



Holocene paleohydrology of playa lakes in northern and central Spain: a reconstruction based on the mineral composition of lacustrine sediments

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Abstract

The focus of this study is the reconstruction of Holocene limnic conditions of playa lakes in central Spain using inorganic components of their sediments. It is demonstrated that the mineralogical sediment characters provide valuable paleoenvironmental information: If dolomites originate from authigenic precipitation or early diagenetic dolomitization, the Mg–Ca-ratio of dolomites, derived from the position of dolomite's major X-ray diffraction line, turns out to be an indicator for the reconstruction of paleosalinity. In contrast, the concentrations of carbonates and sulphatic evaporites and their changing proportion to siliciclastic sediments point to changing depositional environments. The comparison of investigations from different playa lakes and drainage basin systems shows that the interpretation of mineralogical sediment features always has to consider the petrographic, hydrologic, and geomorphic features of the catchment. As for the lacustrine sediments investigated there are no data available yet, a preliminary chronological framework is derived by comparison with results from neighbouring areas. Based on this the hypothesis is put forward that during the so-called *Little Ice Age* subhumid environmental conditions occurred over the central part of the Iberian Peninsula, while today climatic conditions are dry-subhumid to subarid. Also for times older than the *Subatlantic* distinct changes of environmental conditions are noticed, but various hiatuses in the sediments make correlation difficult. © 2000 Elsevier Science Ltd and INQUA. All rights reserved.

1. Introduction

Core-based paleoenvironmental investigations of lacustrine sediments are mostly dominated by micro-paleontological, mainly pollen-based, studies. The focus of this study is the reconstruction of Holocene limnic and paleohydrological conditions of today playa lakes in central Spain using the mineralogical composition of their sediments.

Lake-level fluctuations of endorheic basins are among the best indicators for climatic fluctuations during the Holocene, determined by relief, geology, soils, vegetation, and paleohydrology of their watersheds as the main factors (Street-Perrott, 1980). The magnitude and frequency of lake-level fluctuations can be reconstructed from geomorphological and sedimentological analyses (e.g. beach ridges, beach terraces, cliff edges) in conjunction with knowledge of the present-day water balance of the lake (Street-Perrott and Harrison, 1985). In addition

to these indicators in the shore area, the mineralogical properties of sediments from the playa lakes allow the reconstruction of lake phases (ephemeral, perennial) and paleolimnic environments (i.e. salinity, brine composition). Apart from the deposition of allochthonous detritus, lacustrine sediments are characterized by precipitation of authigenic minerals from aqueous solutions. Because this process is substantially influenced by lake water salinity and brine composition, such sediments are particularly of interest for the reconstruction of the paleolimnic environments of playa lakes. For this purpose the overall mineralogy, but predominantly the character of carbonates of lacustrine sediments, is investigated to obtain information about the paleohydrology of playa-lake systems.

In this paper the results from five different areas, all located in central Spain (Fig. 1), are compared. Climatic conditions in all these areas are characterized by highly negative annual water balances and typical Mediterranean climates, with dry conditions in summer and precipitation mainly in autumn and spring. Mean annual precipitation totals 300–350 mm. Summer aridity lasts

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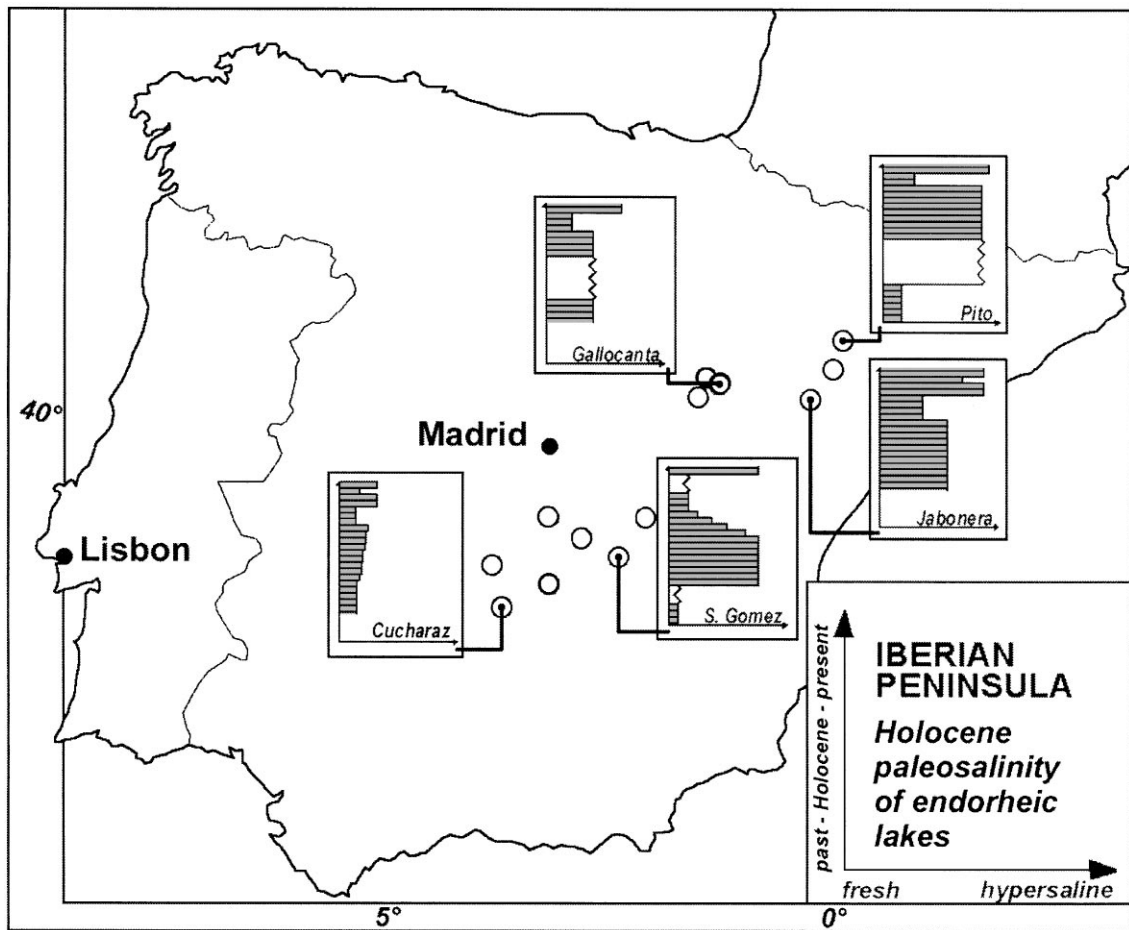


Fig. 1. Location of study areas on the Iberian Peninsula and development of Holocene paleosalinity in playa-type lakes in northern and central Spain. (○ drillings in the project Ba 1000/7, ◐ drillings discussed in this paper).

on average four months and the average annual precipitation–evapotranspiration ratio (P-ET ratio) assigns the areas of investigation to the subarid to dry-subhumid dryland zones (UNEP, 1991). Different geological, hydrological, and geomorphological conditions in the catchment areas cause the systems to respond differently to changing climatic and anthropogenic influences.

2. Methods

Cores were taken in the center of the playa lakes (Table 1). To avoid core loss and to control sediment compaction by drilling, two parallel cores were taken with about 0.5 m vertical displacement. A modified KULLENBERG corer with a hydraulic core catcher and a diameter of 40 mm was used to obtain undisturbed sediment samples.

Analyses of the sediments included first a sedimentological description to identify stratigraphical units by macroscopic characters (color, lamination, sedimentary

structures, facies). Preparation of samples started with drying them at 50°C in a drying cabinet and homogenizing them in an agate swing sledge mill. Organic and inorganic carbon contents were determined by an infrared cell in a LECO high-frequency induction oven (detection limit = 0.02 wt% C). Analyses of mineralogical compounds were carried out by X-ray powder diffraction analyses using a copper k_{α} -tube (Siemens DIFFRAC AT/D 5000). Concentrations of calcite and dolomite were estimated by calibration of the intensity of major diffraction peaks of calcite and dolomite (cps) by inorganic carbon contents (Behbehani, 1987). The position of dolomite's major diffraction line was determined to obtain data about the Mg–Ca ratios of the carbonates after calibration of the diffractogram with reference to the major diffraction line of quartz (Tennant and Berger, 1957; Weber and Smith, 1961; Langbein et al., 1981). Data were traced with two decimals but presented with three decimals wherever they show average values. Bulk chemistry of samples was determined by X-ray fluorescence analyses (Siemens SRS 2000). PH-value of the

Table 1
Location of drilling and character of study areas

Drilling	Easting	Northing	Lake hydrology	Area	Bedrock of catchment area	
	UTM-coordinates				Lithology	Stratigraphy
Laguna de Pito	737 200	4588 750	Ephemeral	Las Plañas de Bujaraloz (central Ebro Basin)	Limestone, gypsum	Miocene
Laguna Jabonera	736 600	4547 500	Dry	Desierto de Calanda (Iberian Piedmont)	Slightly cemented clay rocks	Miocene
Laguna de Gallocanta	627 200	4537 000	Ephemeral	Laguna de Gallocanta (central Iberian Chain)	Quartzite limestone	Ordovician/Trias
Laguna de Sancho Gomez	514 000	4364 450	Ephemeral	La Mancha	Gypsum, rañas	Miocene/Pliocene
Laguna de Cucharaz	400 450	4290 850	Ephemeral	Campos de la Calatrava	Quartzite gypsum, clay rock	Ordovician/Miocene

sediments was measured in a suspension of one part dried sediments to five parts H₂O after a 30 min reaction time (Schlichting et al., 1995, p. 132).

The drainage basins were also surveyed. Besides the study of geological, geomorphological, and land use settings, the main emphasis was put on hydrological conditions. In the watershed the level of perched-groundwater was measured in wells using a light plumb line. Additionally, water samples from wells were taken and chemical composition was analysed in the laboratory using ion chromatography.

3. Results

3.1. Laguna de Pito (Central Ebro basin)

3.1.1. Geographical setting

Las Plañas de Bujaraloz is a plateau in the Los Monegros area (Fig. 1). It is an endorheic region, limited to the south by an escarpment towards the Ebro River and to the east by the La Valaurna creek. Bedrock is Miocene gypsum and limestone with a few intercalated beds of calcareous sandstone (Quirantes Puertas, 1969). Surficial and subsurface drainage of the Las Plañas de Bujaraloz area are strongly influenced by regional tectonics. Fracturing combined with the high solubility of the bedrock causes the karst landscape of this area. Some valleys have developed from strings of solution depressions related to the fracturing of limestone and gypsum formations (Sánchez Navarro et al., 1989). Laguna de Pito is a collapsed hollow in the Las Plañas de Bujaraloz area. It has a depth of 20 m and a diameter of c. 1 km and is covered by an ephemeral, hypersaline lake (Schütt, 1998a).

Actual subsurface solution at the Las Plañas de Bujaraloz area is evident by the high concentration of solutes in the groundwater with an average dry residue of

6658 mg/l (Sánchez et al., 1993). Predominance of sulphates in the chemical composition of groundwater ($\mu = 2885 \text{ mg/l SO}_4^{2-}$, std = 1886, $n = 26$) reflects the origin from solid Miocene sulphates. Composition of cations also points to solution of sulphates with calcium, magnesium, and sodium ions predominating ($\mu_{\text{Ca}} = 533 \text{ mg/l Ca}^{2+}$, std = 180; $\mu_{\text{Mg}} = 353 \text{ mg/l Mg}^{2+}$, std = 458; $\mu_{\text{Na}} = 484 \text{ mg/l Na}^+$, std = 1179; $n = 26$) (Schütt, 1997). Perched groundwater in the Las Plañas de Bujaraloz area was sampled in March 1994; parallel groundwater level measurements showed variations between -1.7 and -9.5 m below surface.

3.1.2. Core sedimentology

A 195 cm long core of lacustrine sediments, underlain by Miocene gypsum, was extracted from the centre of Laguna de Pito. The most noticeable characteristic of the core sediments is the very low concentration of organic carbon (less than 1 wt% C_{org}) and two layers of gravel (c. 4–7 mm \varnothing) at a depth of 150 and 180 cm. Relatively pure calcites dominate the mineralogical composition of the core from its base up to a depth of 131 cm (stratigraphic unit 1; Table 2). Dolomite occurs in these basal sediments in traces; the average position of the dolomite's major diffraction line is located at $30.895 \text{ }^\circ 2\theta \text{ Cu K}_\alpha$. Above 130 cm (stratigraphic unit 2) carbonates and gypsum occur together (Fig. 2). In this part of the core calcite occurs as a minor component while dolomite concentrations increase and reach an average of $\mu_2 = 3.8 \text{ wt\% CaMg(CO}_3)_2$ (std₂ = 2.10, $n_2 = 9$). The average angle of the dolomite major diffraction line totals $\mu_2 = 30.916 \text{ }^\circ 2\theta \text{ Cu K}_\alpha$ (std₂ = 0.057, $n = 9$). Between 25 and 5 cm (stratigraphic unit 3), calcite is again a major component with concentrations up to 20.9 wt% CaCO₃. Simultaneously, the position of dolomite's major diffraction peak shifts down to $30.830 \text{ }^\circ 2\theta \text{ Cu K}_\alpha$. In the uppermost sediments, above 4 cm (stratigraphic unit 4), the mineralogy of the sediments is similar to those from stratigraphic

Table 2
Laguna de Pito: Mineralogical composition of lacustrine sediments

Stratigraphic unit	Depth (cm)	Calcite	Dolomite	Gypsum	Bassanite	Anhydrite	Halite	Quartz	Clay Minerals	Overall mineralogical character
4	2	+++ ^a	++	+++	++	+	++	+	+	Gypsum rich
3	8	+++	++	+++	+	++	++	++	++	
	19	+++	++	+++	++	+	++	+	+	
2	31	++	++	+++	++	++	++			
	46	++	++	+++	++	++	++			
	66		++	+++	++	+	++		+	
	84	++	++	+++	++	+	++	+	+	
	96	++	++	+++	++	+	++	++	+	
	106	++	++	+++	++	+	++	+	+	
	112	++	++	+++	++	+	++	+	+	
	121	+++	++	+++	++	+	+	++	+	
1	133	+++	+	+	+	+			+	
	141	+++	++		+	+		+	+	
	147	+++	+			+				
	150					gravel-layer				
	166	+++	+		+	+		++	+	
	170	+++	+		+	+		++	+	
	174	+++	+		+	+		++	+	
	180					gravel-layer				
	189	+++	+	+		+		+	+	
	195	+++	+	+	+	+		+	+	

^aMax counts: +++ major components, ++ minor components, + traces.

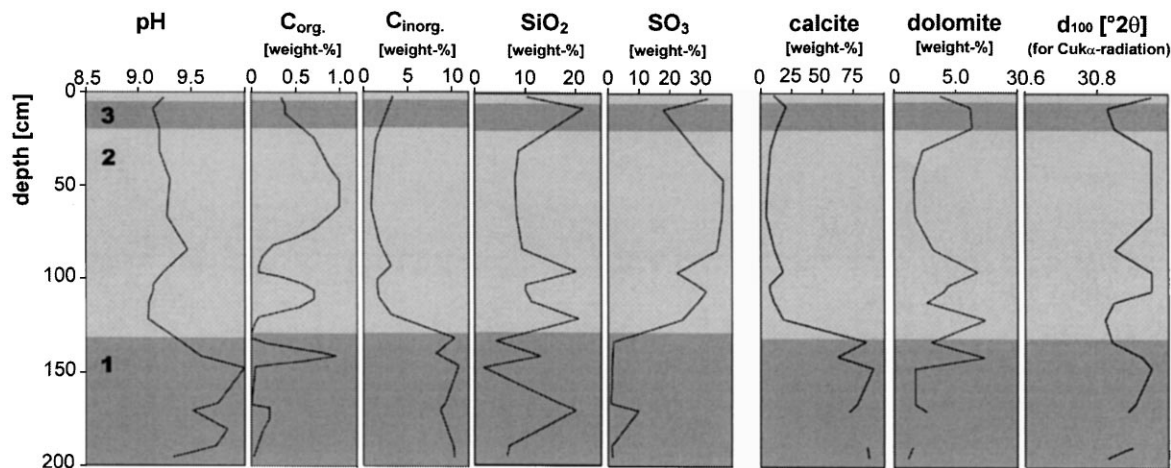


Fig. 2. Laguna de Pito: pH, Chemical and mineralogical stratigraphic variation of lacustrine sediments. Organic carbon (C_{org}), inorganic carbon (C_{inorg}), silica (SiO_2), sulphur (SO_3), calcite and dolomite content are shown in wt%; location of the diffraction angle of dolomite's major diffraction line is shown (d_{100} °2 θ Cu k_{α} -radiation). Background shading of stratigraphic units: □ subarid to dry-subhumid environment, ■ subhumid environment.

unit 2 (130–26 cm). For stratigraphic units 2–4 graphs of sulphur (substituted by SO_3) and dolomite concentrations are running invertly ($\alpha < 0.01$) (Fig. 2).

Corresponding to the mineralogical character, carbonates (C_{inorg}) are the predominant geochemical component

in the section from 131 to 195 cm depth (Fig. 2). Above a depth of 130 cm increasing sulphur concentration marks the onset of gypsum precipitation. In the strata between 96 and 195 cm depth concentrations of silica show large oscillations, whereas in the section from 26 to

96 cm depth silica concentrations are relatively low, and only show another strong deflection in stratigraphic unit 3.

3.2. Laguna de Jabonera (Iberian Piedmont)

3.2.1. Geographical setting

The bedrock geology of the Desierto de Calanda southwest of Alcañiz, located in the Iberian piedmont (Fig. 1), is characterized by Miocene fine-grained detrital formations with secondary precipitated sulphates along their joint system and Pliocene paleochannels of calcareous sandstone (Riba et al., 1983). The Desierto de Calanda is drained by the Guadalupe River, a tributary of the Ebro River. Endorheic basins developed during the Holocene in combination with subsurface erosion of gypsum and deflation of outcropping clay strata (Ibáñez, 1973; Sanchez Navarro et al., 1991; Schütt, 1998b). Laguna de Jabonera is an endorheic basin in the Desierto de Calanda with a depth of c. 20 m and a lake bed diameter of c. 0.7 km. This playa lake is dry all year around.

Actual subsurface solution is evident by the high concentration of solutes in the perched groundwater with an average electric conductivity of $\mu_{\text{ec}} = 6347 \mu\text{S}$ (std = 3802, $n = 13$). Predominance of sulphates in the solutes ($\mu = 3640 \text{ mg/l SO}_4^{2-}$, std = 2207, $n = 13$) reflects their origin from solution of underlying sulphates. Composition of cations also points to solution of sulphates with calcium, magnesium, and sodium ions predomina-

ting ($\mu_{\text{Ca}} = 526 \text{ mg/l Ca}^{2+}$, std = 143; $\mu_{\text{Mg}} = 457 \text{ mg/l Mg}^{2+}$, std = 305; $\mu_{\text{Na}} = 569 \text{ mg/l Na}^+$, std = 730; $n = 13$). During sampling in March 1994, the table of perched groundwater at Desierto de Calanda varied between -0.8 and -5.2 m below surface.

3.2.2. Core sedimentology

A 305 cm long core of lacustrine sediments, underlain by Miocene clay strata, was extracted from the centre of Laguna de Jabonera. Lacustrine sediments are greyish brown (7.5 YR 4/4) at the basal layers and to the top continuously change to a more reddish color (2.5 YR 5/4 in 240 cm depth). From 240 cm depth to the surface sediments are uniformly brownish grey. At the lake floor, the surface concentration of organic carbon (C_{org}) totals 1.02 wt%, but below surface rapidly decreases and averages $\mu = 0.12 \text{ wt\% } C_{\text{org}}$ (std = 0.15, $n = 24$) in the strata below 5 cm depth (Fig. 3).

The whole core is characterized by simultaneous occurrence of gypsum and carbonates with gypsum predominant in the parts below 130 cm depth, and carbonates in the upper part (Table 3). Thin sections show that idiomorphic carbonates and gypsum crystals are embedded in an alternating medium- to fine-grained groundmass of carbonates and gypsum in the whole core. In the most recent sediments carbonates occur as grains, most likely of detrital origin (stratigraphic unit 4). Calcite contents continuously increase from bottom to top (stratigraphic units 2–4). Dolomite contents decrease from bottom to top between 69 and 165 cm depth

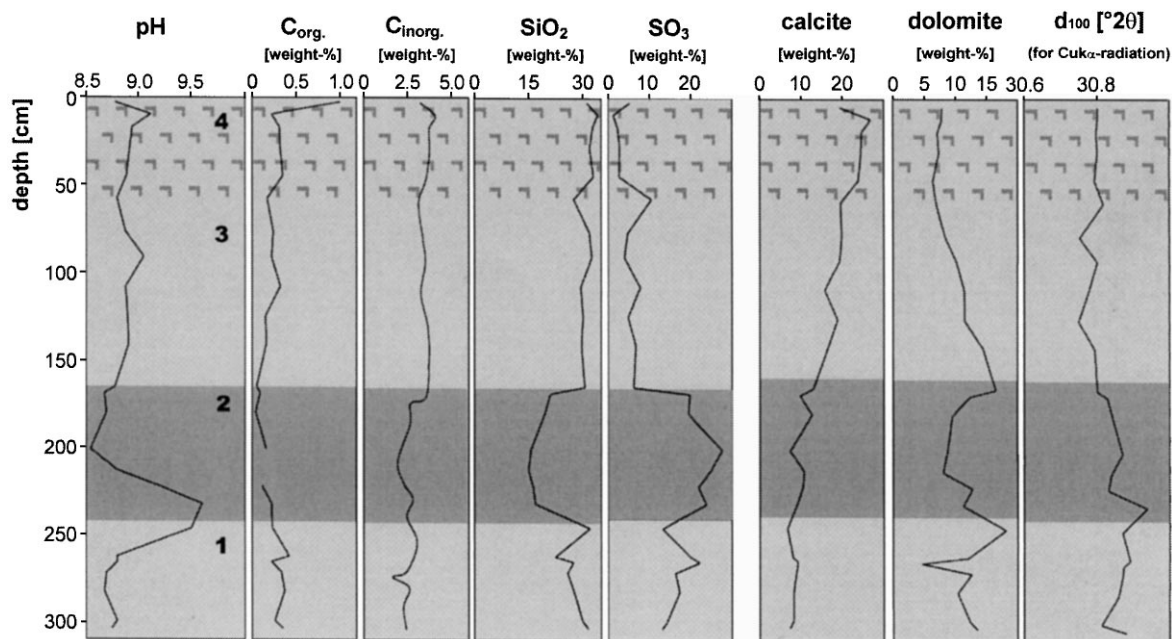


Fig. 3. Laguna de Jabonera: pH, Chemical and mineralogical stratigraphic variation of lacustrine sediments. Organic carbon (C_{org}), inorganic carbon (C_{inorg}), silica (SiO_2), sulphur (SO_3), calcite and dolomite content are shown in wt%; location of the diffraction angle of dolomite's major diffraction line is shown ($\text{dol}_{100} \text{ } ^\circ 2\theta \text{ Cu } K_\alpha$ -radiation). Background shading of stratigraphic units: □ subarid to dry-subhumid environment, ■ subhumid environment, ▨ climatic influence modified by soil erosion processes.

Table 3
Laguna de Jabonera: Mineralogical composition of lacustrine sediments

Stratigraphic unit	Depth (cm)	Calcite	Dolomite	Gypsum	Bassanite	Anhydrite	Halite	Quartz	Phyllosilicates	Goethite	Overall mineralogical character
4	3	+++ ^a	++	++		+	++	++	++	+	← Detrital carbonates Carbonate rich and Quartz rich →
	10	+++	++	+		+	++	++	++	+	
	18	+++	++	++		+	++	++	++	+	
	29	+++	++	++		+	++	++	++	+	
	45	+++	++	++		+	++	++	++	+	
	58	+++	++	++	+	+	++	++	++	+	
3	77	++	++	++	+	+	++	++	++	++	← Gypsum rich →
	91	+++	++	++	+	+	++	++	++	++	
	108	+++	++	++	+	+	++	++	++	++	
	125	+++	++	++	+	+	++	++	++	++	
	141	++	++	++	+	+	++	++	++	++	
	165	+	++	++	+	+	++	++	++	++	
2	173	+	++	++	+	+	++	++	++	+	← Quartz and gypsum rich →
	180	++	++	++	+	+	++	++	++	+	
	201	++	++	++	+	+	++	++	++	+	
	213	+	++	++	+	+	++	++	++	+	
	232	++	++	++	+	+	++	++	++	+	
	246	+	++	++	+	+	++	++	++	++	
1	261	++	++	++	+	+	++	++	++	+	← Quartz and gypsum rich →
	265	++	++	++	+	+	++	++	++	+	
	271	+	++	++	+	+	++	++	++	+	
	282	+	++	++	+	+	++	++	++	+	
	292	++	++	++	+	+	++	++	++	+	
	303	+	++	++	+	+	++	++	++	++	

^aMax counts: +++ major components; ++ minor components; + traces.

(stratigraphic unit 3; $\alpha < 0.05$) and in stratigraphic unit 4 they stagnate. For the four stratigraphic units defined, calcite and dolomite contents are correlated negatively in the basal and the top stratigraphic units ($\alpha < 0.05$) while in stratigraphic unit 2 (166–240 cm depth) a relationship is missing (Fig. 3). The major diffraction line of dolomite varies along the whole core about $\mu = 30.828^\circ 2\theta$ Cu k_α (std = 0.046, $n = 25$). In stratigraphic unit 2 the position of dolomite's major diffraction line averages $\mu_2 = 30.859^\circ 2\theta$ Cu k_α (std = 0.042, $n = 6$) and does not differ significantly from the average position of dolomite's major diffraction line in the underlying and overlying sediments ($\alpha > 0.05$).

The chemical composition of the sediments varies more than the mineralogical composition. In the basal part of the core (stratigraphic unit 1; < 241 cm depth) strong alterations of silica and sulphur concentrations occur. In stratigraphic unit 2 gypsum and calcite occur simultaneously (Table 3), as well as constant and relatively low concentrations of silica (Fig. 3). At a depth of 170 cm (stratigraphic unit 3) there is a change in sediment composition: from the lower to the higher layer sulphur concentrations decrease distinctly ($\mu_{3;4} = 5.02$ wt% SO_3) while the concentrations of silica increase. At a depth of 50–70 cm the sulphur graph again shows a marked deflection, while concentrations of silica are reduced. All over the core the graph of sulphur concentration is inversely correlated to the graph of silica concentrations ($\alpha < 0.05$).

3.3. Laguna de Gallocanta (central Iberian Chain)

3.3.1. Geographical setting

The Laguna de Gallocanta is an isolated lake basin in the central part of the Iberian Chain and has a drainage basin area of 531.6 km². It developed as a result of the structural setting in an appendix of the Calatayud-Daroca graben zone (Gonzalez Lopez et al., 1983). The basin forms a flat upland area approximately 1000 m a.s.l. It is composed of several partial lake basins of which Laguna Grande, the biggest lake basin of the Laguna de Gallocanta, is c. 1–2 km wide and 5 km long.

Bedrock outcropping in the watershed is mainly of Paleozoic and Mesozoic age with some areas covered by Tertiary fluvial sediments (rañas). Impermeable marls (Keuper, Upper Triassic) underlying the Quaternary sediments seal the lake basin (Comin et al., 1983). Mesozoic calcareous bedrock outcrops southwest of the NW–SE striking axis across the deepest part of the lake basin and dips to the northeast. Northeast of this axis, and at the southeastern end of the basin, Paleozoic (Ordovician) quartzites outcrop in the surrounding mountain ranges. During the Quaternary, alluvial fans were formed at the base of these ranges and covered extensive parts of the watershed (Gracia Prieto, 1990). These Quaternary detrital sediments directly underlie the

lacustrine sediments of Laguna Grande. Most recently, Laguna Grande is an ephemeral lake that has desiccated six times during the 20th century (Comin et al., 1990). The brine of Laguna Grande is hypersaline, composed predominantly of Na^+ , Mg^{2+} , and Cl^- -Ions (Comin et al., 1983).

Perched groundwater in the watershed of the Laguna de Gallocanta, sampled from wells in February 1995, corresponds with an average electric conductivity of $\mu_{\text{ec}} = 611 \mu\text{S}$ (std = 136, $n = 15$) to freshwater. Chemical composition of perched groundwater ($\mu_{\text{SO}_4} = 89$ mg/l SO_4^{2-} , std = 101; $\mu_{\text{Ca}} = 76$ mg/l Ca^{2+} , std = 24; $\mu_{\text{Mg}} = 103$ mg/l Mg^{2+} , std = 141; $\mu_{\text{Na}} = 10$ mg/l Na^+ , std = 9; $n = 15$) points to the solution of solid carbonates as the predominant source of solutes (cf. Gracia Prieto, 1990). The table of perched groundwater varied between – 1.6 and – 5.1 m below surface.

3.3.2. Core sedimentology

In Laguna Grande a 95 cm long core of lacustrine sediments, underlain by Quaternary fluvial deposits, was extracted. These lacustrine sediments are light grey in colour, changing to black in the uppermost layers. Sediments are clayey, not laminated, and only weakly cemented. Organic carbon content totals in the uppermost sediments (stratigraphic unit 3) in average $\mu_3 = 0.887$ wt% C_{org} (std₃ = 0.278, $n_3 = 6$), and has higher values than in the underlying sediments of stratigraphic units 1 and 2 ($\mu_{1,2} = 0.1438$ wt% C_{org} , std_{1,2} = 0.243, $n_{1,2} = 26, 2$) ($\alpha < 0.001$).}

Quartz dominates the mineralogical composition of the lacustrine sediments and other silicates only occur as traces (Table 4). At a depth of 24 to 55 cm (stratigraphic unit 2), quartz is replaced by gypsum and carbonates as the dominant mineral components. Gypsum is not present in the basal parts of the lacustrine sediments and first appears at 85 cm depth. Above 23 cm depth (stratigraphic unit 3), carbonates and quartz are the predominant mineral components. Thin sections show that quartz, in general, is detrital and is embedded in a matrix composed of carbonates and clay minerals. Gypsum crystals show an idiomorphic texture and are typically developed along desiccation cracks. The halite content increases towards the top of the core section, occurring as a minor component in the sediments above 23 cm depth. In contrast, above 23 cm depth dolomite only occurs in traces, whereas the content of calcite in the sediments above 55 cm depth increases constantly. The diffraction angle of the dolomite's major diffraction line (dol_{100}) varies between 30.804 and 30.940 $^\circ 2\theta$ Cu k_α and shows lowest values in stratigraphic unit 2 with $\mu_2 = 30.830^\circ 2\theta$ Cu k_α (std = 0.014, $n = 13$) (Fig. 4).

The chemical composition of the sediments shows similar trends to the mineralogical composition. Silica concentrations are dominant below 55 cm and above 24 cm (stratigraphic units 1 and 3), and can be used as an indicator of quartz and silicate contents. Corresponding

Table 4
Laguna de Gallocanta: Mineralogical composition of lacustrine sediments

Stratigraphic unit	Depth (cm)	Calcite	Dolomite	Gypsum	Halite	Quartz	Muskovite	Overall mineralogical character
3	7	++ ^a		+++	++	+++	+	
	10	++		+++	++	+++	+	
	12	+		+++	+	+++	+	
	18	++		+++	++	+++	+	
	19	++		++	+	+++	+	
	22	++	++	++	++	+++	+	
2	24		++	++		+++	+	
	27	+	++	+++	+	+++	+	
	29	+	++	+++	+	+++	+	
	31		++	+++	+	+++	+	
	36		++	+++	+	++	+	
	39		++	+++	+	++	+	
	41		++	+++	+	++	+	
	48		++	+++	+	+	+	
	51		++	+++	+	++	+	
	53		+++	+++	+	+++	+	
	1	56		+++	++	+	+++	+
60			+++	+	+	+++	+	
63			++	++	+	+++	+	
65			++	++	+	+++	+	
72			++	+	+	+++	+	
75			++	+	+	+++	+	
77			++	+	+	+++	+	
82			+++	+	+	+++	+	
85			+++	+	+	+++	+	
89			+++	+	+	+++	+	
92			+++	+	+	+++	+	
95		+++	+	+	+++	+		

^a Max counts: +++ major components; ++ minor components; + traces.

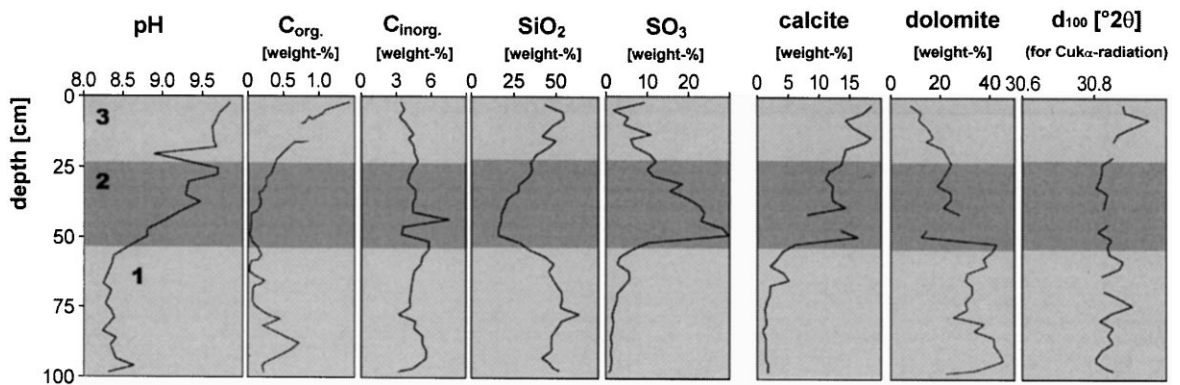


Fig. 4. Laguna de Gallocanta: pH, Chemical and mineralogical stratigraphic variation of lacustrine sediments. Organic carbon (C_{org}), inorganic carbon (C_{inorg}), silica (SiO_2), sulphur (SO_3), calcite and dolomite content are shown in wt%; location of the diffraction angle of dolomite's major diffraction line is shown ($dol_{100} \text{ } ^\circ 2\theta \text{ Cu } k_\alpha$ -radiation). Background shading of stratigraphic units: □ subarid to dry-subhumid environment, ■ subhumid environment.

to the increasing gypsum content, sulphur concentrations are highest in the section from 24 to 55 cm depth, where parallel SiO_2 concentrations are relatively low

(stratigraphic unit 2). Along the whole core profile graphs of silica and carbonate concentrations are negatively correlated ($\alpha < 0.01$).

3.4. Laguna de Sancho Gomez (La Mancha)

3.4.1. Geographical setting

The La Mancha area forms the eastern part of the Llanura Manchega and belongs to the structural unit of the Tajo-Depression (Pérez González, 1994). It is a flat upland area with a mean elevation of 600–800 m a.s.l. The Guadiana River drains the La Mancha area into the Atlantic Ocean. Since the Tertiary, the La Mancha has been the foreland of the surrounding mountain ranges. It was part of the northern Betic molasse basin, with deposition of carbonate, siliciclastic, and evaporite sequences (Molina, 1975). In the La Mancha area limestone and calcareous sandstone are the predominant outcropping bedrocks. Under subhumid conditions in the Pliocene, uplift of the surrounding mountain ranges caused erosional processes, which resulted in extensive deposition of pebbles in a loamy reddish matrix in the piedmont, the so-called raña sediments (Rommerskirchen, 1978; Pérez González, 1979; Pérez González, 1982). With the onset of Quaternary, geomorphic processes were increasingly influenced by linear fluvial erosion and development of the modern drainage system was initiated. During the Holocene in the eastern La Mancha, karstic solution of Miocene limestones and evaporites started forming an extended pattern of hollows, which, in most cases, are endorheic basins, recently occupied by ephemeral lakes (de la Peña and Marfil, 1986). A sediment core was extracted in the solutional hollow of Laguna de Sancho

Gomez, which is covered by an ephemeral, hypersaline lake.

Wells in the watershed of Laguna de Sancho Gomez were sampled in February 1995 and give some clues to the hydrochemistry of perched groundwater. For the eleven wells investigated high salinity of groundwater is reflected in an average electric conductivity of $\mu_{ec} = 3140 \mu\text{S}$ (std = 1252). Average anion and cation concentrations ($\mu_{\text{SO}_4} = 987 \text{ mg/l SO}_4^{2-}$, std = 780; $\mu_{\text{Ca}} = 348 \text{ mg/l Ca}^{2+}$, std = 144; $\mu_{\text{Mg}} = 43 \text{ mg/l Mg}^{2+}$, std = 25; $n = 11$) point to sulfatic brines resulting from solution of solid Miocene gypsum. The table of perched groundwater varied between -2.6 and -7.9 m below the surface.

3.4.2. Core sedimentology

A 300 cm long core of lacustrine sediments was extracted from the centre of Laguna de Sancho Gomez. Colour changes of the exposed sediments define a preliminary stratigraphy, whereas the texture shows no variation. The substratum is loamy and compact. From 300 and 180 cm depth, sediments show an intense red colour (5 YR 5/6–8). Above this the sediments become more brownish (10 YR 5/6, and 2.5 Y 6/1), and the uppermost strata (≥ 35 cm depth) show lesser density, and the sediment is light grey (7.5 Y 6/1). Below 80 cm depth, organic carbon contents range between 0.1 and 0.2 wt% C_{org} . Above 80 cm depth, organic carbon content increases slightly towards the top, up to a maximum of 0.9 wt% C_{org} in the uppermost strata (Fig. 5).

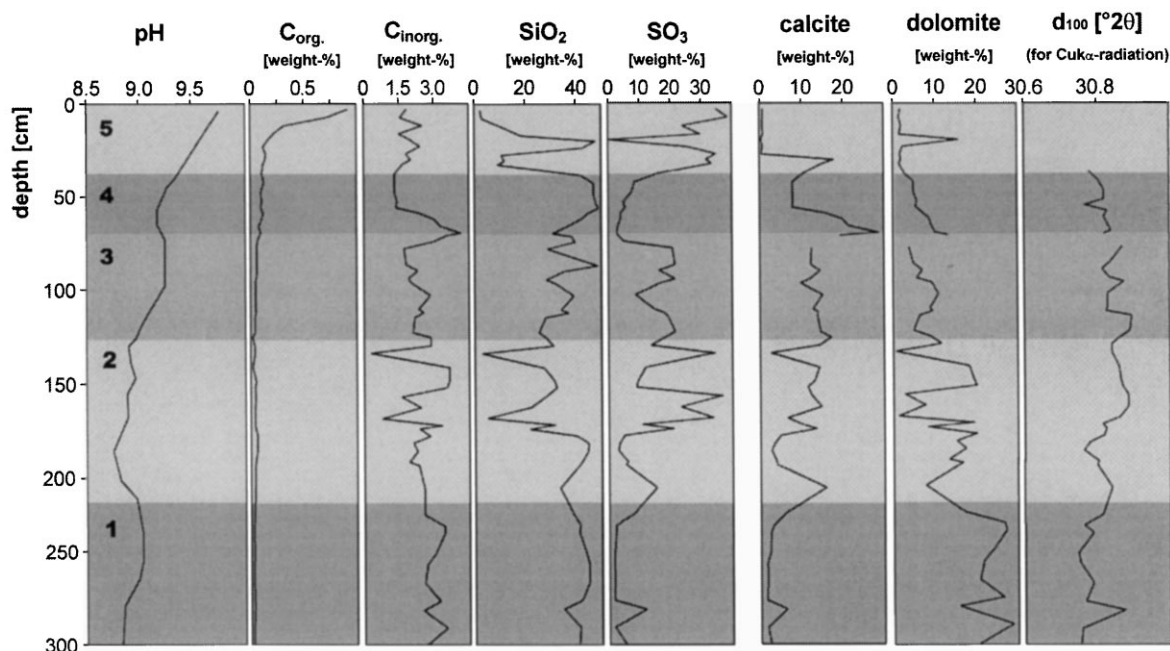


Fig. 5. Laguna de Sancho Gomez: pH, Chemical and mineralogical stratigraphic variation of lacustrine sediments. Organic carbon (C_{org}), inorganic carbon (C_{inorg}), silica (SiO_2), sulphur (SO_3), calcite and dolomite content are shown in wt%; location of the diffraction angle of dolomite's major diffraction line is shown ($\text{dol}_{100} \text{ } ^\circ 2\theta \text{ Cu } k_\alpha$ -radiation). Background shading of stratigraphic units: □ subarid to dry-subhumid environment, ■ subhumid environment.

Table 5
Laguna de Sancho Gomez: Mineralogical composition of lacustrine sediments^a

Stratigraphic unit	Depth (cm)	Calcite	Dolomite	Gypsum	Anhydrite	Bassanite	Halite	Quartz	Muscovite, Clay min.	Geothite	Hematite	Overall mineralogical composition
5	8					+++		+				Gypsum is the major component, quartz layer at 20 cm depth
	13			+		+++		+++	+			
	20		++			+++		+				
	24			+	+	+++						
	28			+	+	+++		+				
	34			+	+	+++		+++	++			
4	39	++	+	++	++	+++	+++	+++	++			Quartz and clacite are the major components
	44	+	+		+	+		+++	++			
	55	++	+		+	+		+++	++			
	61	+++	++		+	++		+++	++			
	68	+++	++		+	++	+	+++	++		+	
	73	+++	++		+	++	+	+++	++	+		
	80		++	++	++	+++		++	++		+	
	90		++	+	++	+++		++	+		+	Gypsum is the major component
	98		+	++	++	+++		++	++	+	+	
	107	+++	++	+	++	++		+++	++	+		
3	119	+	++	+	++	+++	+	++	+		+	
	127	+	+	+	++	+++	+	++	+		+	
	134	+	++	+	++	+++		+++	++		+	
	139		++	+++	+	++		++	++		+	
	146		+++		++	+++		++	++		+	Dolomite, gypsum, and quartz occur alternately as major components
	157		+++	+	+	++		+++	+		+	
	168	+	++	++	+	+++	+	++		+		
	174		++	+++		++		+	++			
	178	+	+++		++	++	+	+++	++		+	
	184		+++	++	++	+		+++	++		+	
2	192	++	++	+	+	++		+++	++		+	
	198	++	++		+	+++		+++	++		+	
	200		+++	++	+	+++		+++	++		+	
	213	++	+++	+	++	++		+++	++	+		
	228		+++	+	++	++		+++	++	+	+	Dolomite is the major component, but quartz can also occur in high quantities
	238		+++	+	+	+		+++	++	+	+	
1	249		+++	+	+	+		+++	++	+	+	
	255		+++	+	+	+		+++	++	+	+	
	266		+++	+	+	+		+++	++	+	+	
	276		+++		+			+++	++	+	+	
	291		+++					+++	++	+	+	
	300		+++	+	+	+		+++	++	+	+	

^a Max counts: +++ major components; ++ minor components; + traces.

The lacustrine sediments are composed of carbonates, sulphates, silicates, and halite (Table 5). The mineralogical composition of the sediments leads to a differentiation into five stratigraphic units: Below 36 cm depth, quartz and phyllosilicates occur as major or minor elements. Dolomite, a predominant mineral component in the basal sediments (< 221 cm depth), occurs occasionally as a major component from 136 to 220 cm depth and appears between 36 and 135 cm depth only as a minor component. There is no calcite in the basal core sections, but its concentrations increase and fluctuate in the stratigraphic units 2–4 (from 36 to 220 cm depth). In the uppermost sediments, above 35 cm depth, gypsum is the dominant mineral component, with a quartz layer at 20 cm depth. Gypsum also occurs as a major component from 76 to 135 cm depth (stratigraphic unit 3) and occasionally below 136 cm depth. Thin sections show that gypsum is idiomorphic, whereas carbonates and silicates predominantly occur as grains, most likely of detrital origin.

Dolomites in the exposed sediments occur exclusively as non-stoichiometric dolomites. In stratigraphic unit 1 the position of dolomite's major diffraction line averages $\mu_1 = 30.781^\circ 2\theta$ Cu k_α (std = 0.041, $n = 9$) and is significantly smaller than in stratigraphic unit 2 ($\mu_2 = 30.832$, std = 0.039, $n = 15$) ($\alpha < 0.05$) (Fig. 5). While the average position of dolomite's major diffraction line in stratigraphic units 2 and 3 do not vary ($\alpha > 0.05$), it shifts down to $\mu_4 = 30.810^\circ 2\theta$ Cu k_α in stratigraphic unit 4 (std = 0.024, $n = 10$) and, thus, is significantly lower than in stratigraphic unit 3 ($\mu_3 = 30.849^\circ 2\theta$, std = 0.028, $n = 12$) ($\alpha < 0.05$). All over the core graphs of dolomite and sulphate contents show a negative linear trend ($\alpha < 0.05$); for statistical analysis, SO_3 wt% was substituted for sulphates.

In the basal part of the exposed sediments (< 213 cm depth), high silica contents characterize the chemical composition, and without distinct oscillations average $\mu_1 = 41.9$ wt% SiO_2 (std = 2.85, $n = 9$). Above 213 cm depth, CaO and SO_3 concentrations increase and together, they average more than 40 wt% $\Sigma(\text{CaO}, \text{SO}_3)$ in stratigraphic units 2 and 3. In stratigraphic unit 4 average silica concentration increases to another high with $\mu_4 = 42.6$ wt% SiO_2 (std = 5.80, std = 10) while sulphur and carbonate concentrations decrease distinctly. In stratigraphic unit 5 concentrations of carbonates and sulphates increase again. Correspondingly, silica concentrations decrease ($\mu_5 = 17.8$ wt% SiO_2 , std = 16.46, $n = 9$), but show a short interval with high concentrations at 20 cm depth.

3.5. Laguna de Cucharaz (Campo de Calatrava)

3.5.1. Geographical setting

The Campo de Calatrava is the southwestern spur of the Llanura Manchega situated between the Sierra

Morena and the Montes de Toledo, both composed of Paleozoic quartzites. The Argamasilla de Calatrava basin is part of the Campo de Calatrava; it is located in an anticlinal depression which is bordered by the foothills of the Sierra de Navalenguilla to the north and east and by the Sierra de Calatrava to the south (Garcia Rayego, 1995). During the Miocene and Pliocene limestone-series were deposited on the faulted basin area. The sediments are essentially made up of dolomites and marls; calcites are mainly found in surficial calcareous formations. In the transitional zone, leading to the elevated areas, the surface is covered by detritus and alluvial fans, predominantly composed of quartzite. Tertiary volcanic activity occurred at the eastern borders of the Argamasilla de Calatrava basin (Garcia Rayego, 1995). The Argamasilla de Calatrava basin is drained by the Argamasilla River, a tributary of the Guadiana River. A structural high separates the Argamasilla de Calatrava basin from the *Depression anticlinal de Abenójar* in the west, a basin flanked by hogbacks comparable to the Appalachian-relief type (Garcia Rayego, 1995), and, thus, obstructs outflow of the Argamasilla River into the Guadiana River.

Karstification of limestones of the Argamasilla de Calatrava basin caused the development of several dolines with diameters up to 1.5 km and c. 15 m depth. Due to the damming of the main drainage channel the Argamasilla de Calatrava basin was broadly flooded until the beginning of Roman settlement (Carrasco Serrano, 1996). Today, the karstic hollows are the relics of the now desiccated wetland area. Laguna de Cucharaz is the largest of these subsidence hollows, covered by an ephemeral, brackish lake. Perched groundwater in the Argamasilla de Calatrava basin is slightly saline ($\mu_{\text{ec}} = 1203$ μS , std = 955, $n = 5$), composed of carbonate aqueous solution ($\mu_{\text{Ca}} = 135$ mg/l Ca^{2+} , std = 191.1, $\mu_{\text{Mg}} = 35$ mg/l Mg^{2+} , std = 11.6; $n = 5$). During sampling in February 1995 the level of perched groundwater in the watershed varied between – 4.1 and – 10.2 m below surface.

3.5.2. Core sedimentology

A 297 cm long core was extracted in Laguna de Cucharaz. Hardly any distinctions can be made macroscopically for the extracted core profile. Underneath 100 cm depth, the silty texture and yellowish brown colour (5 Y 6/3, 2.5 Y 7/4) are uniform. In the top meter of the core the colour turns darker (2.5 Y 5/2) and is interrupted by fine gravel layers in 57 and 65 cm depth. Below 100 cm depth organic carbon concentrations of lacustrine settings are below detection limit but above 100 cm depth continuously increase up to 1.2 wt% C_{org} at the sediment surface (Fig. 6).

The mineralogical analysis shows that quartz is the predominant mineralogical component of the lacustrine sediments over the entire profile (Table 6). It originates

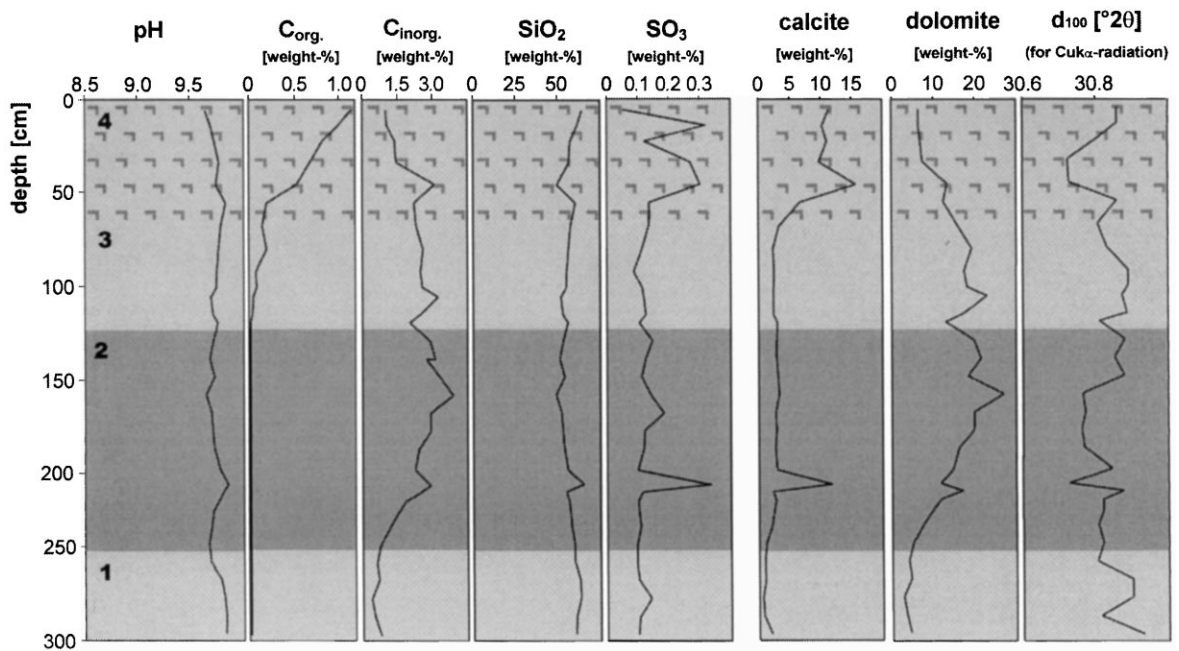


Fig. 6. Laguna de Cucharaz: pH, Chemical and mineralogical stratigraphic variation of lacustrine sediments. Organic carbon (C_{org}), inorganic carbon (C_{inorg}), silica (SiO_2), sulphur (SO_3), calcite and dolomite content are shown in wt%; location of the diffraction angle of dolomite's major diffraction line is shown (d_{100} $^{\circ}2\theta$ Cu k_{α} -radiation). Background shading of stratigraphic units: □ subarid to dry-subhumid environment, ■ subhumid environment, ◻ climatic influence modified by soil erosion processes.

from the surrounding mountain ranges consisting of Paleozoic quartzites. Corresponding to these high quartz contents silica concentrations are high (Fig. 6), but show no significant variations and, thus, do not provide any information about the paleoenvironment. Phyllosilicates are minor elements (Table 6). The minor component analcime, found below 50 cm depth, is a typical feldspar substitute in extrusive rocks. Dolomite alternates throughout the core being a major or minor component. Carbonates, in general, only occur in the matrix. Analysing thin sections, detrital carbonates were only traced in the most recent strata (stratigraphic unit 4, 0–65 cm depth). Quartz is a detrital component, partly well rounded and with a large range of sizes.

In the basal sediments carbonates occur in traces ($\Sigma(\text{calcite, dolomite}) = 4.56$ wt%, $\text{std} = 1.011$, $n = 4$) with calcite concentrations constantly below 1 wt% $CaCO_3$. Carbonate deposition increases above 250 cm depth, but calcite does not occur as a minor element until from 65 cm depth to the top; its content reaches merely a sporadic 10 wt% $CaCO_3$ at 217 cm depth (Fig. 6). Dolomite and calcite contents only correlate very little ($\alpha > 0.05$). Comparison of the average angles of dolomite's major diffraction line in the four stratigraphic units identified shows a systematic pattern ($\alpha < 0.05$): in stratigraphic unit 1 (250–297 cm depth) the major diffraction line of dolomite averages $\mu_1 = 30.870$ $^{\circ}2\theta$ Cu k_{α} ($\text{std} = 0.058$, $n = 5$), which decreases to an average of $\mu_2 = 30.798$ $^{\circ}2\theta$ Cu k_{α} ($\text{std} = 0.044$, $n = 11$) in strati-

graphic unit 2 (130–249 cm depth), and again increases to an average diffraction angle of $\mu_{3,4} = 30.839$ $^{\circ}2\theta$ Cu k_{α} above 130 cm depth ($\text{std} = 0.049$, $n = 16$; stratigraphic units 3 and 4). A short interval in the uppermost stratigraphic unit between 30 and 50 cm depth allows the diffraction angle of dolomite's major diffraction line to drop to 30.725 $^{\circ}2\theta$ Cu k_{α} .

Chemical composition of lacustrine sediments from the Laguna de Cucharaz only shows minor variations. Corresponding to high quartz and silicate contents silica concentrations dominate the chemical composition along the whole core profile ($\mu = 57.1$ wt% SiO_2 , $\text{std} = 1.77$, $n = 33$) and show only very little variations. Sulphur concentrations are altogether small (in stratigraphic units 1–3 $\mu_{SO_3} < 0.15$ wt% SO_3) and only in the uppermost layers increase up to an average of $\mu_4 = 0.26$ wt% SO_3 ($\text{std} = 0.149$, $n = 5$; stratigraphic unit 4).

4. Discussion

4.1. Organic carbon in playa-lake-type sediments

In perennial lakes the decomposition of suspended organic matter is predominantly controlled by oxidation, whereas after deposition, decomposition of organic matter is continued by anaerobic bacteria (Meyers and Ishiwatari, 1993). Early diagenetic decomposition of organic matter occurs in both the aerobic and anaerobic

Table 6
Laguna de Cucharaz: Mineralogical composition of lacustrine sediments

Stratigraphic unit	Depth (cm)	Calcite	Dolomite	Quartz	Muscovite, Clay min.	Analcime	Overall mineralogical composition
4	15	++	+	+++	+		
	23	++	++	+++	++	lay min.	
	35	++	++	+++	++		
	48	++	++	+++	++		
	57		gravel-layer				
	59	+	++	+++	++	+	
	65		gravel-layer				
3	70		++	+++	++	+	
	83		++	+++	++	+	
	96		++	+++	++	++	
	104		++	+++	++	++	
	109		+++	+++	++	++	
	119		++	+++	++	++	
	124		++	+++	++	++	
2	134		+++	+++	++	++	
	144		+++	+++	++	++	
	154		++	+++	++	++	
	164		++	+++	++	++	
	174		+++	+++	++	++	
	184		+++	+++	++	++	
	194		++	+++	++	++	
	206		++	+++	++	++	
	218		++	+++	++	++	
	229	++	++	+++	++	++	
	237		++	+++	++	++	
	247		++	+++	++	++	
1	257		+	+++	++	++	
	267		+	+++	++	++	
	277		+	+++	++	++	
	287		+	+++	++	++	
	297		++	+++	++	++	

^aMax counts: +++ major components; ++ minor components; + traces.

limnic environment and can result in the total decay of organic matter (Livingstone, 1984). Altogether, water soluble organic materials such as carotenoids and chlorophyll are more strongly affected by decomposition than insoluble materials such as cellulose, chitin, or lignin (Vallentyne, 1962). The gradient of decreasing organic carbon contents from the top to the underlying beds results from the decomposition rate which is forced by light, high temperatures, and oxygen (Vallentyne, 1962). Consequently, in ephemeral lakes high decomposition rates can be expected during desiccation, and, therefore, high rates of biomass production in saline environments (Evans and Kirkland, 1988) do not necessarily result in high organic carbon values in the corresponding lacustrine sediments.

In general, organic carbon contents in the extracted lacustrine sediments are very low. In the uppermost sediments from top to bottom continuously decreasing contents of organic carbon suggest a progressively

early diagenetic decomposition of organic matter (Rheinheimer, 1974). Additionally, it has to be considered that the high amounts of organic carbon content in the uppermost sediments might be influenced by increasing soil erosion rates in the youngest past (Dunne et al., 1991).

4.2. Information about the paleolimnic environment from mineralogy

Apart from allochthonous detritus authigenic carbonates, sulphates, and chlorides precipitated from brines make up the mineralogical composition of playa lakes. Early diagenetic processes, controlled by salinity and chemistry of brines and pore water can modify the mineralogical properties. The influence of lake water salinity is predominant over the authigenic mineral fabric and early diagenetic modification of minerals. Therefore, the mineralogical sediment properties of playa lakes can

provide valuable information for the reconstruction of paleoenvironments, especially for the reconstruction of the salinity and the composition of brines and for the reconstruction of the lake paleohydrology (ephemeral, periodic, perennial).

4.2.1. Carbonates

Calcareous mud is the predominant form of carbonate deposits in the playa lakes investigated. Its origin can be explained by strong mechanical stress on detrital carbonates (Kelts and Hsü, 1978) as well as by authigenic calcite precipitation (Schröder et al., 1983). Essentially, the autochthonous development of calcareous mud (= auto-micrite) in lacustrine environments is due to water chemistry changes effected by decomposition of organic matter, biological assimilation of CO_2 , or temperature increases with resulting salinity deviations (Flügel, 1978). Warming of the water body in summer and evaporation can also lead to deposition of carbonates, especially in shallow-water areas (Schäfer, 1972). As salinity in the playa lakes investigated is high and magnesium as an indispensable prerequisite of dolomite formation is available in all these systems (Folk and Land, 1975), also authigenic dolomite precipitation is possible (Morrow, 1982).

The Mg–Ca ratio of authigenic dolomites is a helpful indicator for the reconstruction of paleosalinity. When using the Mg–Ca ratio as a paleosalinity indicator it must be taken into account that the dolomites developed as a result of authigenesis or early diagenetic dolomitization in lacustrine settings (Behrens and Land, 1972; Dekker and Last, 1988). In the case that these conditions are not given and detrital dolomites dominate, the Mg–Ca ratio of dolomites is no good indicator of salinity conditions during authigenesis or early diagenetic dolomitization in the lacustrine environment. ‘Burial’ dolomitization can be excluded for the lacustrine sediments investigated because the field boundary between calcite and dolomite suggests that for this process temperatures between 80 and 90°C are necessary (Usdowski, 1994).

If dolomites show lattice spacing higher than 2.8879 Å, the dolomite is non-stoichiometric and called “protodolomite”. As the radii of calcium-ions ($R_{\text{Ca}^{2+}} = 1.00$) are bigger than the radii of magnesium-ions ($R_{\text{Mg}^{2+}} = 0.72$) the lattice spacing of dolomite becomes larger the smaller the Mg–Ca ratio is (Langbein et al., 1981). This is portrayed when using an X-ray-diffractogram with $\text{Cu } k_\alpha$ -radiation, where the major diffraction line of stoichiometric dolomite shifts from $30.94^\circ 2\theta$ $\text{Cu } k_\alpha$ to smaller angles with decreasing Mg–Ca ratio (Tennant and Berger, 1957; Royse et al., 1971; cf. Fig. 7). Because magnesium-ions relatively accumulate, whilst brines are confined and calcium carbonates and sulphates are precipitated, the Mg–Ca ratio of dolomites reflects lake water salinity during dolomite formation, regardless whether dolomites originate from authigenic or early

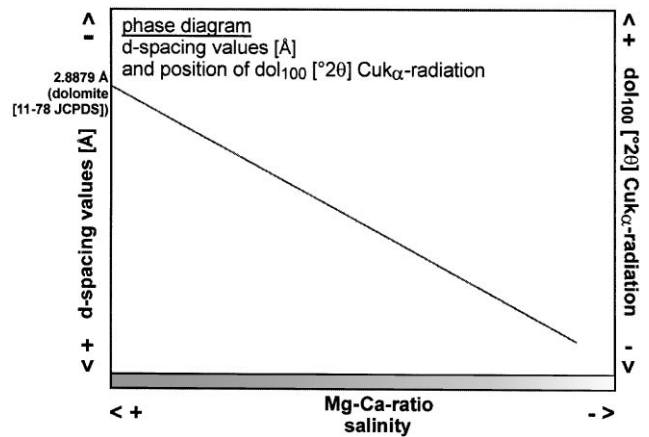


Fig. 7. D-spacing value (Å) of protodolomites protodolomite's strong reflection [2θ] ($\text{Cu } k_\alpha$ -radiation) of lacustrine sediments as a paleosalinity indicator.

diagenetic processes (Folk and Land, 1975; Morrow, 1979).

The quantitative relationship between the Mg–Ca ratio of dolomites and lake water salinity was first discussed by Folk and Land (1975). They demonstrated that the conditions for authigenic dolomite formation respectively early diagenetic dolomitization vary with the lake water chemistry and salinity: in fresh-water environments a Mg–Ca ratio of 1 : 1 is enough for dolomite formation, whereas ratios of 5–10 : 1 are required in hypersaline environments. These results were revised in later studies (i.e., Morrow, 1979; Lumsden and Chimahusky, 1980; Mattess and Mountjoy, 1980). The relationships between Mg–Ca ratios, lake water salinity, and stoichiometric conditions of the corresponding (genetically different) dolomites concluded by Morrow (1982) also show indications of dimension, and do not imply any specific factors. While in these studies of the 1970's and early 1980's, in general, the hydrochemical aspect was highlighted as the most important factor influencing the character of carbonates, Last (1994) presented a much more complex model including basin morphology, basin hydrology, and water salinity.

In conclusion, lake water salinity can only be inferred indirectly from the Mg–Ca ratio, determined by the lattice spacing of protodolomites; quantifying this connection is impossible without preceding determination of the overall chemistry and especially of the inflowing surface and subsurface waters. Additionally, it has to be considered that also re-dissolution of evaporites precipitated during preceding lake phases influences brine salinity. When considering the complexity of input factors, it seems to be questionable to transfer the individually established relationships between the angle of dolomite's major diffraction line and the brine salinity during authigenesis of dolomites associated with early diagenetic dolomitization to watersheds with different

properties. Although constant petrographical and hydrological drainage basin characters are required, the Mg–Ca ratio is an appropriate semi-quantitative indicator for approximating salinity of limnic environments during dolomite formation.

4.2.2. Sulphates

In playa lakes precipitated authigenic sulphates frequently occur. Using X-ray powder diffraction analysis, among gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) also bassanite ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) and anhydrite (CaSO_4) were detected while magnesium-sulphates might occur, but contents were below detection limits. In general, autochthonous gypsum precipitates from brines with a density $> 1.115 \text{ g/cm}^3$ (Sonnenfeld, 1984, p. 102). In contrast, anhydrite can be precipitated from brines or might be a diagenetic product from gypsum (Usdowski, 1974). Diagenesis of gypsum is controlled by temperature, pressure, and lake water salinity (Holser, 1979).

In playa lakes also bassanites can develop by dehydration of gypsum when the lake-floor desiccates or by hydration of anhydrites (Braitsch, 1971, p. 9). Dehydration of gypsum appears predominantly in the capillary fringe under high temperatures and high evaporation rates (Sonnenfeld, 1984, p. 453). As bassanites are metastable they again transform to gypsum under the effect of surface- and pore-water (Hardie, 1967). Thus, it seems to be evident that bassanites detected by X-ray powder diffraction analysis (i.e. in cores of Laguna de Pito, Laguna de Jabonera, Laguna de Sancho Gomez), are an artefact of sample preparation in the drying cabinet. Comparison tests with samples without preceding preparation in the drying cabinet showed that gypsum and anhydrite were present in these samples while bassanite was missing and, thus, point out that the experimentally fixed temperature range of 75–80°C for the dehydration of gypsum might be too high (cf. Gay, 1965, Chapter 2).

4.3. Laguna de Pito (central Ebro basin)

In the sediments of the Laguna de Pito (Fig. 2, Table 2) the relatively pure calcites in stratigraphic unit 1 correspond to chalk as defined by Merkt et al. (1971; calcium carbonate content $\geq 90\%$) and indicate a period with a freshwater lake (McKenzie, 1985). The absence of gypsumiferous sediments, despite a rich source within the drainage basin, is attributed to low concentration brines and, perhaps, to exterior drainage during this phase. The particles from the two gravel layers at 150 and 180 cm depth are interstratified with the calcareous muds. They are interpreted as remnants of a detrital deposition event triggered by excessive rainfall. They were deposited in a calcite-saturated lacustrine environment which prevented further decomposition of rock fragments (cf. Trudgill et al., 1980).

The former existence of a freshwater lake indicates a humid or subhumid climate, whereas precipitated gypsum in the sediments above 130 cm indicates increased aridity, corresponding to an increased salinity of the limnic environment (Warren, 1989). The transition zone between stratigraphic units 1 and 2 shows an abrupt change between high calcite and low sulphate concentrations in the underlying sediments and low calcite and high sulphate concentrations in the overlying sediments, and, thus, points to a possible hiatus.

As dolomites are not present in the bedrock of the watershed, dolomites in the lacustrine sediments are most likely authigenic or a result from early diagenetic dolomitization. The relatively high mean position of dolomite's major diffraction line in stratigraphic unit 2 corresponds to a relatively small lattice spacing and, thus, compared to the underlying strata points to an increased Mg–Ca ratio in the brine (Langbein et al., 1981). In stratigraphic units 2–4 negatively correlated graphs of sulphur (substituted by SO_3) and dolomite ($\text{CaMg}(\text{CaCO}_3)_2$) point to the obstructive influence of sulfatic brines on processes of authigenesis of dolomites respectively early diagenetic dolomitization (Braddock and Bowles, 1963; Mazor and Mantle, 1966). At the top of the core (stratigraphic unit 3), short-term increased calcite contents coincide with decreasing angles of the dolomite major diffraction line, thus, with increased lattice distances of protodolomites as corresponding to decreased Mg–Ca ratios. The deposition of these sediments documents a short period of increased humidity producing a temporary perennial lake with a relatively low salinity. In the recent past these conditions changed again so that today the Laguna de Pito is once more an ephemeral lake with a hypersaline limnic environment (Schütt, 1997).

Summarising: A freshwater lake covered the lake basin of Laguna de Pito during deposition of sediments in stratigraphic unit 1. These relative wet environmental conditions changed to a subarid climate and resulted in a hypersaline lake with predominant sulphate precipitation (stratigraphic unit 2). These environmental conditions last until today, interrupted by a short period with more humid conditions in the recent past (stratigraphic unit 3). Rapid change of sediment character between stratigraphic units 1 and 2 points to a possible hiatus.

4.4. Laguna de Jabonera (Iberian Piedmont)

In the Desierto de Calanda surface input from evaporitic sediments may be excluded, as there are almost no outcrops of evaporitic sediments within the watershed. Precipitation of evaporites in the Laguna de Jabonera therefore has to be explained by increased subsurface inflow of aqueous solution, which will mostly take place in response to relatively more humid conditions (Schütt, 1998a). In general, during humid phases the vegetation

cover obstructs surface runoff and erosion, and infiltration rates increase (Horton, 1945). As conditions are reversed during arid phases, surface erosion increases and infiltration rates and subsurface flow are reduced (Dunne et al., 1991; Rogers and Schumm, 1991).

Solution of underlying gypsum and deflation of outcropping clay strata formed the endorheic basins of the Desierto de Calanda (Sanchez Navarro et al., 1991). During the subsequent time subarid climatic conditions led to predominant deposition of silica clastics (stratigraphic unit 1), while, simultaneously, in these sediments carbonates and gypsum are of minor importance. In opposite to that, sediments in stratigraphic unit 2 are predominantly evaporitic, with silicates only as minor components. In the Desierto de Calanda such a composition of lake sediments is typical for subhumid phases, as only such climatic conditions allow the increased input of brines necessary for large evaporite precipitation.

In the lacustrine sediments of Laguna de Jabonera these paleoenvironmental changes are not reflected by the Mg–Ca ratio of the dolomites (Fig. 3) as the position of the dolomite' major diffraction line does not vary significantly between stratigraphic units. High inflow rates of solutes during wetter phases are compensated by high evaporation rates during drier phases. Thus, the salinity of lake water is always high and without marked changes. Consequently, for the lacustrine sediments of Laguna de Jabonera the Mg–Ca ratio of dolomites does not offer useful information for the reconstruction of paleosalinity. Also it has to be considered that dolomites might be due to detritals eroded from the Pliocene paleochannels in the watershed. In stratigraphic unit 3 the calcite content is increasing from bottom to top while dolomite content is decreasing. This might be due to the downward continuing process of early diagenetic dolomitization.

In stratigraphic unit 3 silicate contents increase stepwise, and precipitation of sulphates is less important. This change in composition is attributed to a change in related processes: Sedimentation of stratigraphic unit 2 was mainly caused by subsurface inflow and reduced surface runoff and only little input of clay and detrital quartz occurred. These processes may be due to subhumid climatic conditions. In contrast, sedimentation of stratigraphic units 3 and 4 was due to reduced subsurface inflow and high rates of surface runoff or aeolian input corresponding to high erosion and deflation rates in a subarid to dry-subhumid environment. During deposition of these sediments a decreased vegetation cover favoured surficial erosion and deposition of detritic sediments, while subsurface input by aqueous solution was reduced. But for the most recent sediments (stratigraphic unit 4) also human impact has to be considered (Stevenson et al., 1991). Thus, increased detritic components in stratigraphic unit 4 indicate anthropogenically induced soil erosion processes (Faust and Diaz del Olmo, 1997).

Sediments at a depth between 50 and 60 cm again indicate a brief subhumid phase, as noted in the deflection of the sulphur graph.

Summarizing: Subarid to dry-subhumid climatic conditions led to the predominant detrital deposits in stratigraphic unit 1. In contrast, composition of stratigraphic unit 2 is typical for subhumid environmental conditions while sedimentation was due to subsurface inflow and surface runoff was reduced. In stratigraphic unit 3 a change in sediment composition is again attributed to processes in a subarid to dry-subhumid environment, dominated by surface runoff. These relatively dry environmental conditions still occur today, interrupted by a brief phase of increased humidity in the recent past and modified by soil erosion processes (stratigraphic unit 4).

4.5. *Laguna de Gallocanta (Central Iberian Chain)*

Graphs of silicate and carbonate contents show an inverse trend, which is mostly caused because they are the two major components. But nevertheless, for the drainage basin of the Laguna de Gallocanta this relationship is — because of the particular drainage basin characteristics — a useful paleoenvironmental indicator. The Laguna de Gallocanta is located at the base of the Iberian Chain, which is locally formed of Paleozoic quartzites. The mean hydraulic gradient in this northeastern part of the drainage basin averages 2.8–3.2°. Alluvial fans cover extensive portions of the base of the mountain ranges, thus, providing a source of detrital silicates available for erosion. Deposition of detrital silicates in the Laguna Grande, therefore, requires only minimal erosion and transport distances. In contrast, the hydraulic gradient of the southwestern slopes is low, averaging only 1.2–1.5°. Therefore, despite the high hydraulic conductivity of the joint aquifer (Mesozoic limestones; MdAPA, 1988), groundwater velocity is low. Accordingly, deposition of carbonates requires processes of solution and transport, which, in average, do not dominate under the present climatic conditions (Csa-climate sensu Köppen) (Schütt, 1998b). During such subarid periods a negative water balance with low groundwater recharge will result in increasing salinity of brines, but however, input of detrital silicates by runoff or aeolian processes will dominate (stratigraphic units 1 and 3). In contrast, high carbonate concentrations in stratigraphic unit 2 are caused by increased subsurface inflow from the southwestern part of the drainage basin, due to increased annual precipitation and changing seasonality of rainfall (Kuhn et al., 1997).

In the outer banks of Laguna Grande dolomites occur in a small area in the southwestern part (Jurassic carbonates exposed in a horst close to the settlement Las Cuerlas; IGME, 1983) and, thus, are possible sources of detrital dolomites in the lacustrine settings. Simultaneously, it has to be considered that the decrease in dolomite content above 55 cm might be connected to the

increasing precipitation of sulphates, due to processes of dedolomitization and reduced precipitation of authigenic dolomites under the influence of sulphur-rich solutions (Braddock and Bowles, 1963; Mazor and Mantle, 1966). If dolomites are authigenic, the smaller mean diffraction angle of dolomite's major diffraction line of the sediments in stratigraphic unit 2 indicates significantly lower Mg–Ca ratios of the dolomites than in the stratigraphic units 1 and 3. These lower Mg–Ca ratios of dolomites in stratigraphic unit 2 point to a brackish limnic environment during dolomite formation, while the relatively high mean Mg–Ca ratios of the dolomites in stratigraphic units 1 and 3 indicate phases of an increased salinity of the corresponding limnic environment during authigenic dolomite precipitation or early diagenetic dolomitization (Morrow, 1982). The reconstruction of a lake with a brackish environment during deposition of sediments of stratigraphic unit 2 indicates that the increased gypsum contents above 55 cm depth mark a postdepositional desiccation phase of Laguna Grande, where high evaporation rates caused ascending groundwater and, therefore, gypcrete-like secondary deposition of sulphates in pores.

From the bottom to the top, increasing halite contents (Table 4) indicate an increasing aridity (Sonnenfeld, 1984, p. 154; Warren, 1989, p. 97). But it has to be considered that halite precipitated during desiccation is partially remobilized during the lake's renewed infill. Thus, however, high solubility of sodium causes repeated resolution and therefore the residual brine — and correspondingly, the uppermost strata — is enriched in sodium and easily causes a misinterpretation of a 'paleoclimatic' trend (Spencer et al., 1985).

Summarising: In Laguna Grande basal lacustrine sediments were deposited in a saline lake under subarid to dry-subhumid environmental conditions, while sediments of stratigraphic unit 2 were deposited in a brackish lake under subhumid environmental conditions. Sudden change in sediment composition between stratigraphic units 1 and 2 points to a possible hiatus. The actual subarid climate causes the Laguna Grande to be an ephemeral, hypersaline lake, reflected in the sediments of stratigraphic unit 3.

4.6. *Laguna de Sancho Gomez (La Mancha)*

As dolomites do not occur in the drainage basin of the Laguna de Sancho Gomez, dolomites in the lacustrine sediments originate from autochthonous dolomite precipitation or from early diagenetic dolomitization of calcites (Morrow, 1982). In the saline to hypersaline limnic environment of Laguna de Sancho Gomez calcites as well as dolomites might be due to authigenic precipitation (Flügel, 1978; Morrow, 1982). In stratigraphic units 2 and 3 the relative high mean diffraction angle of dolomite's major diffraction line is consistent with an

authigenic dolomite precipitation or an early diagenetic dolomitization while the Mg–Ca ratios in the aqueous solution were high (Morrow, 1982). High Mg–Ca ratios as well as the high sulphate precipitation rates in these stratigraphic units indicate a saline to hypersaline limnic environment (van der Borch, 1976; van der Borch and Lock, 1979). Correspondingly, halite precipitation, which is limited to these stratigraphic units, also indicates a subarid environment (Warren, 1989). In contrast, stratigraphic units 1 and 4 tend to have lower mean diffraction angles of dolomite's major diffraction line. This points to high lattice spacing of the dolomites (Langbein et al., 1981), which is due to relatively low Mg–Ca ratios of the aqueous solution during authigenesis of dolomites respectively early diagenetic dolomitization (Morrow, 1982). Altogether, a brackish or slightly saline limnic environment during deposition of sediments in stratigraphic units 1 and 4 can be inferred from this interpretation backed up by the increased contents of silica and the decreased contents of sulphur and carbonates. During freshwater lake-phases, low salinity impeded precipitation of sulphates, and thus silicates in the lacustrine sediments gain importance. In contrast, during arid phases in a saline to hypersaline limnic environment sulphate precipitation dominates deposition of lacustrine sediments and silicates get secondary. The negative trend between graphs of silica and sulphur concentration is due to these processes.

In the uppermost sediments (stratigraphic unit 5), the predominance of sulphates corresponds to the recent depositional factors as described for neighbouring Laguna de Alcahozo (2 km west of the Laguna de Sancho Gomez) by Ordóñez et al. (1994). Like the brines of Laguna de Sancho Gomez those of Laguna de Alcahozo have a Na–Mg–SO₄–Cl composition, from which sulphates and halites are precipitated during desiccation (Ordóñez et al., 1994). Influence of lake water salinity on dolomite formation is also reflected in dolomite and SO₃ contents; the negative trend between both components indicates the negative effect of increasing sulphate contents on authigenesis of dolomites' early diagenetic dolomitization rates (Braddock and Bowles, 1963).

A short-term increase of quartz and silica concentration in 20 cm depth (Table 5, Fig. 5) is due to a thin layer of wind-blown sand with an origin in extended eolian sand patches c. 2 km west of Laguna de Sancho Gomez. It has to be considered that also in the older lacustrine settings layers of wind-blown sand might be interbedded, but because of early diagenetic processes or mixing after deposition are not identified as eolian strata any more.

Summarising: In Laguna de Sancho Gomez lacustrine sediments point to repeated changes of dry and wet phases. While the basal sediments (stratigraphic unit 1) were deposited under relative wet conditions, the character of overlying strata (stratigraphic units 2 and 3) indicates a dry-subhumid to subarid environment.

During deposition of stratigraphic unit 4 environmental conditions were again characterized by increased humidity. The composition of the most recent sediments (stratigraphic unit 5) is due to the actual dry-subhumid environmental conditions. A sudden change of the sedimentary fabric between stratigraphic units 4 and 5 points to a possible hiatus.

4.7. Laguna de Cucharaz (Campo de Calatrava)

Laguna de Cucharaz was formed as a solutional hollow in the basin of Argamasilla de Calatrava (Garcia Rayego, 1995). Today, it is an ephemeral lake, mainly fed by surficial groundwater. Geomorphological and pedological indicators point out that Laguna de Cucharaz most recently lies in the centre of a former wetland area which, in the past, covered large parts of the Argamasilla de Calatrava basin (Carrasco Serrano, 1996).

Carbonates, calcites as well as dolomites, might be due to erosional processes as solid dolomites and marls outcrop in the margin of the basin. But thin sections show that detrital carbonates do not occur below 65 cm depth. Calcareous mud is the predominant form of carbonate deposits below 65 cm depth. Thus, it is supposed that carbonates below 65 cm depth might be due to authigenic deposits (Flügel, 1978). In the basal strata (stratigraphic units 1–3) calcite is found only in traces (< 5 wt% CaCO₃), whereas the dolomite contents are subject to strong variations. Increased contents of detrital calcites in the most recent sediments (stratigraphic unit 4) are most likely the result of continuous soil erosion within the catchment area of the basin (Faust and Diaz del Olmo, 1997). Thus, also the calcitic fine gravel layers in 57 and 65 cm depth are due to soil erosion processes. Altogether low, but increased sulphur contents in this stratigraphic unit, coinciding with a dark sediment colour, might be due to decomposition of organic matter (Dean and Fouch, 1983).

Summarising: The limnic environment of Laguna de Cucharaz is characterised by freshwater conditions during deposition of lacustrine sediments. Variations in lake salinity caused only short periods of brackish lake environments. Low sulphate contents of the lacustrine sediments confirm the freshwater conditions during the depositional history of the lacustrine settings. In the most recent sediments (stratigraphic unit 4) increasing detrital contents point to the increasing influence of soil erosion on geomorphic processes in the drainage basin.

5. Holocene paleosalinity and lake phases of playa-lake systems in central Spain

For the lacustrine sediments investigated there is no chronological control available. Correlations with investigations from neighbouring areas, therefore, have to

back up the preliminary time assignment. Thus, the chronological framework achieved so far only gives a rough estimation of the period of sediment deposition (Fig. 1).

For the lacustrine sediments of *Laguna de Pito* no dates are available. To get a rough estimate about the time scale, Schütt and Baumhauer (1996) tried to calculate sedimentation rates in Laguna de Pito, including the factors drainage basin area, actual annual precipitation and evaporation rates as well as salinity and chemical composition of brines and groundwater. They suggested that the karstic hollow of Laguna de Pito collapsed approximately during the *Boreal* period and the lacustrine sediments of stratigraphic unit 1, reflecting freshwater conditions and a subhumid environment, may have been deposited during the late *Boreal* or early *Atlantic* (Schütt and Baumhauer, 1996). Followed by a possible hiatus, it is assumed that sediments of stratigraphic unit 2 reflect the more or less subarid to dry-subhumid depositional environment since the *Subboreal*. Several sedimentary features of stratigraphic unit 3 point to short-term increased humidity in the recent past, conditions which might coincide with the climatic pessimum of the *Little Ice Age* as it has been shown in other Ebro basin sites (Davis, 1994). Today these conditions changed once more so that Laguna de Pito is again an ephemeral lake with a hypersaline limnic environment (Schütt, 1997).

For the lacustrine sediments of *Laguna de Jabonera*, comparison with pollen analyses from neighbouring playa lakes in the Desierto de Calanda (*Laguna Pequeña*; Davis, 1994) allows to assign the Holocene environmental history to a preliminary time scale. Thus, the subhumid environmental conditions as reconstructed for the depositional phase of stratigraphic unit 2 could correspond to the late *Subboreal*, while the oldest lacustrine sediments (stratigraphic unit 1), deposited under subarid or dry-subhumid environmental conditions, are coherent with the *late Atlantic* (Davis, 1994; Macklin et al., 1994). Subarid to dry-subhumid environmental conditions also determined deposition of lacustrine sediments during the *Subatlantic* (stratigraphic unit 3), in the most recent past increasingly modified by soil erosion processes (stratigraphic unit 4). Corresponding to Laguna de Pito, the short subhumid phase documented in the uppermost sediments (50–60 cm depth) might be related to the *Modern Times* climatic pessimum of the *Little Ice Age*.

For *Laguna Grande* (basin of Laguna de Gallocanta) a preliminary time assignment of the environmental changes during deposition of lacustrine sediments can be made by correlation with the work of Davis (1994) and Burjachs Casas et al. (1996), who also extracted cores from the lake. Davis identified the *olive rise* (ca. 0.4 ka BP) from the pollen record in 14–15 cm depth. Comparison of the chemical composition from the core introduced in this paper with carbonate and sulphate contents of the sediment sequence described by Davis (1994) indicates that the perennial phase of Laguna Grande

(stratigraphic unit 2) discussed in chapter 4.5 coincides with the olive rise. In an additional study of Laguna Grande (Burjachs Casas et al., 1996), this most recent period of increased humidity is dated to 1842 using ^{210}Pb and, thus, coincides with the final stage of the *Little Ice Age*. In contrast to these very young, historical sediments of stratigraphical units 2 and 3, the underlying sediments of stratigraphic unit 1, deposited under subarid to dry-subhumid environmental conditions, are situated directly on Pleistocene alluvial sediments (Gonzalez Lopez et al., 1983) and form the oldest lacustrine sediments of Laguna Grande, approximately deposited during the *Middle Holocene* (Burjachs Casas et al., 1996). Thus, thickness of stratigraphic unit 1 of only 40 cm suggests that this stratigraphic unit is interrupted by at least one hiatus (Schütt, 1998c).

The timing for the sedimentary history of *Laguna de Sancho Gomez* is not yet possible. Comparison with studies from SE Spain indicates a distinct but short subhumid phase during the *Subboreal* which might correspond to the sediments in stratigraphic unit 4 (Mariscal, 1991). Correspondingly, the low thickness of stratigraphic unit 5 indicates a possible hiatus in these most recent sediments. The character of sediments in stratigraphic units 2 and 3 points to subarid to dry-subhumid environmental conditions, but dating is not yet possible. Basal lacustrine sediments of Laguna de Sancho Gomez were deposited in a freshwater lake and, thus, indicate subhumid environmental conditions which might be related to a *Boreal* wet phase as described by Florschütz et al. (1971) and Jalut et al. (1997).

Chronological dates for the *Laguna de Cucharaz* or neighbouring lake basins in the Campo de Calatrava area do not exist. Altogether, the limnic environment of Laguna de Cucharaz during deposition of the lacustrine sediments discussed was characterised by freshwater conditions and increasing salinity caused at most a brackish environment. Until the beginning of Roman settlements the Argamasilla de Calatrava Basin was broadly flooded due to the damming of the main drainage channel (Carrasco Serrano, 1996). Concluding, in the Argamasilla de Calatrava basin changes in salinity of lake water might be due to climatic influences as well as to regional tectonics influencing the draining of the basin by the Argamasilla River. First the reports of Plinius sen. in his *Historia Naturalis* (XXXIII) provide some information that the intense agricultural use of the Argamasilla de Calatrava basin appeared with the dewatering of the area in the *Roman* period. Due to these increasing land use intensity soil erosion processes in the watershed occurred and lacustrine sediments are increasingly composed of detritals (stratigraphic unit 4). In the most recent past the environmental conditions in the Laguna de Cucharaz like in several other of the playa lakes presented in this study, were characterised by a short period of reduced salinity (cf. Laguna de Pito, Laguna de Jabonera, Laguna Grande).

6. Conclusions

The analysis of lacustrine sediments from playa lakes demonstrated that their inorganic compounds provide evidence for the reconstruction of environmental changes and paleohydrological fluctuations. Mineralogical composition and, particularly the analysis of carbonate phases are valuable paleoenvironmental indicators. The varying concentrations of carbonates and sulphatic evaporites and their changing proportion to siliciclastic sediments allow to identify different depositional environments. Additionally, the Mg–Ca ratio of the dolomites, inferred from the position of the dolomite's major diffraction line, gives information about salinity during dolomite formation (Fig. 7). The comparison with the results from different drainage basins shows that any interpretation of mineralogical parameters always must consider the local petrographic, hydrologic, and geomorphic features of the watershed. Doing this, information about environmental change is gained which is a valuable addition to information obtained from analysing pollen or microfossils.

These techniques were applied to investigate the paleoenvironmental changes of five different playa lakes in northern and central Spain (Fig. 1). As a dating of investigated sediments is not yet available, the chronological framework is backed up by comparison with studies from neighbouring areas and only gives a rough estimation. Based on these preliminary time scales it seems that in the most recent past more humid environmental conditions than today occurred in central Spain. This subhumid period might be due to the climatic pessimism of the so-called *Little Ice Age*, which ended on the turn of the 19th century. The distinct environmental change noticed for the basal settings of Laguna de Pito and Laguna de Sancho Gomez points possibly to a climate change from relatively wet to dry-subhumid or subarid conditions. A similar trend from the *Boreal/early Atlantic* to the *late Atlantic/early Subboreal* is also documented by Jalut et al. (1997) for a South–North transect along the Mediterranean coast of the Iberian Peninsula. The absence of time control precludes a correlation with these data.

In spite of chronological uncertainties the records clearly show the presence of dry and wet phases during the Holocene and also the great potential — and limitations — of these playa-lake systems as paleoenvironmental archives.

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