although the Salada Mediana depression is excavated within the alluvial infill, suggesting a younger age. A preliminary AMS-based chronology (Valero-Garcés *et al.*, 2000) suggests that sedimentation in the Salada Mediana started after the last glacial maximum and most of the sedimentary sequence belongs to the late glacial period (14 000–10 000 years BP).

Most of the Salada Mediana basin is a seasonal saline pan (Fig. 2A). A cliff of aeolian and lacustrine sediments, up to 4·25 m high, occurs on the southern and eastern lake margins. At the SW margin the cliff is higher and is only composed of aeolian sediments (Fig. 2B). In the SE margin, two well-developed lake terraces are present at 170 and 50 cm above the lake floor, and a small one at 10 cm above the recent maximum flood level. The ages of these aeolian and lacustrine sediments are unknown. A halophytic plant community of *Salicornia* L. and other genera of the *Suaedetum brevifoliae* association colonizes the lake margins. The main organic producers in the lake are algal communities including *Microcoleus desmazières*, *Dunaliella salina*, and diatoms of the *Hantzschia* genus. They form mats up to 4-mm thick that almost completely cover the lake floor during wet periods, are detached and reworked by wave and wind action (Fig. 2C), and become partially encrusted with evaporites during dry periods. The algal mats are ephemeral features, which are not annually added to the sediments. Crustaceans (*Artemia salina* L.), some protozoans and flagellates characterize the lake biota.

Hydrology and hydrochemistry

The Salada Mediana waters are of ($SO_4^=$)–(Cl^-)–(Na^+)–(Mg^{2+}) type, with low carbonate and calcium contents, and high Mg/Ca ratios (Table 1). Brine salinity and composition vary greatly during the year (Mingarro *et al.*, 1981; Auqué *et al.*, 1995). The lake is fed by rainfall, groundwater and runoff. The Salada Mediana is the discharge zone of shallow, unconfined aquifers in detrital sediments of the infilled valleys, the remains of Pleistocene Ebro terraces, and the pediment (Fig. 1C). Diffuse seepage occurs in the southeastern and northern margins. The lake dries up almost every year, although it may remain wet during rainy periods. As in most lakes in the region, groundwater flow is restricted by the low permeability of the Tertiary aquifers and aquitards (Auqué *et al.*, 1995; García-Vera, 1996), and its contribution to the saline lake water budgets has not been quantified.

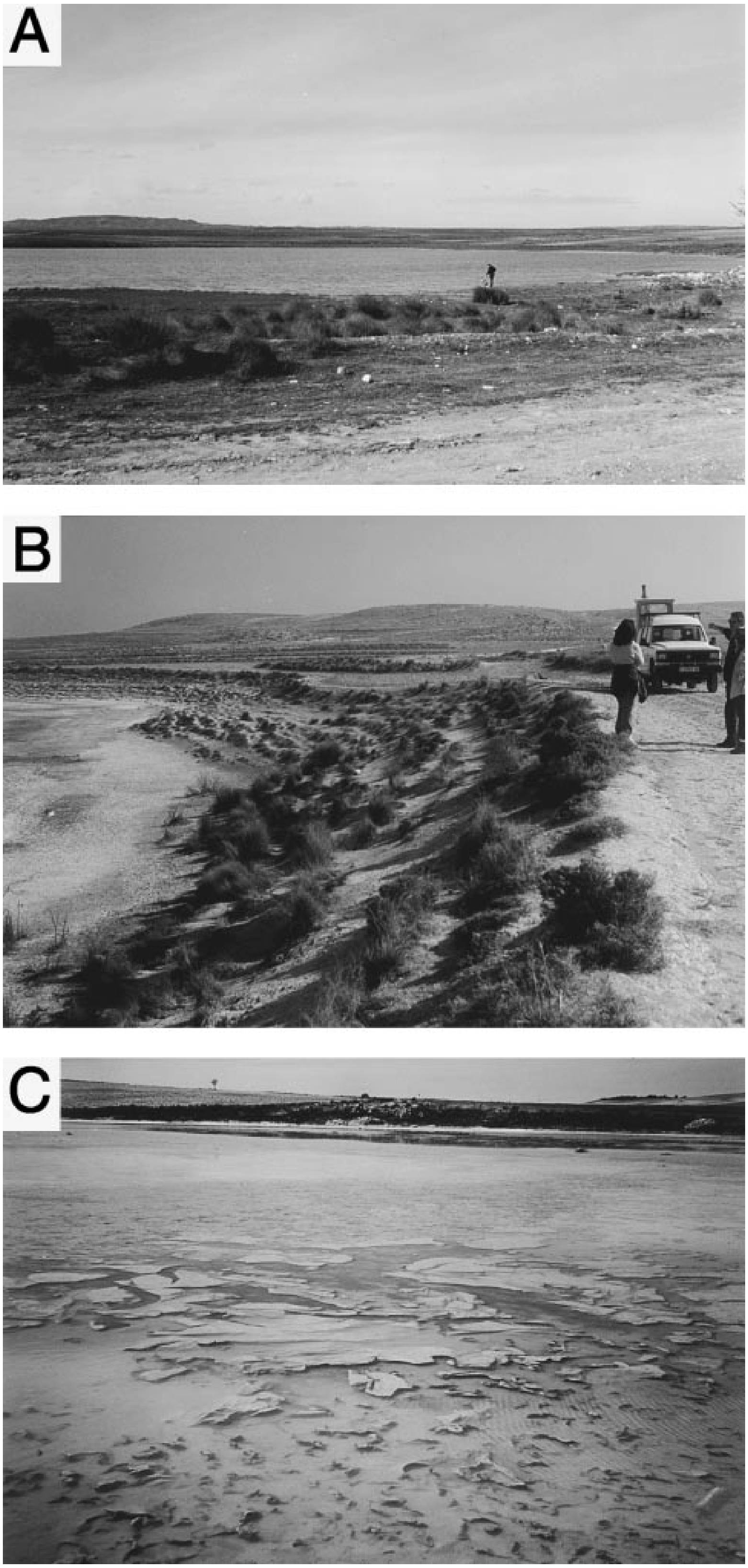

Fig. 2. (A and B) The Salada Mediana during the flood period (A; winter–spring) and during the dry-out period (B; summer–fall). Note the cliff developed in the southern edge, the terraces, and the halophytic vegetation (B). (C) Floating cyanobacterial mats during late spring.

Table 1. Electric conductivity (dSm^{-1}), major ion concentrations ($meq\ l^{-1}$) and stable isotope ($\delta^{18}O$, $\delta^{2}H$, SMOW) range of compositions from different water sources in the Salada Mediana area during the survey period (February–June 1997).

	Ginel spring	Ginel river	Cistern	Salada Mediana
EC	1·68–1·69	3·9–4·2	1·64–1·96	28·3–78·7
Cl^-	4·9–5·0	10·5–11·6	0·36	120·5–262·4
SO_4^{2-}	7·6–9	27·5–29·5	24	360–1500
HCO_3^-	1·96–2·44	1·33–4·17	1·1–1·71	0·682–2·05
Na^+	5·12–5·25	11·4–12·2	0·07–1·06	302·1–1004·8
K^+	0·08–0.1	0·15	0·22–0·31	0·7–7
Mg^{2+}	4·82–5·40	5·2–11·8	0·76–1·06	124·8–1015·2
Ca^{2+}	6·78–10·88	29·8–38·0	37·42–47·54	29·6–48·6
Sr^{2+}	0·04	0·2	0–0·06	0
B^{3+}	0·03	0·072–0.087	0·027	0·3–1·12
Li^+	0·007–0.009	0·02	0·001–0.0005	0·2–1·1
$\delta^{18}O$	(−7·97)–(−8·41)	(−7·6)–(−7·9)	(−4·3)–(−9·4)	(−6·36)–(+6·75)
δD	(−18·7)–(−60·2)	(−57·1)–(−61·1)	(−43·0)–(−61·4)	(−56·1)–(+22·3)

The ultimate source of the solutes in the groundwaters and playa lakes in the central Ebro basin is dissolution of Quaternary and Tertiary carbonates and evaporites (Pueyo-Mur, 1979; Mingarro *et al.*, 1981; Sánchez-Navarro *et al.*, 1998). Significant gypsum and carbonate dissolution causes the high SO_4^{2-} and CO_3^{2-} contents of the water. The high Mg^{2+} content of the water needs sources in addition to carbonate dissolution because Miocene limestones have a low Mg content (1·6% $MgCO_3$) and dolomite- and magnesite-rich facies are minor (Quirantes, 1978; Mata *et al.*, 1988). The Miocene evaporite formations (Zaragoza, Lerin, and Falces) contain dolomite and magnesite associated with clay and evaporite layers, and also as several-centimetre-thick carbonate beds (Mata *et al.*, 1988; Salvany & Ortí, 1994). The Zaragoza Formation provides Mg to the groundwaters through dissolution of small amounts of soluble salts, cation-exchange processes in the clay fraction, and dissolution of magnesite and dolomite. Another significant source of Mg is the weathering of sepiolite–paligorskite type clay minerals. Mg-rich clay minerals are abundant in the Tertiary Ebro Basin (Torres-Ruiz *et al.*, 1994) and are also present in some playa lakes of Los Monegros (Pueyo-Mur & Inglés-Urpinell, 1987a, b). Quaternary sediments (infilled valleys) and soils also provide a significant amount of the salts. Indeed, Quaternary sediments in the watershed and the soils contain high concentrations of Mg^{2+} (up to 60 meq L^{-1}) and Na^+ (up to 20 meq L^{-1}), and significant amounts of K^+ (up to 7 meq L^{-1}), and Li^+ (up to 0·14 meq L^{-1}; Navas & Machín, 1997).

Groundwater and rainfall isotope data for the region are scarce, and restricted to the central plateau of Los Monegros. Stable isotope compositions ($\delta^{18}O$ and δD) of groundwaters in the Monegros endorheic area show high variability (García-Vera, 1996). On average, the deuterium excess is very small (±1) and $\delta^{18}O$ ranges from −7·3 to −4·6‰ SMOW. The $\delta^{18}O$ values of groundwaters do not increase with TDS, which suggests that dissolution is more important than evaporation for the increase of salinity in groundwaters. The average $\delta^{18}O$ composition of rain in the Central Ebro basin is about −7 to −8‰ SMOW, although available data show a clear seasonality, as expected in semi-arid zones, and a large variability even during the same month (García-Vera, 1996; Fig. 3). Spring and summer rains have heavier $\delta^{18}O$ and δD-values, and a smaller deuterium excess than fall and winter rains. This seasonal variability is controlled by changes in the isotopic composition of the air masses, and the kinetic effects associated with evaporation of the rainwater during precipitation.

Modern deposition

The geochemical evolution of the Salada Mediana brine shows seasonal cycles governed by temperature and brine concentration (Pueyo-Mur, 1979; Auqué *et al.*, 1995). During late autumn, winter and early spring, when the water levels are higher and temperatures colder, the Salada Mediana precipitation sequence is dominated by mirabilite, because of its low solubility at low temperatures, although small amounts of carbonate and gypsum also precipitate (Pueyo-Mur, 1979; Auqué *et al.*, 1995). Mirabilite dehydrates to thernardite, which forms pseudomorphs after mirabilite and microcrystalline aggregates. During the late spring and summer, when temperatures are higher, and the water level decreases, the precipitation sequence changes to carbonate–gypsum–halite. Small amounts of dolomite, calcite, and high-

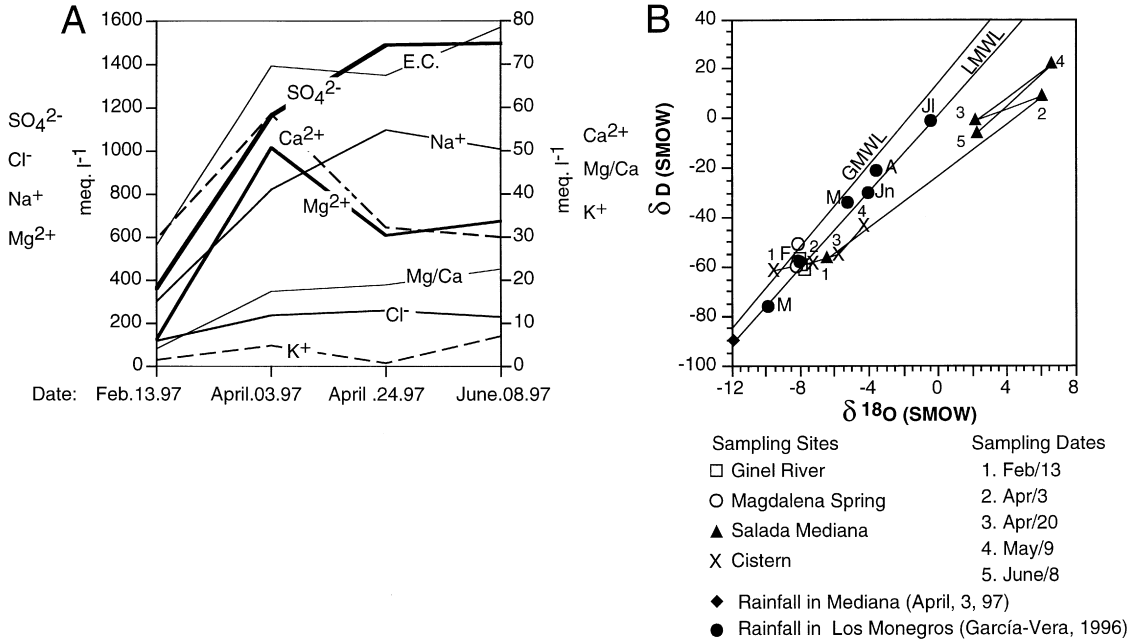

Fig. 3. (A) Evolution of the major ion concentrations, Mg/Ca ratios, and electrical conductivity (EC) of lake waters during the survey period (February – June 1997). (B) Isotopic composition ($\delta^{18}O$ and δD) of different water sources in the Salada Mediana area. The Monegros rainfall values (García-Vera, 1996) correspond to the period 1992–94 (F, February; M, May; Jn, June; Jl, July; A, August); global, GMWL, and local meteoric water lines (LMWL).

magnesium calcite (HMC) also precipitate, but the bulk of the evaporites is gypsum. Gypsum precipitates from the brine as prismatic crystals, 100 μm to several millimetres long. As the water level decreases and brine concentrates, halite crystals also form in the central area of the salada. Direct precipitation of thenardite and bloedite during the summer has been documented in the Salada Mediana and other saline lakes in the Central Ebro Basin (Pueyo-Mur, 1979). The mineralogical distribution follows a concentric pattern: gypsum and small amounts of thenardite in the marginal areas; towards the inner areas, thenardite dominates, although gypsum, bloedite and glauberite are also present; the central zone consists of bloedite and thenardite, with small amounts of halite (Pueyo-Mur, 1979; Mingarro *et al.*, 1981; Auqué *et al.*, 1995). Efflorescent salt crusts form in the saline mud flat when the Salada Mediana is dry from early summer until late autumn.

RESULTS

Hydrology and modern carbonate deposition

The water survey (Fig. 3A) shows a rapid chemical and isotopic enrichment of lake waters after the February rains, and dilution after the mid-April and mid-May rains. Sulphate concentration increased threefold during the rainless February–April period, whereas Mg^{2+} increased sixfold, and Cl^-, Ca^{2+} and the electric conductivity (EC) increased twofold. The boron and lithium concentrations in February were already much higher in lake waters than in the river, spring and cistern (Table 1). The cistern, a concrete tank, 6 m diameter with high walls, is only fed by rainfall. The amounts of B and Li in the lake water sharply increased as a result of evaporative concentration, and remained high (about 1 meq L^{-1}) for the rest of the sampling period. The mid-April rains only slightly decreased the EC. The Ca^{2+} and Mg^{2+} concentrations decreased to half of their previous values (Mg^{2+} an order of magnitude more than Ca^{2+}), whereas sulphate, chloride and sodium concentrations increased. The Mg^{2+} and Ca^{2+} behaviour suggests that the amount of carbonate (dolomite and calcite) precipitated is small, and most of the Mg^{2+} is being used up in other phases.

The algal mat sampled in late spring contained evaporites (mirabilite, thenardite, bloedite and halite), low magnesium and high magnesium calcite (LMC 10%, HMC 35% Mg), and clays (illite). The dry algal mat sampled in summer also contained gypsum, and small amounts of dolomite and quartz. The position of the XRD peaks indicates a nearly stoichiometric, non-calcian, non-ferroan dolomite (Goldsmith & Graf, 1958b; Goldsmith *et al.*, 1961; Runnells, 1970; Al-Hashimi & Hemingway, 1974).

The Ginel River water isotope composition, electric conductivity and pH remained constant during the survey period (February–June 1997) at the two sampling sites, near the village of Mediana and at the headwaters (Magdalena spring; Fig. 3A and B; Table 1). Immediately after a rainy period in February, δD compositions of the Ginel river, the Magdalena spring, the Salada Mediana and the cistern were similar (about −60‰; Fig. 3B). The cistern showed the lightest values in both $\delta^{18}O$ and δD.

Lake waters at the beginning of the survey were also already chemically concentrated (28·3 dS m^{-1} electric conductivity) compared with the freshwaters of the cistern (1·64 dS m^{-1}). After a month without rain (measured April 3), the lake waters were enriched by almost 12‰ and 60‰ in $\delta^{18}O$ and δD respectively (Fig. 3B), and their conductivity increased to 70 dS m^{-1} (Fig. 3A). The $\delta^{18}O$ composition of the cistern waters only increased by 2‰, δD increased only slightly and conductivity remained in the same range (1·96 dS m^{-1}). Rainy periods in mid-April and late May decreased lake water $\delta^{18}O$ values by 4‰ and δD by 10‰. However, the lake water remained highly concentrated (electric conductivity 68 dS m^{-1}), and soon after the rain events, its isotopic composition returned to high values. Although rainfall isotopic compositions were highly variable, values between −9 and −7‰ are the typical composition of the input waters to the lake. The large evaporation rates in the area, even during the winter, and the high surface to depth ratio of the playa lake, produce a rapid isotopic evolution that small rain events cannot counterbalance. As a result, during carbonate precipitation in spring and summer, lakewaters can be enriched by 8–12‰ relative to the average rainwater.

The Quaternary sedimentary sequence

Sedimentary facies

Sedimentary structures (mainly lamination), colour and lithology allow definition of three main sections in the core (Fig. 4): (i) the Lower section (150–107 cm) is composed of massive grey muds with intercalated thin gypsum layers; (ii) the Middle section (107–19 cm) is composed of massive to banded (up to several cm thick) grey,

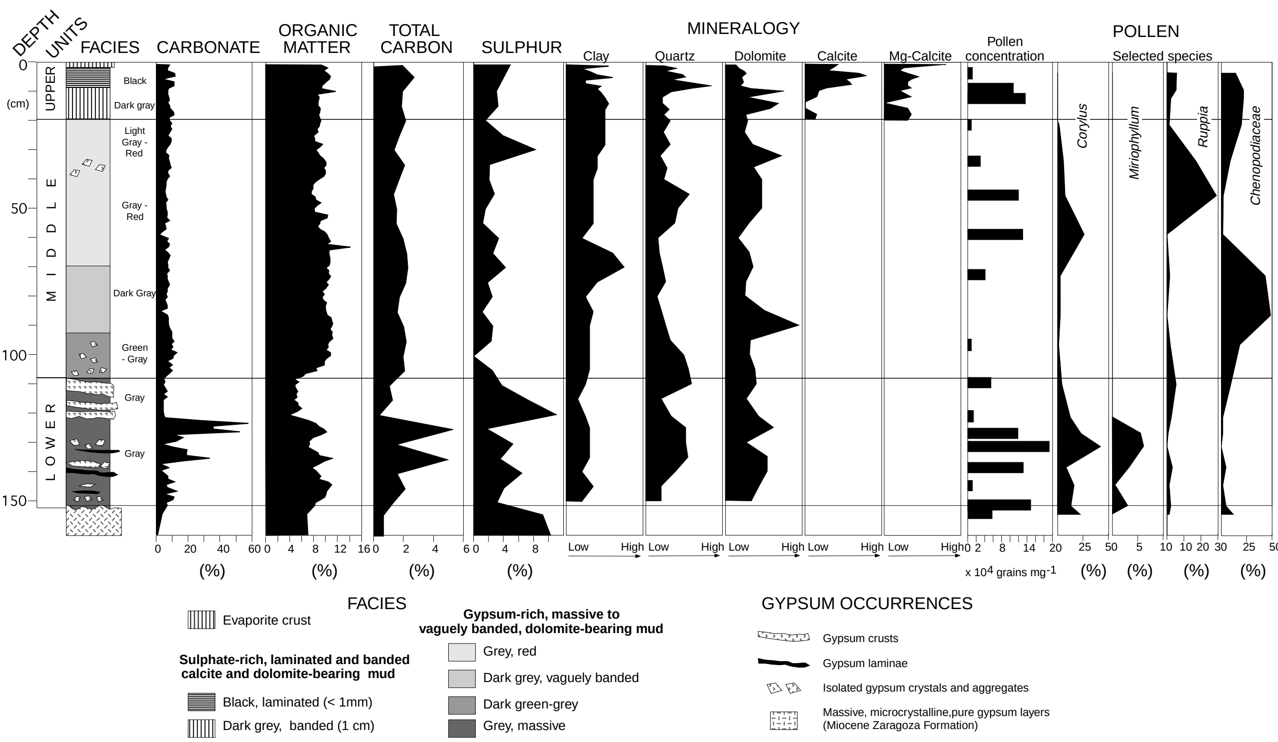

Fig. 4. Sedimentary facies, sediment composition (carbonate, organic matter, total carbon and sulphur), semi-quantitative carbonate and silicate mineralogy, pollen concentration, and percentages (without *Pinus*) of selected pollen taxa: deciduous tree (*Corylus*), freshwater aquatic plant (*Miriophyllum*), saline aquatic plant (*Ruppia*) and halophytic grasses (*Chenopodiaceae*) of the Mediana core.

greenish and reddish muds, which contain several intervals with isolated gypsum crystals; and (iii) the Upper section (19–0 cm) is composed of dark grey, banded (layer thickness around 1 cm) and black, laminated (lamina thickness <1 mm) muds. Coring was stopped by a massive, microcrystalline, pure gypsum layer that probably corresponds to the Miocene Zaragoza Formation.

The core muds are fine grained (<20 μm), and mainly composed of gypsum, dolomite, illite and organic matter. SEM and EDAX observations of the salt layer show a mesh of algal filaments, elongated prisms of magnesium sulphates, clusters of gypsum crystals, and some halite crystals (Fig. 5A). Within the muds, gypsum occurs as millimetre-sized isolated crystals, or euhedral (prismatic, plates) crystals, tens to hundreds of microns long, and grouped in clusters (Fig. 5B). Dolomite crystals are a few microns long, and anhedral to rounded (Fig. 5D); calcite crystals are a few microns long, euhedral to subhedral, and isolated (Fig. 5C). The degree of ordering (Goldsmith & Graf, 1958a,b) in the five measured dolomite samples ranges from 0·6 to 0·9, which indicates it is well ordered. Dolomite and calcite crystal sizes are similar (about 5 μm), but the dolomite is more rounded than the calcite (Fig. 5C and D).

The lower sediments (150–121 cm depth) consist of alternating massive, structureless muds and intervals with abundant gypsum laminae and isolated crystals. Gypsum laminae (about 5 mm

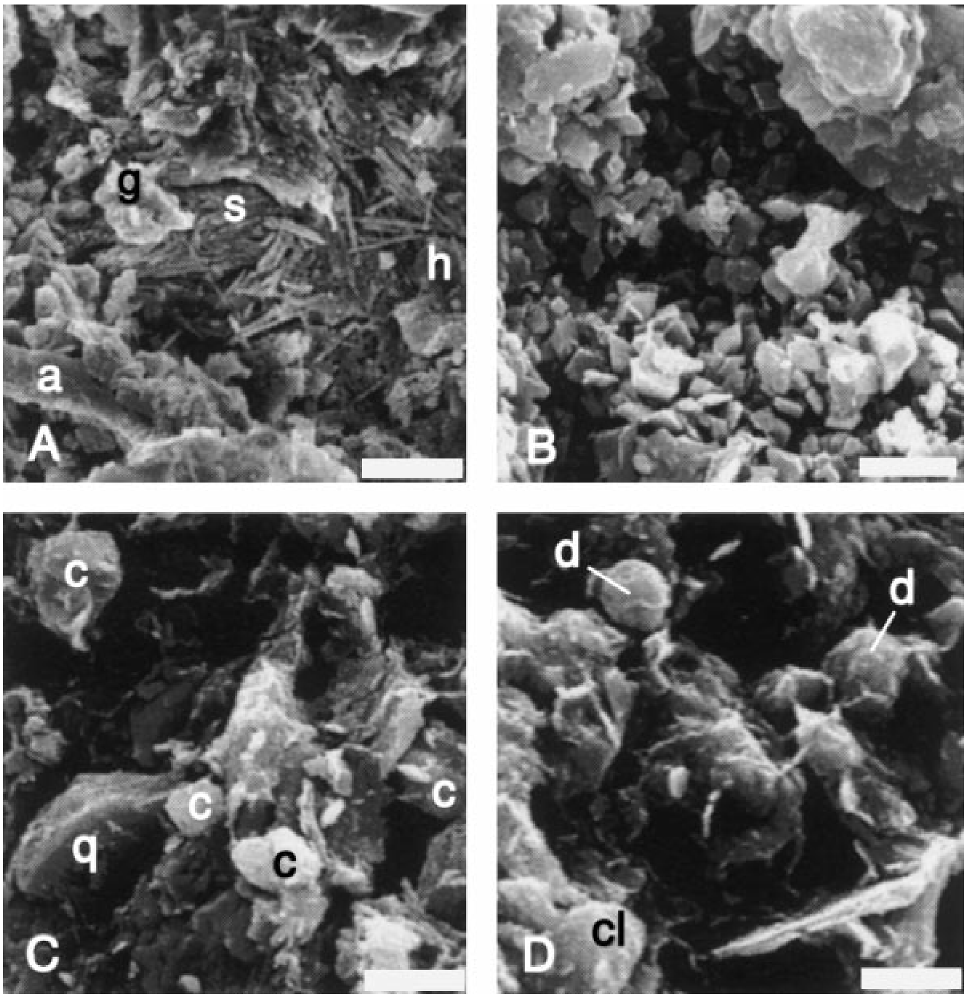

Fig. 5. SEM photographs of Mediana sediments. (A) Cyanobacterial mat encrusted with salts (top of unit 1): a mesh of algal filaments (a), with elongated magnesium sulphate crystals (s: mirabilite, thenardite?), gypsum (g) and halite (h). (B) Microcrystalline gypsum: prisms and clusters (unit 5). (C) Calcite crystals (c) at the top of unit 2. Note the euhedral shapes and smaller size than quartz crystals (q). (D) Dolomite crystals (d) with some clay minerals (cl) at the top of unit 2. Note the equant, more rounded crystal morphologies of dolomite compared to calcite. Scale bars for all photographs: 10 μm.

thick) are composed of up to 1 mm long euhedral gypsum crystals with low matrix content. The crystals have no preferred orientation and contain no matrix inclusions. A thicker gypsum-rich interval occurs between 121 and 107 cm. The gypsum crusts are composed of long (up to 2 cm) gypsum crystals, with no preferred orientation, and aggregates within a mud matrix. Displacive textures and matrix mud inclusions in the crystals suggest that the crusts formed as a result of intrasediment growth. The muds from the Middle core section (107–19 cm depth) are vaguely bedded to banded (several centimetre-thick layers). Gypsum occurrences and colour are the main sedimentary criteria that subdivide this section. Gypsum laminae are absent, but displacive gypsum euhedra occur as isolated crystals and crystal aggregates at the base (107–92 cm depth) and at the top (40–30 cm depth). The lower part of the section, corresponding to a gypsum-rich interval (107–92 cm depth), is dark-green. The section between the two gypsum-rich intervals is grey–red, and grades to lighter red colours at the top of the section (30–19 cm depth). An abrupt colour transition occurs at the base of the Upper section. Dark grey, weakly banded muds (19–9 cm depth) change upwards to laminated (<1 mm), black muds capped by a salt layer encrusting the cyanobacterial mat.

Sediment composition and mineralogy help to define sedimentary facies and units in the core (Fig. 4). Mud intervals from the Lower section have the highest carbonate (dolomite) content of the core. The gypsum-rich intervals (particularly at the top of the section: 121–107 cm depth) have the lowest carbonate, organic matter and clay mineral content, and also small amounts of thenardite and bloedite. An abrupt increase in organic matter and carbonate suggest an unconformity between the Lower and Middle sections. The Middle section muds have relatively constant carbonate (about 10%), organic matter (10%) and sulphate (2–4% sulphur) contents. Two clay-rich intervals occur at 80–60 cm depth and at the top of the Middle section (lower part of the Upper section 30–9 cm depth). The Upper section (19–0 cm depth) is characterized by calcite (high and low magnesium), and higher contents of mirabilite, thenardite and bloedite.

Geochemistry

Figure 6 summarizes the bulk chemical composition of the Mediana core sediments. Calcium primarily reflects the changes in gypsum content,

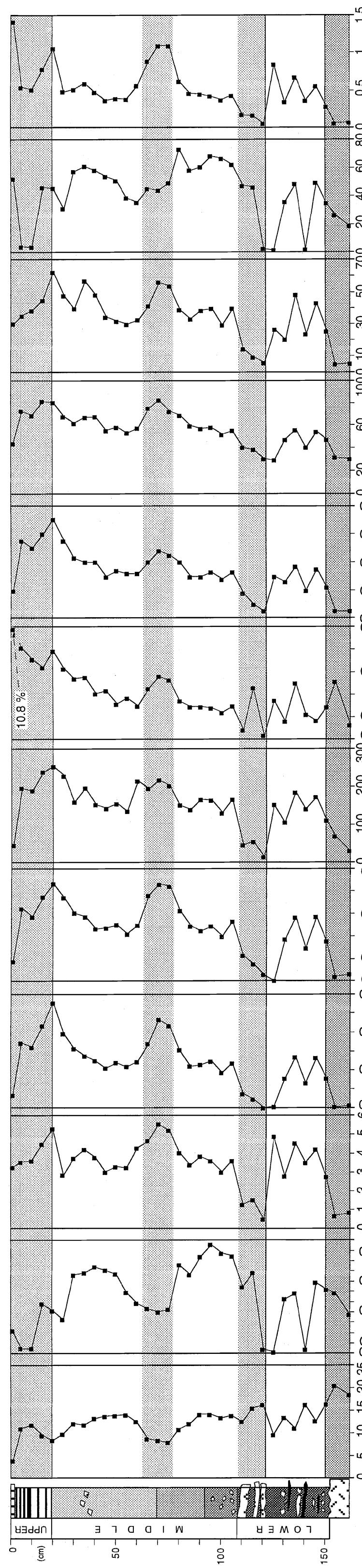

Fig. 6. Chemical composition of the Mediana core sediments.

and to a lesser extent carbonate (dolomite and calcite). As expected, the decreasing trend and the peak values in the Lower section (Fig. 6) parallel the sulphur content trends (Fig. 4). However, carbonate-rich intervals are not reflected in similar peaks in calcium, suggesting that dolomite is a subordinate source of calcium. The upward decrease in calcium in the Middle section correlates with lower gypsum and dolomite contents, and the low values (80–60 cm depth interval) correlate with higher clay mineral contents. The relative increase in calcium in the Upper section may also be related to the presence of calcite. Strontium occurs in sulphates and carbonates (particularly dolomite) as a substitute for Ca^{2+}, and consequently it is more abundant in the gypsum- and dolomite-rich facies than in the clay-rich facies.

The other elements show similar patterns: (i) moderate and fluctuating values in the Lower section, (ii) a sharp decline in the gypsum-rich interval (121–107 cm depth), (iii) two cycles in the Middle section, and (iv) a decreasing trend in the Upper section. Aluminium, iron and manganese trends follow the clay mineral content, which suggests that they are indicators of detrital (aeolian) input. Iron and manganese may be adsorbed on clays, or precipitated as colloids and oxides. Magnesium shows a slightly different pattern. It increases from <1% in the underlying Miocene gypsum to as much as 5% in carbonate-rich intervals of the Lower section, a response to the higher dolomite content and the presence of small amounts of bloedite. Although only illite was detected, the positive correlation with clay mineral content and negative correlation with dolomite in the Middle section suggest that magnesium is mainly adsorbed to clays, incorporated into Mg-bearing clays, or related to small amounts of soluble salts within the muddy sediments. Potassium, boron, sodium and lithium have similar trends in the sequence, which are related to clay and salt content. Sodium does not show this decrease in the Upper section. After a small decrease at the base, sodium content increases, reflecting the presence of halite, mirabilite, and thenardite in the crust that covered the lake bottom during the sampling period.

Pollen

Variations in the most important ecological taxa correspond to sediment changes in the Salada Mediana core (Fig. 4). The maximum development of *Corylus* and other deciduous trees, and the minimum of halophytic grasses (*Chenopodiacea*) indicate a relatively large arboreal cover in the area, and a deciduous forest around Salada Mediana during deposition of the Lower section. The presence of *Myriophyllum* sp., a freshwater aquatic plant, indicates periods of very low salinity correlating with the carbonate-rich intervals. The demise of *Corylus* and *Myriophyllum* sp., and the progressive increase in *Chenopodiaceae*, indicative of more arid conditions, are synchronous with the gypsum-rich interval. Very low percentages of saline aquatic plants (*Ruppia*), the highest *Chenopodiaceae* content, the low taxa variability, and the low pollen concentrations all indicate frequent desiccation events and grass colonization of the lake floor in the lower part of the Middle section. A change in sediment composition at 60 cm depth correlates with an increase in *Corylus*, and a decrease in grass pollen, congruent with more humid conditions and increased lake level. The presence of *Ruppia* points to more permanent saline waters during deposition of the upper part of the Middle section. Decreasing pollen concentration, *Corylus* and *Ruppia* percentages, and increasing *Chenopodiaceae* indicate more frequent desiccation periods during deposition of the top part of the Middle section. The absence of *Corylus* – a tree that at present does not grow in the central Ebro valley – characterizes the Upper section. The increase of *Ruppia* in the upper part, and the high percentages of *Chenopodiaceae*, favour large seasonal or pluri-annual oscillation in the water level.

Stable isotopes

There is no comprehensive study of isotope composition of the Miocene carbonate formations near the Salada Mediana. In the Los Monegros area, the limestone $\delta^{18}O$ compositions range between −9 and 0‰ PDB, and dolomite-bearing samples between −6 and +4‰ PDB (Arenas *et al.*, 1997). The isotopic compositions of dolomites from the Middle and Upper Salada Mediana sections are within this range, but the Lower section has heavier compositions (Fig. 7A). The $\delta^{18}O$ compositions of Miocene limestones from the Salada Mediana area, and from the Ebro terrace gravels near the lake are considerably lighter (between −7 and −4·7‰) than calcites from the Upper section (about −2‰), and calcite precipitated in the bacterial mats (0·44 and 0·77‰; Fig. 7B and C). Unlike the saline lakes of Los Monegros, where calcite is also provided by detrital local sources (Pueyo-Mur &

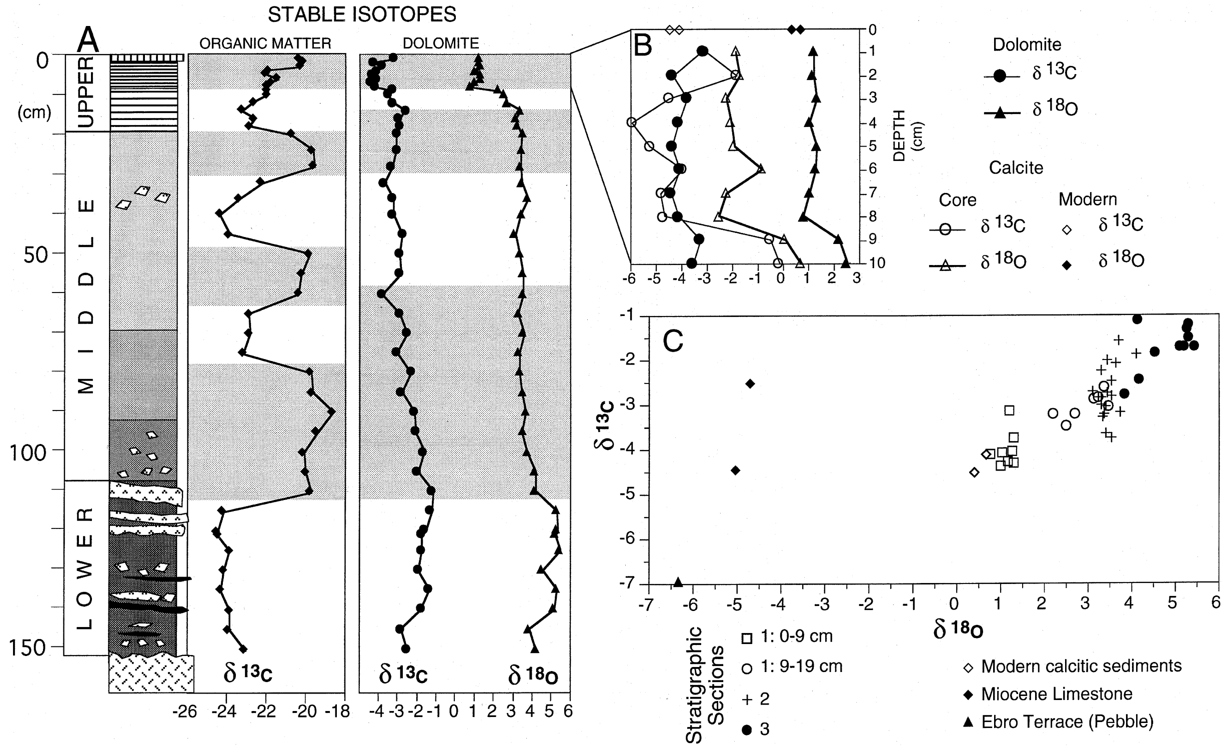

Fig. 7. Stable isotope composition of the sediments. (A) $\delta^{18}O$ and $\delta^{13}C$ values of dolomite samples from the core. (B) $\delta^{18}O$ and $\delta^{13}C$ values of dolomite and calcite from the upper sediments (0–9 cm depth). (C) Cross plot of the isotopic composition of dolomite from the core, the modern calcite in the cyanobacterial mats, and samples of the Miocene limestones and limestone clasts from the Ebro river terrace.

Inglés-Urpinell, 1987a,b), the restricted occurrence of calcite, and the isotope data favour an authigenic origin for calcite in Salada Mediana.

The $\delta^{13}C$ and $\delta^{18}O$ values of the dolomite have a strong positive correlation (Fig. 7A). They generally decrease from the bottom to the top of the section and there is a sharp negative shift between 9 and 12 cm depth. The $\delta^{13}C$ calcite values decrease downcore in the upper 4 cm (from about −1 to −6‰) reaching the lowest values in the whole core at the transition between the black and grey laminated muds.

The $\delta^{13}C$ organic matter curve shows two distinct populations: (i) samples with $\delta^{13}C$ values between −25 and −22‰ (Lower section, and the 80–60, 45–30 and 19–15 cm depth intervals), and (ii) samples with $\delta^{13}C$ values between −22 and −19‰ (Fig. 7A). The two main organic carbon sources in Salada Mediana have distinctive $\delta^{13}C$ values similar to these two populations (Fig. 8): cyanobacterial mats have values between −12·8 and −11·2‰, terrestrial halophytic plants have measured values between −20 to −24‰.

DISCUSSION

Hydrology and carbonate formation in Salada Mediana

Brine evolution models for the Central Ebro basin saline systems based on field observations (Pueyo-Mur, 1979; Pueyo-Mur & De la Peña, 1991), and experimental studies (Auqué *et al.*, 1995), suggest that small amounts of calcite and dolomite precipitate in the Salada Mediana during the spring and summer, before the main phase of salt precipitation. Calcite precipitation could also be associated with peak algal growth and freshwater input to the lake during the spring. Although calcite and dolomite are found in the modern cyanobacterial mats, the present data are not conclusive on modern dolomite formation. The water survey shows that the evolution of ionic concentrations reflects a complex interplay of evaporite dissolution and precipitation, solute introduction, and brine concentration changes by evaporation and rainfall. The de-coupling of salinity and $\delta^{18}O$ values indicates that factors other than evaporation and rainfall control the

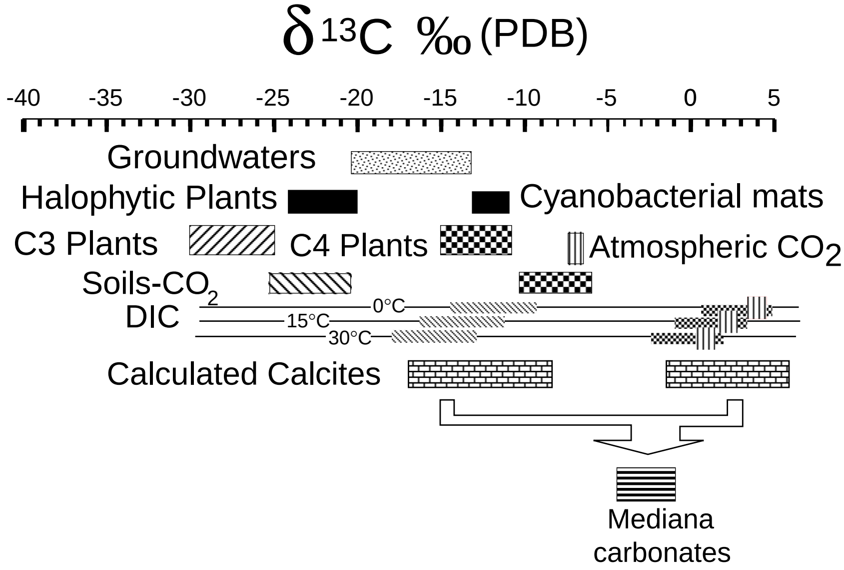

Fig. 8. Sources of carbon in the Salada Mediana: C3 and C4 plants (Deines, 1980); halophytic plants and cyanobacterial mats; groundwaters from Los Monegros (García-Vera, 1996); atmospheric CO_2 (pre-industrial values of −6·5‰; current values −8‰; Friedli *et al.*, 1986), and soil-CO_2 (about 4·5‰ heavier than the vegetal biomass; Cerling, 1984). Isotopic calculations (DIC and calcites) assumed a calcite-bicarbonate enrichment of 1‰ (independent of the temperature) and used the calcite-CO_2 equation of Romanek *et al.* (1992) for temperatures of 0 °C, 15 °C and 30 °C.

brine concentration. High chemical concentrations were most probably maintained during late spring by the dissolution of previously precipitated salts. Furthermore, the isotopic composition of the brine is more variable than the chemical composition of isotopically depleted and low salinity inflows. Small inflows do not greatly decrease the brine concentration, and evaporites formed prior to the rains would buffer brine concentration. The Salada Mediana illustrates the complex relationship between salinity and $\delta^{18}O$ composition observed in other saline lakes (Chivas *et al.*, 1993; Ordoñez *et al.*, 1994; Valero-Garcés *et al.*, 1995, 1997).

The carbonate minerals in Salada Mediana have different origins: (i) aeolian input, (ii) dolomitization, (iii) sulphate-reduction and (iv) precipitation from the lake or interstitial waters.

Aeolian input. Aeolian processes are of great importance in the central Ebro basin, as shown by the occurrence of large wind-blown accumulations on the lee side of many saline lakes in the Monegros area (Pueyo-Mur & Inglés-Urpinell, 1987b; Pueyo-Mur, 1979). The Miocene limestones are a negligible source of detrital dolomite because it is rare in the Central Ebro area (Quirantes, 1978). Dolomite is a minor component associated with Miocene evaporites and carbonates in the Ebro Basin (Mingarro *et al.*, 1981; Mata *et al.*, 1988; Salvany & Ortí, 1994; Salvany *et al.*, 1994; Mayayo *et al.*, 1996), and it is also present in some Mesozoic and Palaeozoic rocks in the Iberian Range. The presence of dolomite in only a restricted number of surface playa lake sediments in the Ebro Basin (Mingarro *et al.*, 1981) suggests that dolomite-bearing formations are only local suppliers of detrital dolomite and not regional sources for the Ebro valley. The dolomite-bearing formations in the Salada Mediana watershed are the Miocene Zaragoza Formation, the Quaternary lacustrine and aeolian deposits surrounding the Salada Mediana, and the saline soils (Solonchak and Gypsisols) developed in the Salada Mediana fringes. They probably contribute some aeolian dolomite to the lacustrine sediments. Dolomite is absent in the Calcisols developed on the Ebro terraces and pediment. Deflation of Salada Mediana lacustrine sediments could be a local source of dolomite for the aeolian sediments.

Dolomitization. In Salada Mediana, the highly Mg-enriched brines could contribute to early dolomitization of the calcite, as proposed in other Spanish saline lakes (Pueyo-Mur & De La Peña, 1991). The increase in dolomite content with depth (from 5 to 30%) in several playa lakes in the Monegros area, and its association with magnesite were interpreted as a signature of a diagenetic origin for dolomite and magnesite (Pueyo-Mur, 1980; Pueyo-Mur & Inglés-Urpinell, 1987a,b). In some lakes of the Ebro Basin, where more than one core was studied, the largest amounts of dolomite were found in the marginal areas (Monegros lakes: Pueyo-Mur & Inglés-Urpinell, 1987a,b; and Gallocanta: Comín *et al.*, 1990), where less saline groundwater seepage and mixing with the hypersaline lake waters favour dolomitization. The absence of calcite in the lower sections of the Mediana core could indicate that replacement of calcite by dolomite occurred. However, the large range in isotopic composition (almost 5‰) and the presence of rapid shifts correlating with sediment changes are not consistent with diagenetic overprint.

Sulphate reduction. Another possible source of diagenetic carbonate in sulphate-rich environments such as Salada Mediana is via sulphate reduction. Sulphate-reducing bacteria rapidly oxidize organic matter to H_2S and HCO_3^-, and this could lead to the precipitation of calcite with light $\delta^{13}C$ values (Kelts, 1988; Komor, 1994). The $\delta^{13}C$ dolomite values in the upper 9 cm are fairly constant, indicating a relatively stable carbon reservoir after the sharp shift between 1 and 9 cm depth (Fig. 7B). The $\delta^{13}C$ calcite values decrease downcore in the upper 4 cm (from about −1 to −6‰), reaching the lowest values in the whole core at the base of the black laminated muds. These isotopic data may indicate that some HCO_3^- used for calcite precipitation was derived from decomposition of organic matter in the reducing upper sediments. Pore waters in Salada Mediana probably have the oxygen isotopic composition of evaporated lake waters. The carbon isotopic composition, however, could be affected by sulphate reduction and, consequently, calcite precipitated during early diagenesis would have lighter $\delta^{13}C$ values. The larger $\delta^{13}C$ range for calcite compared with dolomite suggests a double origin for the calcite, primary from the lake waters, and diagenetic from the pore waters. However, similar $\delta^{13}C$ calcite and $\delta^{13}C$ dolomite in the interval below the black muds (4–9 cm depth), and the consistent 3‰ shift in $\delta^{18}O$ values support precipitation of both carbonates from the same lake or interstitial brine. Organic matter and sulphate concentrations in the upper part of the core suggest that sulphate reduction may take place in the Salada Mediana. Organic matter content is moderate (about 8–10%) and decreases slightly with depth in the upper 30 cm. Total sulphate content also decreases with depth in the upper sediment section, although generally high organic matter content in the sediments suggests low sulphate reduction rates. Lyons *et al.* (1994) show low sulphate reduction rates in the algal mat – carbonate platform of Freefight lake (Saskatchewan, Canada), a similar environment to Salada Mediana. In conclusion, although sedimentary and isotopic data suggest that sulphate reduction occurs in Salada Mediana, there is no conclusive evidence that this results in the formation of diagenetic calcite.

Precipitation from lake or interstitial waters. Although carbonate alkalinity is lower, other sedimentological and chemical features of the lake are similar to most modern dolomite-bearing lacustrine environments: shallow playas, saline waters with high Mg/Ca ratios, NaCl type, and high sulphate concentrations (Last, 1990). The only study of modern carbonate-forming conditions in the Ebro Basin saline lakes was carried out in Gallocanta (Comín *et al.*, 1990). They concluded that low-magnesium calcite and dolomite precipitated from the brine. Modern calcite from the Salada Mediana has $\delta^{13}C$ values similar to, and $\delta^{18}O$ values heavier than, the uppermost samples of the Upper section (Fig. 7), indicating a similar carbon reservoir, but different hydrological conditions during the sampling period (probably greater evaporation effects). Although dolomite was detected by XRD in the summer cyanobacterial mats, the amounts were too small to measure its isotopic composition. Isotope data strongly support a primary origin for the modern calcite and for dolomite and calcite of the Upper section, either directly from lake water or from interstitial pore water. Considering that water temperature during the day in the Salada oscillates between 25 and 35 °C, and applying the equation of Kim & O'Neil (1997), the measured $\delta^{18}O$ values of modern calcitic (LMC and HMC) sediments formed in the bacterial mats during late spring (+0·44 and +0·77‰) suggest that calcite precipitated in isotopic equilibrium with lake waters ($\delta^{18}O$ between +2 and +6‰).

The oxygen isotopic values of calcites from the upper 9 cm (−2·5 to −1·7‰) are about 3‰ lower than dolomite (0·8 to −1·3‰). It has been determined experimentally at high temperatures that dolomite formed from a precursor carbonate fractionates approximately +3‰ (Land, 1985). Considering the equations of Irwin *et al.* (1977) and Kim & O'Neil (1997) for dolomite and calcite, respectively, these isotopic compositions support a cogenetic origin for minerals from the same evolved waters (between −1 and +3‰ SMOW at temperatures between 20 and 40 °C; Fig. 9).

The well-ordered structure and stoichiometric composition of the Salada Mediana dolomite are not unequivocal signatures for a detrital origin. About one-third of the Quaternary lacustrine occurrences listed by Last (1990) are stoichiometric, and about half are well ordered. The better studied examples include the west Texas playas (Reeves & Parry, 1965), saline lakes from the northern Great Plains of the US and Canada (see

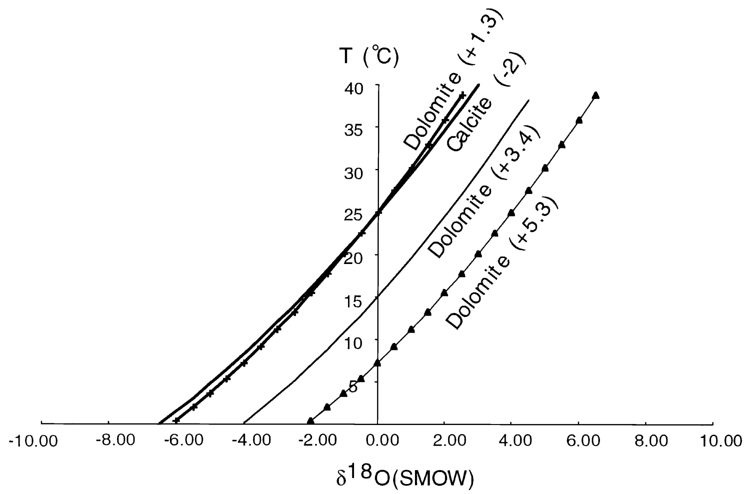

Fig. 9. Temperature-$\delta^{18}O$ (water) curves for different $\delta^{18}O$ (carbonate) compositions, according to the equations of Irwin *et al.* (1977) and Kim & O'Neil (1997). Acid fractionation factors used are 1·01044 at 25 °C for the calcite (Kim & O'Neil, 1997) and 1·01065 at 50 °C for the dolomite (Rosenbaum & Sheppard, 1986). Note that dolomites ($\delta^{18}O$ of about +1·3‰ PDB) and calcites ($\delta^{18}O$ of about −2‰ PDB) from the upper sediment (0–9 cm depth) would have formed in equilibrium with water of around 0‰ and +2‰ SMOW over a temperature range of 25–40 °C.

references in Last, 1990), and saline lakes in Australia (De Deckker & Last, 1988, 1989; Rosen *et al.*, 1989). In all cases dolomite was interpreted as a primary precipitate or replacement of a carbonate precursor. Some of the primary dolomite occurs as anhedral crystals (western Victoria lakes, Australia, and Canadian Plains saline lakes) and rounded aggregates (Freefight lake, Canada; Last, 1993) similar to the Salada Mediana crystals (Fig. 5).

In summary, although only one mineral phase has been identified by XRD, dolomite in Salada Mediana probably has several origins. Isotopic and sedimentological data indicate that calcite forms in the modern environment and also formed during deposition of the Upper section of the sequence. Modern environmental conditions and conditions during deposition of the Middle and Lower core sections were also conducive to dolomite formation. Although the aeolian input has not been quantified, there are several possible sources of detrital dolomite.

Depositional evolution of Salada Mediana

Palaeohydrological indicators

Sedimentary facies and geochemistry. The facies succession was mainly governed by fluctuations in hydrological balance, brine composition and salinity; however, aeolian processes (detrital input and deflation), and recycling of salts also played a significant role. The presence of dunes and aeolian accumulation in many lakes, deflation of microcrystalline thenardite crystals from the lake bed (Pueyo-Mur, 1979), and the presence of hiati confirmed by absolute chronologies (Davis, 1994; Valero-Garcés *et al.*, 2000) indicate that aeolian processes contribute greatly to the elimination of salts and sediments from the central Ebro Basin saline lakes.

Sedimentary structures, sediment composition, mineralogy and geochemistry allow a more detailed characterization of the sedimentary facies (Fig. 4). The carbonate and gypsum-rich sediments in the Lower section are consistent with deposition in a saline lake setting (Hardie *et al.*, 1978; Lowenstein & Hardie, 1985; Smoot & Lowenstein, 1991). Intervals in the Middle and Upper sections with higher Ca, Sr, gypsum and dolomite contents are interpreted as saline pan deposits. Clay-rich facies with lower Ca and Sr contents, and higher Al, Mg, Fe and Mn values are interpreted as saline mud flat deposits; Na, K, B and Li also concentrate in these facies. The clay-rich intervals could result from efflorescent crust development and deposition of small amounts of wind-blown material in depressions when the water table was below the sediment surface (Smoot & Castens-Seidell, 1994). Periods of expansion of the mud flats with more frequent desiccation stages, fluctuating Eh conditions, and higher aeolian input would be more conducive to iron and manganese precipitation as colloids and oxides. B and Li concentrate in alkaline lake waters at high-salinity stages as evaporative minerals, adsorbed onto the finer particles, or substituted for other ions in clay minerals (Kyle, 1994).

Oxygen isotopes. The stable isotope analyses of monomineralic carbonate minerals in the lake deposits provide valuable palaeohydrological and palaeolimnological information. Although some detrital input could occur, most dolomite in Salada Mediana is probably authigenic. The large range (almost 5‰) and high $\delta^{18}O$ values (between +0·8 and +5·47‰) of the Mediana dolomite samples (Fig. 7) was expected in a hydrological system dominated by rainfall, groundwater input and evaporation. The oxygen isotopic composition of lake water is controlled by (1) the isotopic composition of the rainfall, its seasonality, temperature and quantity, (2) relative humidity, (3) potential evaporation and (4) groundwater inflow (Talbot, 1990; Chivas *et al.*, 1993; Valero-Garcés *et al.*, 1997). If it is assumed that the bulk of the carbonate precipitates at approximately the same time during the annual cycle, when the range of surface temperatures is about the same each year, variations in δ^{18}O values may primarily represent past changes in the isotopic composition of the water. However, the decoupling between the isotopic and chemical compositions clearly indicates that the δ^{18}O curve cannot be interpreted as a function of simple evaporation from a closed system. Isotopically light waters can be consistent with increased salinity if lake levels were so low that annual floods reset the system.

In the absence of major changes in water sources, decreasing δ^{18}O suggest a more positive hydrological balance, a colder mean air temperature, a warmer lake-water temperature, or a combination thereof (Talbot, 1990; Valero Garcés *et al.*, 1997). Large negative δ^{18}O shifts, such as the one at the 12–9 cm depth interval, most probably represent an increased input of isotopically lighter waters. This could be related to higher effective moisture, a change in the seasonality or rain source, or an increase in groundwater input. As cooler precipitation is isotopically lighter, a decrease in the mean annual temperature or a contribution of more winter precipitation would lighten the isotopic composition of the lake water. The negative δ^{18}O shift at the transition between the Lower and Middle sections correlates with sedimentological, palynological and geochemical changes that suggest an increase in lake water level.

The small δ^{18}O range in the Middle section could be an indication of an isotopic steady state. The presence of high salt concentrations reduces the evaporation rate and affects the isotope fractionation process, because the isotopic thermodynamic fractionation factor becomes a function not only of temperature, but also of salinity and composition (Gat, 1980; Gonfiantini, 1986). Craig *et al.* (1963) demonstrated that a residual evaporated water body reaches a steady-state isotopic composition that does not explicitly depend on the evaporation rate during the final drying-up process in conditions of high relative humidity. This steady-state value represents the isotopic composition of a closed pond under the prevailing climatic conditions in the area. Consequently, the isotopic response to fluctuations in evaporation rate, salinity, and other hydrological parameters could have been buffered during these periods. This scenario, however, does not fully explain why the δ^{18}O curve does not show some of the large hydrological events, such as flooding and complete desiccation, that are recorded by the other sedimentary and geochemical indicators.

Carbon isotopes. Changes in the δ^{13}C of authigenic lacustrine carbonate and lacustrine organic matter reflect variations in the dissolved inorganic carbon (DIC) pool, controlled by input and biological processes, mainly respiration and photosynthesis (Hakänsson, 1985; Talbot & Kelts, 1990). Fluctuations in groundwater input and composition, changes in the limnological and biological parameters of the lake and in the early diagenetic processes are important to the isotopic carbon budget of lakes (Kelts, 1988; Lyons *et al.*, 1994). The dissolved carbon species in the Salada Mediana come from: (i) groundwater and runoff that incorporated dissolved carbon through dissolution of carbonates, decomposition and respiration of plants, and atmospheric CO_2; (ii) equilibration of atmospheric CO_2 with the lake waters; and (iii) oxidation of lacustrine and terrestrial organic matter in the sediments (Fig. 8). There are no groundwater δ^{13}C data from the Mediana area; the available data from the Monegros aquifers show light DIC isotopic compositions (δ^{13}C between −12·7 and −19·7‰ PDB) and no correlation with salinity (García-Vera, 1996). Increasing groundwater inflow could explain the decreasing δ^{13}C trend during periods of decreasing δ^{18}O values (12–9 cm depth).

Overall, δ^{13}C values of carbonates in Salada Mediana are relatively high (−4·3 to −1·1‰) compared with those precipitated in freshwater systems. In arid environments with poor soils and low vegetation cover, the influence of atmospheric CO_2 vs. plant respiration CO_2 in the aquifers and soils increases, and consequently the δ^{13}C DIC in groundwaters and run-off is relatively enriched compared with more vegetated areas (Cerling, 1991). Furthermore, the dominance of bacterial mats as the main organic producers in Mediana and evaporative effects could also contribute to these relatively high values. Cyanobacterial photosynthesis preferentially extracts $^{12}CO_2$ from the micro-environment and, consequently, carbonate precipitated in such environments is isotopically heavier than other carbonate precipitated in the lake (Andrews *et al.*, 1997). Evaporation could also play a role, because extreme ^{13}C enrichment in evaporite brines have been reported in the Dead Sea (Stiller *et al.*, 1985). Some of the trends observed in the $\delta^{13}C$ record could reflect the interplay of lake productivity and evaporation (residence time evolution). Increased photosynthesis produces relatively ^{13}C-enriched carbonates, due to productivity-driven enrichment in DIC (Aravena *et al.*, 1992; Meyers, 1994). Longer residence time and greater evaporation also result in ^{13}C enrichment (Talbot, 1990; Talbot & Kelts, 1990). Decreasing organic productivity in the lower part of the Middle section (107–60 cm depth), parallel to the increasing dominance of saline mud flats, could account for the decreasing $\delta^{13}C$ trend. Slightly higher $\delta^{13}C$ dolomite values related to lower organic matter content (Lower section, 60–45 cm and 30–19 cm depth intervals) suggest a dominance of residence time evolution factors in the carbon isotopic budget. The decreasing trend in the 45–30 cm depth interval corresponds to increasing organic-matter content, low $\delta^{13}C$ o.m. values, and a slight increase in $\delta^{18}O$ dolomite. These indicators are consistent with stronger evaporative effects during periods of expanded mud flats.

Carbon isotopic ratios of bulk organic matter provide palaeolimnological information, such as organic matter sources, lake palaeoproductivity, and changes in vegetation and catchment hydrology (Aravena *et al.*, 1992; Meyers, 1994). The general correspondence of heavier $\delta^{13}C$ o.m. intervals with saline pan facies (107–70 cm, 60–50 cm and 12–0 cm depth intervals), and the absence of parallel trends in $\delta^{13}C$ dolomite values suggest that changes in the particulate organic matter and not in the DIC are the main controls of the isotopic composition of the bulk organic matter. The sharp positive shifts in $\delta^{13}C$ o.m. (up to 4‰) are not reflected in the $\delta^{13}C$ dolomite curve, suggesting that the change in the type of organic matter in the sediments did not greatly affect the DIC from which carbonate precipitated. The different behaviour of the $\delta^{13}C$ dolomite and $\delta^{13}C$ o.m. curves could be due to limited post-depositional recycling of organic matter in the saline pan. Most of the organic matter incorporated into the sediments would be particulate, from cyanobacterial mats and terrestrial plant fragments. The predominant reducing conditions in the Salada Mediana favour organic matter preservation and, consequently, the $\delta^{13}C$ o.m. curve reflects the relative input of cyanobacterial lacustrine (−12 to −11‰) compared with terrestrial (−20 to −24‰) organic matter. The negative $\delta^{13}C$ o.m. excursions during the playa lake in the Middle section occur in clay-rich saline mud flat facies (60–80 cm and 50–30 cm intervals). These intervals correspond with periods of dominant halophytic vegetation in the Salada Mediana (Fig. 4). The slight increase in $\delta^{13}C$ dolomite at 60 cm is consistent with an increase in lake productivity during a saline pan period. However, heavy $\delta^{13}C$ o.m. compositions during the lower cycle of the Middle section, and increasing values in the Upper section correspond with decreasing $\delta^{13}C$ carbonate values. Sedimentary and geochemical indicators point to deposition in a receding saline pan during the top of the Middle section (30–19 cm depth), although the $\delta^{13}C$ o.m. are heavier than other intervals interpreted as deposition in a saline mud flat. An increase in lacustrine bacterial and algal organic matter input during the saline lake periods was probably the main driving force for the positive $\delta^{13}C$ o.m. excursions.

The clear covariance between $\delta^{13}C$ and $\delta^{18}O$ dolomite values is a reflection of hydrologically closed conditions, according to Talbot (1990) and Li & Ku (1997). However, some intervals are more strongly covariant than others. The Lower section of the saline lake deposits, which has the heaviest isotopic compositions, shows the clearest covariant trend. Evaporation, increased residence time, and enhanced exchange with atmospheric CO_2 in the saline lake would isotopically enrich waters and DIC. Periods of abrupt and rapid hydrological change in the Salada Mediana, such as the lower part of the Upper section (12–9 cm), also show clear covariant patterns, with carbonates depleted in both heavy isotopes. Covariance is weaker in the playa lake deposits, because of the larger $\delta^{13}C$ variability and the small $\delta^{18}O$ range.

Depositional and hydrological evolution

Sedimentary facies, elemental composition, stable isotope values and pollen data allow the determination of a depositional history for the Salada Mediana. Several AMS dates confirm a Lateglacial age for the Lower and Middle sections of the core, and the presence of unsupported ^{210}Pb in the Upper section indicates a modern age for the upper sediments (Valero-Garcés *et al.*, 2000). The Holocene sequence has been eroded, probably during some of the mid- and late Holocene arid periods that occurred in the Iberian Peninsula (Valero-Garcés *et al.*, 1998). As shown in other lakes in the Ebro basin, sedimentation

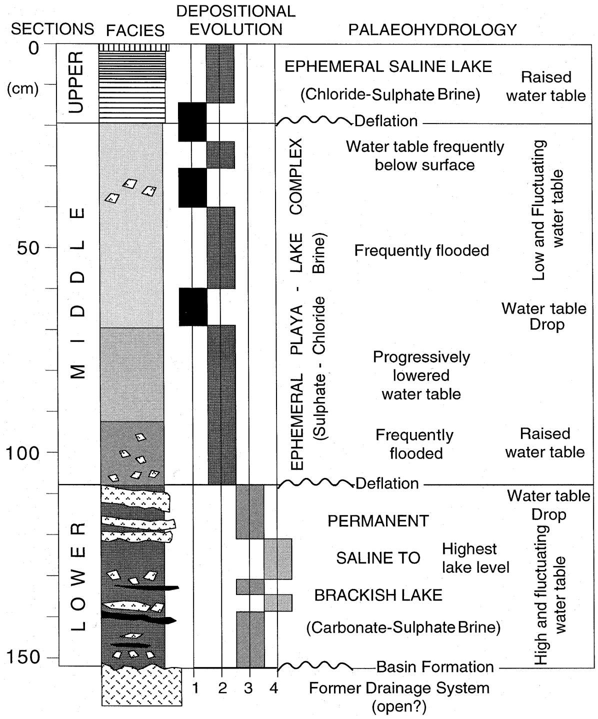

Fig. 10. Depositional evolution and palaeohydrology of the Salada Mediana. Dominant lacustrine subenvironments (shown in the 'depositional evolution' column): 1. saline mud flats; 2. saline pan-ephemeral shallow saline lake; 3. permanent saline lake; 4. permanent brackish lake.

resumed only a few centuries ago with the onset of more humid periods (Davis, 1994; Burjachs *et al.*, 1996). The depositional history is divided into three cycles, based on the presence of sedimentary unconformities, and each cycle is subdivided into several subunits based upon palaeohydrological and palaeoenvironmental information (Fig. 10).

Upper Pleistocene saline lake (Lower section). A karstic depression in the Miocene gypsum substratum led to development of a permanent saline lake. The carbonate-rich muds with intercalated gypsum laminae of the Lower section were deposited in a permanent sulphate–carbonate saline lake with more diluted (carbonate-dominated) and more concentrated (gypsum-dominated) brine stages. The intervals with abundant large gypsum crystals and clusters (particularly in the 121–107 cm depth interval) suggest periods of increased intrasediment gypsum formation in a mud flat.

Geochemical indicators (the lowest values of boron, and relatively low values of lithium and strontium) and palynological evidence (abundance of *Corylus*, and presence of *Myriophyllum* sp.) indicate that carbonate-rich intervals were deposited in a brackish-lake system, probably the freshest of the whole sequence. Increased salinity during more arid episodes was conducive to gypsum precipitation from the brine and as efflorescent crust and intrasediment crystals. The low $\delta^{13}C$ o.m. values suggest that the carbon budget was not dominated by cyanobacterial mats. Pollen data support the sedimentological interpretation of a deeper brackish lake without cyanobacterial mats. High arboreal pollen concentrations (Fig. 4), indicate a more vegetated watershed than later. The high $\delta^{18}O$ values, and the strong isotope covariance point to long residence time, and isotopically evolved waters. Isotopically enriched carbonates during saline lake stages (Lower section) compared with playa-lake stages (Middle section) could reflect longer residence times and greater volumes of evaporated water during periods of higher lake level. Isotopically heavy, but relatively low-salinity lake water, could have also been attained by changes in the moisture sources or seasonality (more summer precipitation). A period of desiccation resulted in the formation of intrasediment gypsum crusts, and probably sediment deflation.

Upper Pleistocene saline pan – saline mud environments (Middle section). The abrupt increase in organic matter and carbonate content at the onset of the Middle section suggests that an unconformity formed after deposition of the gypsum-rich interval (121–107 cm). The weakly banded nature of the sediments in the lower part of the Middle section, and the relatively high organic matter and low carbonate contents, are consistent with an ephemeral shallow saline lake – saline pan where evaporite crusts may have formed, but were dissolved by the input of more dilute waters (saline pan). The increase in lake level allowed colonization of the saline pan by bacterial-algal mats, and the surrounding saline mud flats by halophytic vegetation. The dominance of bacterial mats as primary producers in the saline pan increased the $\delta^{13}C$ o.m. values. Higher quartz contents in the lower part (107–100 cm depth) suggest increased run-off during more frequent flooded stages.

Small changes in topography and hydrological fluctuations controlled the extent of the saline pan and saline mud flat. The increase in boron, lithium, sodium and clay contents, the abundance of *Chenopodiaceae* pollen, and a sharp decrease in $\delta^{13}C$ o.m. values at this interval reflect the progressive dominance of desiccation (saline mud flat) compared with flooded (saline pan) stages. However, dolomite isotope composition ($\delta^{13}C$ and $\delta^{18}O$) slightly decreased during deposition of the lower cycle. Isotopically lighter waters and increased salinity, as interpreted from chemical indicators, can be attained in a number of scenarios: annual floods that reset the system and dissolve previously precipitated salts, steady-state isotopic processes, increase in the relative groundwater ratio, and changes in moisture source or seasonality.

After the arid period recorded in the 60–50 cm depth interval, saline pan environments dominated again. Increased water levels during deposition of the lower part of this cycle produced a sharp decrease in sodium, boron and lithium content in the sediments, and shrinkage of the mud flats. Higher quartz content, and *Ruppia* peaks indicate increased run-off during more frequent flooded stages, and more permanent saline water. An increase in *Corylus* also indicates moister climatic conditions. The $\delta^{18}O$ curve shows similar values during this salinity fluctuation, suggesting low-salinity waters and an isotopic steady-state for the lake. The intervals of increased isolated gypsum crystals and clay mineral content in the middle and upper parts of this section (intervals at about 45–30 cm, and at the transition to the Upper section) indicate more frequent desiccation periods and increased saline mud flat development. Decreased *Ruppia* content and an increase in *Chenopodiaceae* pollen confirm this trend.

Late Holocene saline pan – saline lake (Upper section). The presence of calcite in the Upper section indicates a different brine composition (higher alkalinity, lower Mg/Ca ratio) which could indicate lower salinity. Preservation of fine lamination, and an increase in quartz content suggest deposition in an ephemeral saline lake or a saline pan with significant periods of flooding. Changes in facies and geochemistry indicate the presence of a sedimentary hiatus, which is confirmed by chronostratigraphic data (Valero-Garcés *et al.*, 2000). The Holocene sequence is missing and the upper sequence only reflects sedimentation during the last few centuries.

Relatively low $\delta^{13}C$ o.m. values, and an increase in *Chenopodiaceae* pollen indicate that saline mud flats covered a significant part of the lake basin. The changes in vegetation and sediment geochemistry predated a large negative shift in the isotopic composition of the brine. The large decrease in $\delta^{13}C$ and $\delta^{18}O$ values in carbonate and the onset of an increasing trend in $\delta^{13}C$ o.m. indicate a major hydrological and limnological change in the lake during the 12–9 cm interval. Precipitation of calcite, and lighter $\delta^{18}O$ and $\delta^{13}C$ (dolomite) values are consistent with an increase in the water level during deposition of the Upper section, although higher amounts of sulphates (gypsum, bloedite and thenardite), and relatively high values of chemical salinity indicators (sodium, boron) attest to a concentrated brine. The progressive enrichment in the most soluble salts during residual stages of closed basin evolution, and the dissolution of previously precipitated salts, explain higher chemical concentrations in isotopically lighter waters. A similar increase in water levels in the recent was noted in several lake records in the Ebro basin (Davis, 1994), suggesting a regional climatic trend.

CONCLUSIONS

At present, the Salada Mediana consists of ephemeral saline pan and saline mud flat environments, which alternate during the rainy and dry seasons. The modern brine is of $Na^{+} – Mg^{2+} – SO_4^{2-} – (Cl^{-})$ type, sulphate dominated, with low carbonate and calcium contents, and high Mg/Ca ratios. The modern sediments are composed of organic matter (dominated by cyanobacterial mats), carbonates (dolomite, Mg-calcite, calcite), evaporites (mostly gypsum and mirabilite; subsidiary thenardite, bloedite and halite), and a minor silicate fraction (quartz and clays, transported by the wind). Cyanobacterial mats cover the lake floor almost completely during wet periods, and become partially encrusted with evaporites and eroded during dry periods. Sedimentological and isotopic data favour primary precipitation of dolomite and calcite from the lake or interstitial brines, but calcite may also form as a result of sulphate reduction. A water survey confirms that evaporation and rainfall are the main factors controlling the isotopic composition of the lake water.

Sedimentary facies, geochemical and isotopic compositions and palynological assemblages provide a coherent depositional history of the Salada Mediana. The Lower and Middle sections represent a Late Pleistocene, pre-Holocene sequence. The Lower section was deposited in a sulphate–carbonate saline lake that ended with a period of desiccation, and probably basin floor deflation.

Subsequent deposition took place in a playa lake system dominated by saline pan and saline mud flat environments. Two cycles of lowered water table and saline mud flat expansion occurred. The Holocene sediments were eroded, and sedimentation resumed only a few centuries ago. Saline pan environments dominated in the Upper section, where laminated, calcite-bearing, sulphate-rich sediments were deposited.

The Salada Mediana sedimentary and isotopic sequences provide a depositional model for small, hydrologically closed Cl^{-}–$SO_4^{=}$–Na^{+}–Mg^{2+} playa lakes that evolved under fluctuating, but generally semiarid climatic conditions. The different depositional environments represent fluctuations in the water table in response to climate change. During periods of more frequent flooding, the most soluble of the previously precipitated salts dissolved, causing abrupt increases in salinity and changes in brine chemistry that were not paralleled by the isotopic composition of the waters. The de-coupling of salinity reconstructions based on bulk-sediment geochemistry and the $\delta^{18}O$ curve underlines the importance of evaporite recycling in the hydrology and hydrochemistry of groundwater-fed playa lakes.

ACKNOWLEDGEMENTS

This research was partly funded by the National Science Foundation, USA, under the EAR 941-8657 programme, and by the EEAD-CSIC project number Z-5-96. We are grateful to Loren Hoppe and Concha Arenas for coring assistance. We appreciate Juan Marín (Estación Experimental Aula Dei-CSIC, Zaragoza) for his assistance with SEM observations. We thank Michael Talbot and Joe Smoot for their very thoughtful and comprehensive reviews, and editor Peter Mozley for final revision of the text, which led to a considerable improvement of the manuscript. This is Limnological Research Center contribution number 527.

REFERENCES

Al-Aasm, I.S., Taylor, B.E. and **South, B.** (1990) Stable isotope analysis of multiple carbonate samples using selective acid extraction. *Chem Geol.*, **80,** 119–125.

Al-Hashimi, W. and **Hemingway, J.E.** (1974) Recent dolomitization and the origin of the rusty crusts of Northumberland: a reply. *J. Sed. Petrol.*, **44,** 271–274.

Andrews, J.E., Riding, R. and **Dennis, P.F.** (1997) The stable isotope record of environmental and climatic signals in modern terrestrial microbial carbonates from Europe. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **129,** 171–189.

Aravena, R., Warner, B.G., MacDonald, G.M. and **Hanf, K.I.** (1992) Carbon isotope composition of lake sediments in relation to lake productivity and radiocarbon dating. *Quatern. Res.*, **37,** 333–345.

Arenas, C., Casanova, J. and **Pardo. G.** (1997) Stable-isotope characterization of the Miocene lacustrine systems of Los Monegros (Ebro Basin, Spain): palaeogeographic and palaeoclimatic implications. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **128,** 133–155.

Auqué, L.F., Vallés, V., Zouggari, H., López, P.L. and **Bourrié, G.** (1995) Geoquímica de las lagunas saladas de los Monegros (Zaragoza). I Determinación experimental de los efectos del reequilibrio mirabilita-solución con la temperatura en un sistema natural. *Estud. Geol.*, **51,** 243–257.

Benito, G., Pérez-González, Gutiérrez, F. and **Machado, J.** (1998) River response to Quaternary subsidence due to evaporite solution (Gállego River, Ebro Basin, Spain). *Geomorphology*, **22,** 243–263.

Burjachs, F., Rodó, X. and **Comín, F.A.** (1996) Gallocanta: ejemplo de secuencia palinológica en una laguna efímera. In: *Estudios Palinológicos, XI Simposio de Palinología* (Ed. B. Ruiz Zapata), pp. 25–29. Universidad de Alcalá, Alcalá de Henáres.

Cerling, T.E. (1984) The stable isotopic composition of modern soil carbonate and its relationship to climate. *Earth Planet. Sci. Lett.*, **71,** 229–240.

Cerling, T.E. (1991) Carbon dioxide in the atmosphere: evidence from Cenozoic and Mesozoic paleosols. *Am. J. Sci.*, **291,** 377–400.

Chivas, A.R., De Deckker, P., Cali, J.A., Chapman, A., Kiss, E. and **Shelley, M.G.** (1993) Coupled stable-isotope and trace-element measurements of lacustrine carbonates as paleoclimatic indicators. In: *Climate Change in Continental Isotopic Records* (Eds P.K. Swart, K.C. Lohmann, J. McKenzie and S. Savin), *Geophys. Monogr.*, **78,** 113–121.

Comín, F.A. and **Alonso, M.** (1988) Spanish salt lakes: their chemistry and biota. *Hydrobiologia*, **158,** 237–246.

Comín, F.A., Julià, R., Comín, M.P. and **Plana, F.** (1990) Hydrogeochemistry of Lake Gallocanta (Aragón, NE Spain). *Hydrobiologia*, **197,** 51–66.

Craig, H., Gordon, L.I. and **Horibe, Y.** (1963) Isotope exchange effects in the evaporation of water: 1. Low temperature experimental results. *J. Geophys. Res.*, **68,** 5079–5087.

Davis, B.A.S. (1994) *Paleolimnology and Holocene environmental change from endoreic lakes in the Ebro Basin, northeast Spain.* Unpublished PhD dissertation, University of Newcastle-Upon-Tyne, UK.

De Deckker, P. and **Last, W.M.** (1988) A newly discovered region of modern dolomite deposition in western Victoria, Australia. *Geology*, **16,** 29–32.

De Deckker, P. and **Last, W.M.** (1989) Modern dolomite in continental evaporitic playa lakes in western Victoria, Australia. *Sed. Geol.*, **64,** 223–238.

Deines, P. (1980) The isotopic composition of reduced organic carbon. In: *Handbook of Environmental Isotope Geochemistry, 1. The Terrestrial Environment* (Eds P. Fritz and J.Ch. Fontes), pp. 329–406. Elsevier, Amsterdam.

De la Peña, J.A. and **Marfil, R.** (1986) La sedimentación salina actual en las lagunas de la Mancha: una síntesis. *Cuad. Geol. Ibérica*, **10,** 235–270.

Friedli, H., Lotscher, H., Oeschger, H. and **Stauffer, B.** (1986) Ice core record of the $^{13}C/^{12}C$ ratio of atmospheric CO_2 in the past two centuries. *Nature*, **324,** 237–238.

García-Vera, M.A. (1996) *Hidrogeología de zonas endorreicas en climas semiáridos: aplicación a Los Monegros (Zaragoza y Huesca).* Publicaciones del Consejo de Protección de la Naturaleza de Aragón, Zaragoza.

Gat, J.R. (1980) Isotope hydrology of very saline lakes. In: *Hypersaline Brines and Evaporitic Environments* (Ed. A. Nissenbaum), *Dev. Sed.*, **28,** 1–7.

Giralt, S., Burjachs, F., Roca, J.R. and **Julià, R.** (1999) Late Glacial to Early Holocene environmental adjustment in the Mediterranean semi-arid zone of the Salines playa-lake (Alicante, Spain). *J. Paleolimnol.*, **21,** 449–460.

Goldsmith, J.R. and **Graf, D.L.** (1958a) Structural and compositional variations in some natural dolomites. *J. Geol.*, **66,** 678–693.

Goldsmith, J.R. and **Graf, D.L.** (1958b) Relation between lattice constraints and composition of the Ca-Mg carbonates. *Am. Miner.* **43,** 84–101.

Goldsmith, J.R., Graf, D.L. and **Heard, H.C.** (1961) Lattice constants of calcium-magnesium carbonates. *Am. Mineral.*, **46,** 453–457.

Gonfiantini, R. (1986) Environmental isotopes in lake studies. In: *Handbook of Environmental Isotope Geochemistry Vol. 2 The Terrestrial Environment, B* (Eds P. Fritz and J.Ch. Fontes), pp. 113–168. Elsevier, Amsterdam.

Hakänsson, S. (1985) A review of various factors influencing the stable carbon isotope ratio of organic lake sediments by the change from glacial to postglacial environmental conditions. *Quatern. Sci. Rev.*, **4,** 135–146.

Hardie, L.A., Smoot, J.P. and **Eugster, H.P.** (1978) Saline lakes and their deposits: a sedimentological approach. In: *Modern and Ancient Lake Sediments* (Eds A. Matter and M.E. Tucker), *IAS Spec. Publ.*, **2,** 7–41.

Irwin, H., Curtis, C. and **Coleman, M.** (1977) Isotopic evidence for source of diagenetic carbonates formed during burial of organic-rich sediments. *Nature*, **269,** 209–213.

Kelts, K. (1988) Environments of deposition of lacustrine petroleum source rocks: an introduction. In: *Lacustrine Petroleum Source Rocks* (Eds A.J. Fleet, K. Kelts and M.R. Talbot), *Geol. Soc. Lond. Spec. Publ.*, **40,** 3–26.

Kim, S.T. and **O'Neil, J.R.** (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. *Geochim. Cosmochim. Acta*, **61,** 3461–3475.

Komor, S.C. (1994) Bottom-sediment chemistry in Devils Lake, northeastern North Dakota. In: *Sedimentology and Geochemistry of Modern and Ancient Saline Lakes* (Ed. R.W. Renaut and W. Last), *Soc. Econ. Paleont. Miner. Spec. Publ.*, **50,** 21–32.

Kyle, R.J. (1994) Evaporites, evaporitic processes and mineral resources. In: *Evaporites, Petroleum and Mineral Resources* (Ed. J. Melvin), *Dev. Sedimentol.*, **50,** 477–533.

Land, L.S. (1985) The origin of massive dolomite. *J. Geol. Educ.*, **33,** 112–125.

Last, W.M. (1990) Lacustrine dolomite – an overview of modern, Holocene, and Pleistocene occurrences. *Earth-Sci. Rev.*, **27,** 221–263.

Last, W.M. (1993) Geolimnology of Freefight Lake: an unusual hypersaline lake in northern Great Plains of western Canada. *Sedimentology*, **40,** 431–448.

Li, H.C. and **Ku, T.L.** (1997) $\delta^{13}C$ -$\delta^{18}O$ covariances as paleohydrological indicator for closed-basin lakes. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **133,** 69–80.

Lowenstein, T.K. and **Hardie, L.A.** (1985) Criteria for the recognition of salt-pan evaporites. *Sedimentology*, **32,** 627–644.

Lyons, W.B., Hines, M.E., Last, W.M. and **Lent, R.M.** (1994) Sulfate reduction rates in microbial mat sediments of differing chemistries: implications for organic carbon preservation in saline lakes. In: *Sedimentology and Geochemistry of Modern and Ancient Saline Lakes* (Eds R.W. Renaut and W. Last), *Soc. Econ. Paleont. Miner. Spec. Publ.*, **50,** 13–20.

Mata, M.P., Perez, A. and **Lopez-Aguayo, F.** (1988) Mineralogía del perfil de 'La Muela', Terciario del sector central de la depresion del Ebro (provincia de Zaragoza). *Estud. Geol.*, **44,** 135–143.

Mayayo, M.J., Bauluz, B., López-Galindo, A. and **González-López, J.M.** (1996) Mineralogy and geochemistry of the carbonates in the Calatayud Basin (Zaragoza, Spain). *Chem. Geol.*, **130,** 123–136.

McCrea, J.M. (1950) On the isotopic chemistry of carbonates and a paleotemperature scale. *J. Chem. Phys.*, **18,** 849–857.

Meyers, P.A. (1994) Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem Geol.*, **114,** 289–302.

Mingarro, F., Ordoñez, S., López de Azcona, M.C. and **García del Cura, M.A.** (1981) Sedimentoquímica de las lagunas de Los Monegros y su entorno geológico. *Bol. Geol. Min.*, **92,** 171–195.

Navas, A. and **Machín, J.** (1997) Assessing erosion risks in the gypsiferous steppe of Litigio (NE Spain). An approach using GIS. *J. Arid Environ.*, **37,** 433–441.

Ordoñez, S., Sánchez Moral, S., García del Cura, M.A. and **Rodriguez Badiola, E.** (1994) Precipitation of salts from Mg^{2-} – (Na^{+}) – SO_4^{2-} – Cl^{-} playa-lake brines: the endorheic saline ponds of La Mancha, Central Spain. In: *Sedimentology and Geochemistry of Modern and Ancient Saline Lakes* (Eds R.W. Renaut and W. Last), *Soc. Econ. Paleont. Miner. Spec. Publ.*, **50,** 61–71.

Pérez, A., Muñoz, A., Pardo, G. and **Villena, J.** (1989) Evolución de los sistemas lacustres del margen ibérico de la Depresión del Ebro (sectores central y occidental) durante el Mioceno. *Acta Geol. Hisp.*, **24,** 243–257.

Pueyo-Mur, J.J. (1979) La precipitación evaporítica actual en las lagunas saladas del área Bujaraloz, Sástago, Caspe, Alcañiz y Calanda (provincias de Zaragoza y Teruel). *Rev. Inst. Inv. Geol. Diput. Prov. Barcelona*, **33,** 5–56.

Pueyo-Mur, J.J. (1980) Procesos diagenéticos observados en las lagunas de tipo playa en la zona Bujaraloz – Alcañiz (provincias de Zaragoza y Teruel). *Rev. Inst. Inv. Geol. Diput. Prov. Barcelona*, **34,** 195–207.

Pueyo-Mur, J.J. and **De la Peña, J.A.** (1991) Los lagos salinos españoles. Sedimentología, hidroquímica y diagénesis. In: *Génesis de Formaciones Evaporìticas. Modelos Andinos E Ibéricos* (Ed. J.J. Pueyo), pp. 163–192. Universidad de Barcelona, Barcelona.

Pueyo-Mur, J.J. and **Inglés-Urpinell, M.** (1987a) Magnesite formation in recent playa lakes, Los Monegros, Spain. In: *Diagenesis of Sedimentary Sequences* (Ed. J.D. Marshall), *Geol. Soc. Lond. Spec. Publ.*, **36,** 119–122.

Pueyo-Mur, J.J. and **Inglés-Urpinell, M.** (1987b) Substrate mineralogy, pore brine compositions and diagenetic processes in the playa lakes of Los Monegros and Bajo Aragón, Spain. In: *Geochemistry and Mineral Formation in the Earth Surface* (Eds R. Rodríguez-Clemente and Y. Tardy), pp. 351–372. CSIC-CNRS, Granada.

Quirantes, J. (1978) *Estudio Sedimentológico Y Estratigráfico Del Terciario Continental de Los Monegros*. Instituto Fernando el Católico, Zaragoza.

Reeves, C.C. and **Parry, W.T.** (1965) Geology of West Texas pluvial lake carbonates. *Am. J. Sci.*, **263,** 606–615.

Renaut, R.W. and **Last, W.M.** (1994) *Sedimentology and geochemistry of modern and ancient saline lakes. SEPM Spec. Publ.*, **50,** Tulsa.

Romanek, C.S., Grossman, E.L. and **Morse, J.W.** (1992) Carbon isotopic fractionation in synthetic aragonite and calcite: Effects of temperature and precipitation rate. *Geochim. Cosmochim. Acta*, **5,** 419–430.

Rosen, M. (1994) The importance of groundwater in playas: a review of playa clasifications and the sedimentology and hydrology of playas. *Spec. Pap. Geol. Soc. Am.*, **289,** 1–18.

Rosen, M.R., Miser, D.E., Starcher, M.A. and **Warren, J.K.** (1989) Formation of dolomite in the Coorong region, south Australia. *Geochim. Cosmochim. Acta*, **53,** 661–669.

Rosenbaum, J. and **Sheppard, S.M.F.** (1986) An isotopic study of siderites, dolomites and ankerites at high temperatures. *Geochim. Cosmochim. Acta*, **50,** 1147–1150.

Runnells, D.D. (1970) Error in X-ray analysis of carbonates due to solid solution variation in the composition of component minerals. *J. Sed. Petrol.*, **40,** 1158–1166.

Salvany, J.M. and **Ortí, F.** (1994) Miocene glauberite deposits of Alcanadre, Ebro Basin, Spain: Sedimentary and diagenetic processes. In: *Sedimentology and Geochemistry of Modern and Ancient Saline Lakes* (Eds R. Renaut and W. Last), *SEPM Spec. Publ.*, **50,** 203–215.

Salvany, J.M., Muñoz, A. and **Pérez, A.** (1994) Nonmarine evaporitic sedimentation and associated diagenetic processes of the southwestern margin of the Ebro Basin (Lower Miocene), Spain. *J. Sed. Res.*, **64,** 190–202.

Sánchez-Navarro, J.A., Pérez, A., Coloma, P. and **Martínez-Gil, F.J.** (1998) Combined effects of groundwater and eolian processes in the formation of the northernmost closed saline depression of Europe, north-east Spain. *Hydrol. Process.*, **12,** 813–820.

Smoot, J.P. and **Castens-Seidell, B.** (1994) Sedimentary features produced by efflorescent salt crusts, Saline Valley and Death Valley, California. In: *Sedimentology and Geochemistry of Modern and Ancient Saline Lakes* (Eds R. Renaut and W. Last), *SEPM Spec. Publ.*, **50,** 73–90.

Smoot, J.P. and **Lowenstein, T.** (1991) Depositional environments of non-marine evaporites. In: *Evaporites, Petroleum and Mineral Resources* (Ed. J. Melvin), *Dev. Sedimentol.*, **50,** 189–348.

Soriano, M.A. (1990) *Geomorfología Del Sector Centromeridional de la Depresión Del Ebro*. Institución Fernando el Católico, Zaragoza.

Stiller, M., Rounick, J.S. and **Shasha, S.** (1985) Extreme carbon – isotope enrichments in evaporite brines. *Nature*, **316,** 434–435.

Talbot, M.R. (1990) A review of the palaeohydrological interpretation of carbon and oxygen isotopic ratios in primary lacustrine carbonates. *Chem. Geol. (Isot. Geosci. Sect.)*, **80,** 261–279.

Talbot, M.R. and **Kelts, K.** (1990) Paleolimnological signatures from carbon and oxygen isotopic ratios in carbonates from organic carbon – rich sediments. In: *Lacustrine Basin Exploration – Case Studies and Modern Analogs* (Ed. B.J. Katz), *Am. Assoc. Petrol. Geol. Mem.*, **50,** 99–112.

Torres-Ruiz, J., López-Galindo, A., González-López, M. and **Delgado, A.** (1994) Geochemistry of Spanish sepiolite-paligorskite deposits: Genetic considerations based on trace elements and isotopes. *Chem. Geol. (Isot. Geosci. Sect.)*, **112,** 221–247.

Valero Garcés, B., Kelts, K. and **Ito, E.** (1995) Oxygen and carbon isotope trends and sedimentological evolution of a meromictic and saline lacustrine system: the Holocene Medicine Lake Basin, North American Great Plains, USA. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, **117,** 253–278.

Valero Garcés, B.L., Laird, K.R., Fritz, S., Kelts, K., Ito, E. and **Grimm, E.R.** (1997) Holocene climate in the northern Great Plains inferred from sediment stratigraphy, stable isotopes, carbonate geochemistry, diatoms and pollen at Moon Lake, North Dakota. *Quatern. Res.*, **48,** 359–369.

Valero-Garcés, B.L., Zeroual, E. and **Kelts, K.** (1998) Arid phases in the western Mediterranean region during the Last Glacial Cycle reconstructed from lacustrine records. In: *Paleohydrology and Environmental Change* (Eds G. Benito, V.R. Baker and K.J. Gregory), pp. 67–80. Wiley & Sons, London.

Valero-Garcés, B.L., González-Sampériz, P., Delgado-Huertas, A., Navas, A., Machín, J. and **Kelts, K.** (2000) Lateglacial and Late Holocene environmental and vegetational change in Salada Mediana, Central Ebro Basin, Spain. *Quatern. Int.*, (in press).

van Zuidam, R.A. (1980) Un levantamiento geomorfológico de la región de Zaragoza. *Geographicalia*, **6,** 103–134.

Manuscript received 16 July 1998;
revision accepted 17 March 2000