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The chemistry of playa-lake-sediments as a tool for the reconstruction of Holocene environmental conditions - a case study from the central Ebro basin

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Abstract

The focus of the presented study is the reconstruction of the Holocene limnic and drainage basin conditions of the Laguna de Jabonera, a today playa-lake-system in the Desierto de Calanda, central Ebro Basin, using the inorganic characters of the lacustrine sediments. Mineralogical fabric helped to reconstruct the overall geomorphic processes and gives clues to the synsedimentary limnic environment (paleosalinity). The chemical composition of the lacustrine sediments largely reflects the mineralogical composition, but the higher resolution of the geochemical data compared to the mineralogical data enables to stratigraphically split the extracted core profile into three stratigraphic units. Supplementally, it is demonstrated that statistics between chemical compounds point to the synsedimentary intensity of weathering and soil forming processes.

As for the lacustrine sediments investigated there are no data yet available 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 to dry-subhumid environmental conditions occurred. Also possibly during the *late Subboreal* distinct wetter environmental con-

ditions than today prevailed. Additionally, it is demonstrated that in the most recent past human impact is causing increased erosion rates and, thus, increased deposition of detritals in the most recent lacustrine sediments.

1 Introduction

Core-based paleoenvironmental investigations of lacustrine settings have been mostly dominated by micro-paleontological and pollen-based studies. Inorganic features of lake sediments are predominantly studied using mineralogical analyses to characterize lake typology (depth of water column, lake phase, salinity). The focus of this research is the reconstruction of Holocene weathering conditions of a today playa-lake-system in the Desierto de Calanda, central Ebro Basin by the analyses of the chemical character of lacustrine sediments, supplementing information about the limnic environment derived from the mineralogical character.

2 Site description

The region of the Desierto de Calanda southwest the town of Alcañiz is characterized by a plain built of slightly cemented Miocene clay strata with paleochannels of calcareous sandstone (Riba et al., 1983). The receiving stream of the Desierto de Calanda is the Río Guadalupe, a tributary of the Río Ebro.

The present climate of the area is subarid Mediterranean with mean annual precipitation between 300-350 mm. Precipitation peaks during autumn and spring when the region is under the influence of westerlies. Summer aridity lasts for four months. Present-day climatic conditions in the Desierto de Calanda induce a mean annual precipitation-evaporation-ratio (P/pET) of 0.45 (García de Pedraza and Reija Garrido, 1994), that means, according to the classification of the aridity-indices as quoted by UNEP (1991), the Desierto de Calanda belongs to the semi-arid dryland regions. Under present conditions, the mean annual groundwater influx into the endorheic basins of the Desierto de Calanda amounts to c. 60 mm, the mean annual surface inflow comes to 15 mm (data estimated according to Sanchez Navarro et al., 1991).

In the Desierto de Calanda endorheic basins were formed by the combined processes of subsurface erosion of underlying gypsum layers and deflation of outcropping clay strata (Ibañez, 1973; Fig. 1). Thus, in an area of approximately 100 km² more than 20 endorheic basins varying in size were built (Sanchez Navarro et al., 1991, 23). The largest of these basins are several hundred metres in diameter and get periodically flooded. Only some basins, predominantly located in the northeast of the Desierto de Calanda, are completely desiccated (Ibañez, 1973). Paleochannels form the boundary of the endorheic basins and elevate up to 20 m above the lake floor. Present processes of surface erosion occur, but forms are peri-

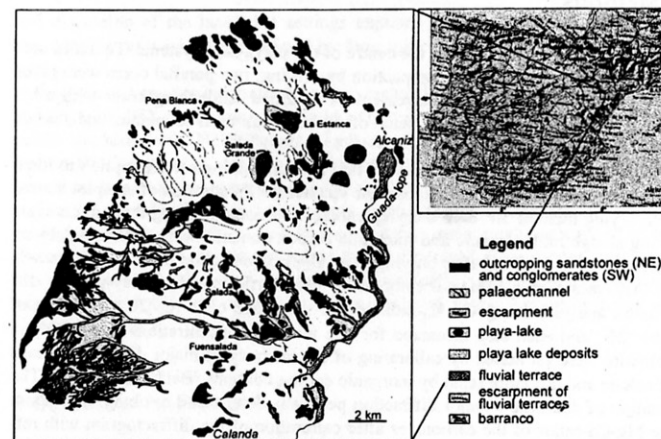


Fig. 1. Geomorphological-lithological map of the Desierto de Calanda (copy from Ibañez, 1973, 23)

odically removed by ploughing of the fields. The present solution of evaporitic rocks is reflected in high groundwater salinity (5765 mg/l TDS, n=13). Predominance of sulphates in the solutes ($\mu=3640$ mg/l SO_4^{2-} , std.=2207, n=13) reflects their origin from solution of solid Miocene sulphates. Composition of cations also points to solution of sulphates with calcium, magnesium, and sodium ions predominating ($\mu_{\text{Ca}}=526$ mg/l Ca^{2+} , std.=143; $\mu_{\text{Mg}}=457$ mg/l Mg^{2+} , std.=305; $\mu_{\text{Na}}=569$ mg/l Na^+ , std.=730; n=13). During sampling in March 1994 table of perched groundwater varied between -0.8 m to -5.2 m below surface (all data are based on field data sampled from wells in the watershed of the Desierto de Calanda in March 1994).

Presently the area is being used for dry farming in which fallow land is used for pasture.

In the Desierto de Calanda cores were taken in the endorheic basins of the Salada Grande (easting 735 000, northing 4548 000; UTM coordinate system), the Laguna Pequeña (easting 733750, northing 4547 500; UTM coordinate system) and the Laguna de Jabonera (easting 736 600, northing 4547 500; UTM coordinate system). As sediments of all three endorheic basins point to the same sedimentary history, results shown in this paper are from the Laguna de Jabonera, an endorheic basin with a depth of c. 20 m and a lake floor diameter of c. 1 km. The lacustrine sediments discussed were extracted in the centre of the basin; coring went down to the Miocene bedrock in 310 cm depth below lake floor.

3 Methods

In general, cores were taken in the centre of the playa-lake-systems. 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. 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 after burning in an O₂-flux (detection limit = 0.02 mass-% C). Analyses of mineralogical compounds were carried out by X-ray powder diffraction analyses using Cu K_α-radiation in the range of 2-70 °2θ with steps of 0.01 °2θ and each step measured for one minute. Concentrations of calcite and dolomite were estimated by calibrating 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 peak was determined to obtain data about the Mg-Ca-ratios of the carbonates after calibration of the diffractogram with reference to the major diffraction peak of quartz (Tennant and Berger, 1957; Langbein et al., 1981); data were traced with two decimals but are presented with three decimals wherever they show average values. Bulk chemistry of samples was determined by X-ray fluorescence analyses (Siemens SRS 2000). For interpretation

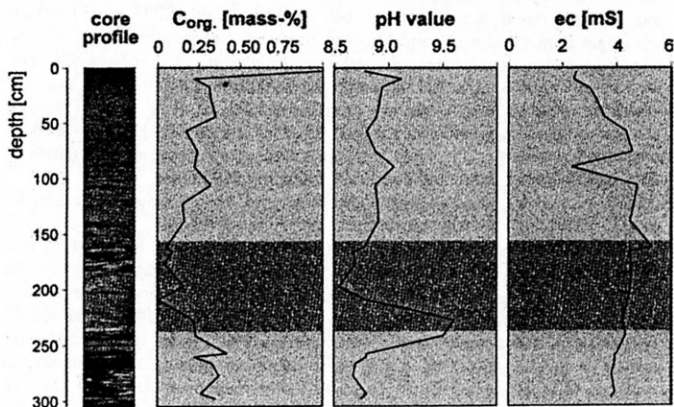


Fig. 2. Bedding of the core profile, organic carbon content (mass-% C_{org}), pH-value, and electric conductivity (ec mS) of lacustrine sediments

and discussion of the lacustrine settings exposed sediments are subdivided into stratigraphic units which are defined by their mineralogical and chemical composition.

Because of very low contents of organic carbon in the playa-lake-sediments, the technique of OSL-dating was chosen to obtain data, executed at the *Forschungsstelle Archäometrie* (Heidelberger Akademie der Wissenschaften, Max-Planck-Institut für Kernphysik). As data are not available yet correlation with investigations from neighbouring areas give a preliminary time scale.

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

4 Sediment character

4.1 General sedimentary fabric

Lacustrine sediments from the Laguna de Jabonera are of a greyish brown at the basal layers (7.5 YR 4/4) and to the top continuously change to a more reddish colour (2.5 YR 5/4 in 240 cm depth), repeatedly interstratified by fibrous gypsum. From 240 cm depth to the surface sediments are uniformly brownish grey. The organic carbon contents in the sediments reach 1.02 mass-% C_{org} close to the lakebed surface but decrease rapidly below 5 cm depth only to oscillate around $\mu_{C_{org}}=0.19$ mass-% C_{org} (std.= 0.153, n=24). The sediments are slightly basic ($\mu_{pH}=8.9$, std._{pH}= 0.23, n=25), only between 230 and 250 cm depth the pH rises to 9.6 (Fig. 2).

4.2 Mineralogical composition

The whole core is characterized by the simultaneous occurrence of quartz, gypsum, and calcite with gypsum predominant in the parts below 130 cm depth, and carbonates in the upper part (Table 1). Thin sections show that along the whole core the mineralogical composition is idiomorphic carbonates and gypsum embedded in an alternating medium- to fine-grained groundmass of carbonates and gypsum; only in the most recent sediments carbonates are detrital. Dehydrated sulphates (anhydrite) can be detected along the entire core profile as traces. Other than sulphates halites exist as evaporitic minerals. Their concentration decreases to the top. They mainly appear as a minor component in the core section below

Table 1. Mineralogical composition of lacustrine sediments

stratigraphic unit	depth [cm]	Carbonates		Sulphates		Halite	Quartz	Phyllo-silicates	Goethite
		Calcite	Dolomite	Gypsum	Anhydrite				
3	3	+++	++	++	+	++	+++	++	+
	10	+++	++	+	+	+	+++	++	+
	18	+++	++	++	+	+	+++	++	+
	29	+++	++	++	+	+	+++	++	+
	45	+++	++	++	+	+	+++	++	+
	58	+++	++	+++	+	+	+++	++	+
	77	+++	++	++	+	+	+++	++	+
	91	+++	++	++	+	+	+++	++	+
	108	+++	++	+++	+	+	+++	++	+
	125	+++	++	++	+	+	+++	++	+
	141	++	++	+++	+	+	+++	++	+
	165	+	+++	++	+	+	+++	++	+
	2	169	+	++	+++	+	++	++	+
180		++	+++	+++	+	++	++	++	+
201		++	++	+++	+	++	++	++	+
213		+	++	+++	+	++	++	++	+
232		++	++	+++	+	++	++	++	+
1	246	+	+++	+++	+	+	+++	+	+
	261	++	++	+++	+	++	++	+	+
	265	++	++	+++	+	++	++	+	+
	271	+	++	+++	+	++	+++	+	+
	282	+	++	+++	+	++	+++	+	+
	292	++	++	+++	++	++	+++	+	+
	303	+	++	+++	+	+	+++	+	+

max. counts p.s. +++ major components
++ minor components + traces

165 cm depth (stratigraphic units 1 and 2) and only as traces above (stratigraphic unit 3). Calcite contents continuously increase from bottom to top ($\alpha < 0.001$) while above 165 cm depth dolomite contents decrease continuously ($\alpha < 0.05$).

The dolomite contents alternate strongly below 165 cm depth (Fig. 3). Between 180 and 220 cm depth the average dolomite content amounts to 8.8 mass-%, in 246 cm depth its content rises up to 18.3 mass-% and fluctuates below 246 cm depth between 4.6-13.6 mass-%. Dolomite's major diffraction line varies along the whole core profile about $\mu_{\text{dol100}} = 30.828 \text{ } ^\circ 2\theta \text{ CuK}\alpha$ (std. = 0.046, n=25). In stratigraphic unit 2 the position of dolomite's major diffraction line averages $\mu_{\text{dol100,2}} = 30.859 \text{ } ^\circ 2\theta \text{ CuK}\alpha$ (std. = 0.042, n=6) and, thus, does not differ significantly from the angles of diffraction in the underlying and overlying sediments ($\alpha > 0.05$).

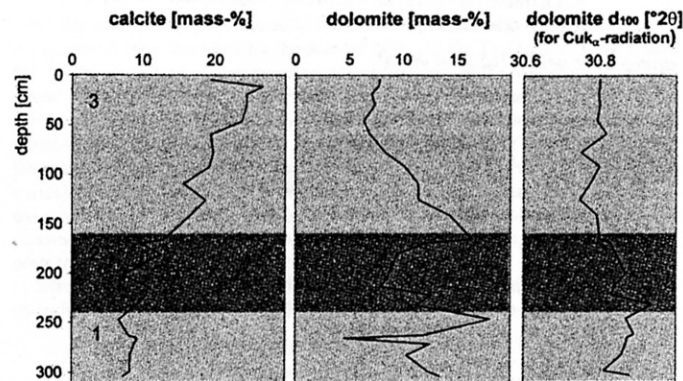


Fig. 3. Calcite and dolomite contents (mass-%) of lacustrine sediments and location of the diffraction angle of dolomite's major diffraction peak 100 (dol₁₀₀ $^\circ 2\theta$ Cu K $_{\alpha}$ -radiation)

4.3 Chemical composition

4.3.1 Major elements

As lacustrine sediments of the Laguna de Jabonera are subdivided into three stratigraphic units (cf., chapter 4.4) mean chemical composition of each stratigraphic unit is summarized in Table 2. These data show evidently that in stratigraphic unit 1 concentrations of SiO₂, MnO, and TiO₂ are distinctly higher and concentrations of S (sulphur content expressed as SO₃) and CaO distinctly lower than in the overlying stratigraphic unit 2 (166-240 cm depth; Fig. 4). At a depth of 165 cm (stratigraphic unit 3; 0-165 cm depth) there is again a marked change in the chemical sediment composition. From the lower to the higher layer, calcium oxide and sulphur concentrations decrease distinctly while the concentrations of the most metal oxides and of silica increase (Table 2). In 50 to 70 cm depth the sulphur graph again shows a marked deflection, coinciding for a short time concentrations of silica and metal oxides are reduced (Fig. 4).

Towards the top continuously increasing phosphate contents ($\alpha < 0.05$) are correlated to the sediment's calcite contents:

$$P_2O_5 \text{ mass-\%} = 0.06237 + 0.00386 \cdot \text{calcite mass-\%} \quad (\text{eq. 1})$$

n=25, r=0.87392, adj. r²=0.75346

$$\text{Al}_2\text{O}_3 \text{ (mass-\%)} = 0.19122 + 2.76116 * \text{Fe}_2\text{O}_3 \text{ (mass-\%)} \quad (\text{eq. 3})$$

n=12, r=0.99822, adj.r²=0.99555

stratigraphic unit 3 (165;0 cm depth):

$$\text{Al}_2\text{O}_3 \text{ (mass-\%)} = 1.84947 + 2.40694 * \text{Fe}_2\text{O}_3 \text{ (mass-\%)} \quad (\text{eq. 4})$$

n=10, r=0.99015, adj.r²=0.97843

stratigraphic unit 1 (310;241 cm depth):

$$\text{Fe}_2\text{O}_3 \text{ (mass-\%)} = 1.23577 + 1.08359 * \text{K}_2\text{O} \text{ (mass-\%)} \quad (\text{eq. 5})$$

n=18, r=0.49884, adj.r²=0.09861

stratigraphic unit 2 (240;166 cm depth):

$$\text{Fe}_2\text{O}_3 \text{ (mass-\%)} = 0.59871 + 1.39093 * \text{K}_2\text{O} \text{ (mass-\%)} \quad (\text{eq. 6})$$

n=12, r=0.99014, adj.r²=0.97547

stratigraphic unit 3 (165;0 cm depth):

$$\text{Fe}_2\text{O}_3 \text{ (mass-\%)} = 2.60917 + 0.96935 * \text{K}_2\text{O} \text{ (mass-\%)} \quad (\text{eq. 7})$$

n=10, r=0.66275, adj.r²=0.38315

4.3.2 Traces

Considering the heavy-metal contents of the lacustrine sediments, evidence of lead cannot be found throughout the core section. The copper, chrome, nickel, and zinc content variations within the lacustrine sediments correspond with the metal oxide contents (Al₂O₃, Fe₂O₃, TiO₂; cf. Fig. 4) and reach maximal values in stratigraphic unit 3 with μ_{Cr}=61 ppm Cr (std._{Cr}=14.5), μ_{Cu}=94 ppm Cu (std._{Cu}=4.2), μ_{Ni}=38 ppm Ni (std._{Ni}=13.8) und μ_{Zn}=81 ppm Zn (std._{Zn}=7.3) (α<0.001). Opposed to this, in stratigraphic units 2 and 3 strontium concentrations correlate highly linear with sulphur contents (α<0.001). Average strontium concentrations prove to have lower values in stratigraphic unit 3 with μ_{Sr}=550 ppm Sr (std._{Sr}=175) than in stratigraphic unit 2 (μ_{Sr}=2830, std._{Sr}=851, n=6) (α<0.001); concurrently, the average strontium contents in stratigraphic unit 2 are lower than in stratigraphic unit 1 (μ_{Sr}=4548, std._{Sr}=3120, n=7) (α<0.01).

4.4 Defining stratigraphical units

Differentiation of the core profile into the three stratigraphic units

- 1 (241 to 310 cm depth),
- 2 (166 to 240 cm depth),
- 3 (0 to 165 cm depth)

was proven by discriminant analysis using the variables 'allothigenic components' and 'position of dolomite's major diffraction peak' (dol₁₀₀). The bulk of allothigenic minerals corresponds to detritals illuviated from the watershed where Mio-

cene clay strata build predominantly the outcropping bedrock. Thus, 'allothigenic components' are substituted by the sum of SiO₂, Al₂O₃, Fe₂O₃, and MnO (mass-%). As the 'authigenic components' are the counterpart of the 'allothigenic components' and both sum up to 100 mass-%, these variables are highly correlated (α<0.001). Thus, the variable 'authigenic components' is not suitable as the second variable for discriminant analysis. As the second variable for discriminant analysis the position (°2θ) of dolomite's major diffraction peak 'dol₁₀₀' was chosen, as this variable is only weakly correlated to the 'allothigenic components' (α>0.05) and, at the same time, the position of dolomite's major diffraction peak reflects the limnic conditions during formation of 'authigenic components' - and, therefore, represents the other fraction of the lacustrine sediments.

Distribution of data lead to a differentiation into three stratigraphic units corresponding to the clusters shown in Fig. 5. Discriminant function Y_{1/2}

$$Y_{1/2} = 1.084 * \text{allothigenic minerals (mass-\%)} + 0.477 * \text{dol}_{100} \text{ (}^\circ 2\theta \text{ Cuk}_\alpha) \quad (\text{eq. 8})$$

allows in all cases correct assignment of data to stratigraphical units 1 and 2 (n=13; Wilk's L=0.205). Also discriminant function Y_{2/3}

$$Y_{2/3} = 0.956 * \text{allothigenic minerals (mass-\%)} - 0.170 * \text{dol}_{100} \text{ (}^\circ 2\theta \text{ Cuk}_\alpha) \quad (\text{eq. 9})$$

allows correct assignment of data to stratigraphical units 2 and 3 in all cases (n=18; Wilk's L=0.078).

5 Paleoenvironmental indications by the inorganic character of lacustrine sediments from playa-lake-systems

5.1 Information about paleolimnic environment from mineralogy

The mineralogical composition of the detrital lacustrine sediments in the area investigated is determined by the parent material. Apart from allochthonously deposited detritus authigenic carbonates and sulphates make up the mineralogical setting of the lacustrine sediments. Early diagenetic processes, steered by salinity and chemistry of brines, i.e. pore water, can modify the mineralogical properties. The influence of brine salinity on the authigenic mineral fabric and early diagenetic modification of minerals is predominant. Therefore, the mineralogical sediment properties provide some valuable information for the reconstruction of the paleoenvironment.

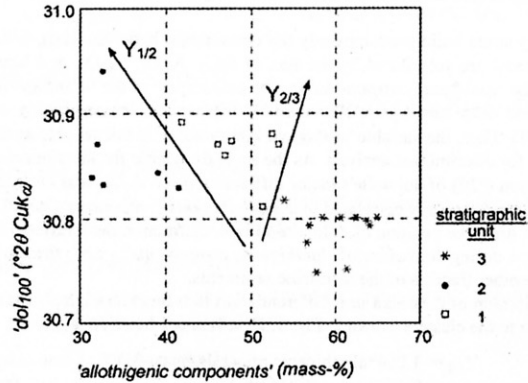


Fig. 5. Scatter-plot of sediment's dolomite's major diffraction peak 'dol100' and 'allothigenic components', substituted by the sum of SiO₂, Al₂O₃, Fe₂O₃, and MnO (mass-%) separated for sections 1-3

For the analysis of the mineralogical composition X-ray powder diffraction of the samples was chosen as this method is a basic tool in the mineralogical analysis of sediments. Data resulting from X-ray powder diffraction are only semiquantitative as shown in Table 1, but with regard to the chemical sediment character also allow to generate discrete mineral contents (cf. Fig. 3). Additionally, this method offers as a by-product information about carbonate's lattice distances and, thus, information about Mg-Ca-ratios of carbonates as presented in chapter 4.2. Thus, even if for detection of carbonate's Mg-Ca-ratios thermal methods such as DTA and DSC provide a higher accuracy, the position of dolomite's major diffraction peak gives an idea on carbonate's Mg-Ca-ratio in the sample. Beneath step-width and goniometer's scan velocity determination accuracy of the position of carbonates major diffraction peak depends on the crystallinity of the the sample and sample's grain-size distribution.

5.1.1 Mineral fabric

Quartz, calcite, and gypsum make up the mineralogical major components of the lacustrine sediments of the Laguna de Jabonera. The analysis of these major components within the lacustrine sediments yields information on some conspicuous environmental changes (Fig. 6).

During periods with a negative water balance a sparse vegetation cover within the catchment, triggering aeolian processes and overland flow, leads to transposition of the parent material due to ephemeral to periodic heavy rains (Dunne et al., 1991; Rogers and Schumm, 1991). Lacustrine sediments which suit these proc-

esses in the Laguna de Jabonera basin include detrital carbonates, quartz, and silicates. Dry environmental conditions also mean a reduction of groundwater recharge and, corresponding, reduced subsurface flow (Horton, 1945). 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. Consequently, lacustrine settings deposited under arid to subarid environmental conditions are rich in allochthonous components (clay minerals, detrital carbonates, and quartz), while autochthonous sediments (carbonates, sulphates, halites) are only of secondary importance. Vice versa, wetter periods allow a denser vegetation cover so the topsoil is protected from being eroded by wind or water. Low relief and vegetation cover support infiltration and, therefore, increase subsurface flow (Horton, 1945; Morisawa, 1959). Precipitation of evaporites in the Laguna de Jabonera therefore has to be explained by groundwater increase and, thus, increased subsurface inflow of aqueous solution, which will mostly take place in response to more humid conditions (Schütt, 1998a, 1998c). Consequently, during wetter conditions in the Laguna de Jabonera basin the reduced erosion combined with concurrent higher influx of sulphate-rich groundwater (SO₄²⁻-Ca²⁺-Mg²⁺-Cl-

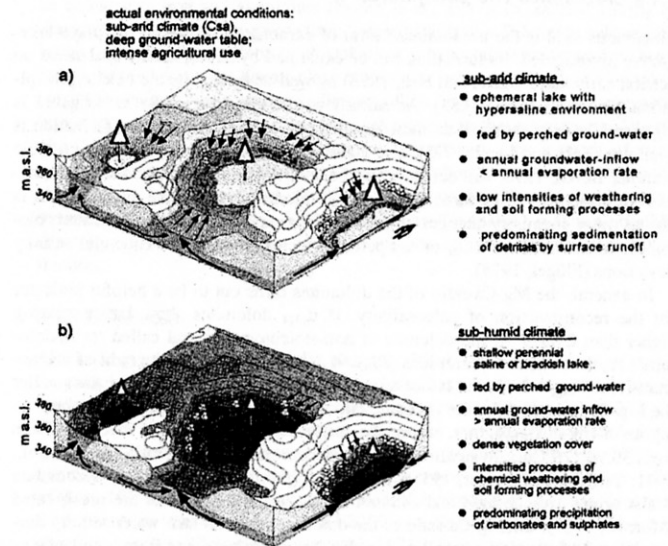


Fig. 6. Reconstruction of climatic influence of environmental and depositional conditions of the Desierto de Calanda: (a) sub-arid climate and (b) sub-humid climate

type) results in increased evaporite concentrations in the correlating lacustrine settings.

Taking these facts into account, the increased sulphate contents in the sediments of core section 2 trace back to a phase of well-balanced water-budget conditions with raised groundwater inflow and thereby high inflow rates of sulfatic aqueous solutions. The detrital carbonates and quartz in the sediments increase to the top because of worsening water-balance conditions and the consequently reduced inflow of aqueous solutions with the groundwater coinciding with increased erosion. A growing influence of soil erosion must also be taken into consideration for the formation of these most recent sediments (Faust and Diaz del Olmo, 1997; Stevenson et al., 1991). These predominant semiarid to dry-subhumid climatic conditions during the sedimentation of the uppermost strata (stratigraphic unit 3) were only briefly interrupted, indicated by a short-term increase of the sulphate contents in the sediments between 50 to 60 cm depth. A similar but less distinct deflection of sulphur graph occurs in stratigraphic unit 1 between 260 to 270 cm depth and, thus, also points to short-term wetter environmental conditions during an altogether dry-subhumid to subarid climatic period during deposition of stratigraphic unit 1.

5.1.2 Carbonates and phosphates

Calcareous mud is the predominant form of carbonate deposits in the playa-lake-system investigated. Its formation 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). As salinity in the playa-type lake investigated is high, and as magnesium as an indispensable prerequisite of dolomite formation is available (Folk and Land, 1975), also authigenic dolomite precipitation is possible (van der Borch, 1976; van der Borch and Lock, 1979). Essentially, the autochthonous development of calcareous mud (=automicrite) in lacustrine environments is due to water chemistry changes effected by decomposition of organic matter, biological assimilation of CO₂, or temperature increases with consequential salinity deviations (Flügel, 1978).

In general, the Mg-Ca-ratio of the dolomites turns out to be a helpful indicator for the reconstruction of paleosalinity. If d_{1014} dolomites show lattice spacing higher than 2.8879 Å, the dolomite is non-stoichiometric and called 'protodolomite'. As the radii of calcium-ions ($R_{Ca^{2+}}=1.00$) are bigger than the radii of magnesium-ions ($R_{Mg^{2+}}=0.72$) the lattice spacing of dolomite becomes larger the smaller the Mg-Ca-ratio of dolomite is (Langbein et al., 1981). This is portrayed when using an X-ray-diffractogram, where the major diffraction peak of dolomite shifts from 30.94 °2θ CuK_α to smaller angles with decreasing Mg-Ca-ratio (Royle et al., 1971; Tennant and Berger, 1957). Because magnesium-ions relatively accumulate whilst brines are confined and calcium carbonates and sulphates are precipitated (Morrow, 1979), the Mg-Ca-ratio of the dolomites reflects lake water salinity during dolomite formation, regardless whether dolomites originate from authigenic or early diagenetic processes (Folk and Land, 1975; Morrow, 1982).

But at all, paleoenvironmental conditions in the watershed of the Laguna de Jabonera as reconstructed on the base of the overall mineral fabric are not reflected in significant changes of lake water salinity as shown by the Mg-Ca-ratio of the dolomites because in the sediments of the Laguna de Jabonera changes in position of dolomite's major diffraction peak do not vary significantly between stratigraphic units (Fig. 3). High inflow rates of solutes during wetter phases get 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 the Laguna de Jabonera the Mg-Ca-ratio of dolomites does not offer useful information for the reconstruction of paleohydrology. In stratigraphic unit 3 the negative trend between calcite and dolomite, corresponding to from bottom to top increasing calcite contents and decreasing dolomite contents, might be due to the downward continuing process of early diagenetic dolomitization. As Mg-Ca-ratios of dolomite show no significant changes in these stratigraphic unit it can be excluded that trends of calcite and dolomite concentrations with depth are due to changes in salinity and, thus, to changing conditions of authigenic carbonate formation.

During precipitation of authigenic calcite dissolved phosphor can be combined and precipitated as apatite (Ca₅(PO₄)₃OH or Ca₅(PO₄CO₃OH)₃(F,OH)) (Stumm and Leckie, 1971; Müller, 1997). In addition, dissolved phosphor compounds can be bounded to iron and aluminium (Eckert et al., 1997). In contrast, during early diagenetic dolomitization magnesium can substitute the PO₄-ions and sodium as well as strontium can substitute phosphate in a hypersaline environment (Nathan, 1984). Nevertheless, the linear, close connection between phosphor(V)-oxide and calcite contents in the lacustrine sediments of the Laguna de Jabonera suggests the importance of calcite for the phosphor precipitation in these sediments. The phosphor(V)-oxide contents in the lacustrine sediments are then a result of primary apatite formation and secondary displacement of phosphor by sodium, magnesium or strontium ions. Due to an altogether low phosphor(V)-oxide content in the sediment ($\mu_{P_{2O_5}}=0.12$ mass-% P₂O₅ \cong 0.28 mass-% apatite) it is not possible to detect apatite in the sediments of the Laguna de Jabonera by X-ray powder diffraction.

5.1.3 Sulphates

Alongside gypsum (CaSO₄ • 2H₂O), also anhydrite (CaSO₄) was found as traces in the samples of the lacustrine sediments of the Laguna de Jabonera. In general, gypsum gets precipitated autochthonously from brines with a density >1.115 g/cm³ (Sonnenfeld, 1984, 102). In contrast, anhydrite can be precipitated autochthonously or might be a diagenesis product from gypsum (Usdowski, 1974). Diagenesis of gypsum is controlled by temperature, pressure, and lake water salinity (Holser, 1979). Anhydrites originating from dehydration of gypsum, in general, show strontium concentrations around 2200 ppm Sr corresponding to the average strontium content of gypsum (Usdowski, 1973). In contrast, in brines strontium gets relatively enriched with continuing evaporation; thus, autochthonous anhy-

drites contain 20000 to 30000 ppm Sr (Usdowski, 1974). Strontium concentrations in the lacustrine sediments of the Laguna de Jabonera, in general, range in the dimension 10^3 and, thus, point to anhydrites formed by dehydration of gypsum – that means by diagenetic processes. Altogether, significant higher strontium concentrations in sediments of stratigraphic unit 1 indicate a distinct negative water balance during gypsum precipitation. In contrast, low strontium concentrations in the most recent sediments reflect 'dilution'-processes by high input rates of detritals (quartz, silicates, carbonates) in consequence of soil erosion processes (Stevenson et al., 1991; cf. chapter 5.2.3).

5.2 Information about erosion and weathering conditions from sediment chemistry

Analogously to the bulk chemistry of the lacustrine sediments the catchment properties of the lakes are recorded and analyzed. That means if occasion arises, the petrography, structure, and relief of the catchment, as well as hydrographical and hydrogeological catchment properties were investigated, as these characters can limit the applicability of individual geochemical sediment properties as paleoenvironment indicators. In opposition to this, climatic factors influence the intensity of the material-mobilisation processes. For the chemical weathering this results from the availability of H_2O as the reaction agent and from the direct influence of the temperature to the speed of the reaction. The influence of the climate on the biomass production and consequently on the provision of vegetable matter should also be considered. Humic acids are produced when vegetable matter is decomposed; they influence the soil pH and, thereby, modify intensity of weathering processes. The climate can also have an effect on the erosion processes which can interfere with weathering and soil-formation processes.

5.2.1 Organic Carbon

The organic carbon is subject to early diagenetic decomposition processes, both, in the limnic environment as well as in the lacustrine sediments (Meyers and Ishiwatari, 1993). These processes take place during different redox-conditions (Evans and Kirkland, 1988) and, as a function of time, can lead to the complete consumption of the organic carbon (Lerman, 1979). The organic carbon in the lacustrine sediments of the Laguna de Jabonera is allochthonous and was transported from the catchment into the basin as a result of surface erosion, or it is autochthonous and developed owing to limnic biomass production (Håkanson and Jansson, 1983). The decomposition processes of organic matter are accelerated in aerobic environments with the presence of light and high temperatures (Vallentyne 1962). Accordingly, organic carbon in sediments close to the surface in ephemeral lakes is subject to quickened decomposition. Hence, the known high primary production in saline environments (Evans and Kirkland, 1988) does not consequently effect increased organic-carbon contents in the sediment. The graph of organic carbon

concentration as shown in Fig. 2 essentially reflects the early diagenetic decomposition of organic matter advancing from the bottom to the top.

Because the components of phytoplankton are generally more soluble than allochthonous plant detritus (cellulose, chitin, lignin) (Vallentyne, 1962) the increased organic carbon contents in stratigraphic unit 1 possibly suggest intensified deposits of difficultly decomposable plant detritus. Additionally, the increased organic carbon concentrations can be an indicator for an altogether increased accumulation rate which induces a relative decrease of the organic carbon decomposition rate in the sediment (Lerman, 1979, 392). Both processes, nevertheless, likewise indicate intensified erosion dynamics for the Laguna de Jabonera catchment during sediment deposition of stratigraphic unit 1 and, thus, confirm subarid to dry-subhumid environmental conditions as already reconstructed by the overall mineral fabric.

5.2.2 Mean chemical composition

The mean chemical composition of the lacustrine sediments largely reflects the mineralogical composition. However, the higher resolution of the geochemical data compared to the mineralogical data enables to stratigraphically split the extracted core profile into three stratigraphic units (eq. 8, eq. 9). Correspondingly, not only the ascendancy of gypsum in the sediments of stratigraphic unit 2 can be verified by the graphs of the sulphur-trioxide concentration in the sediment, moreover, by comparing stratigraphic units 1 and 2 an increased importance of sulphatic precipitations in unit 2 can be observed. Here, the mean silica-, titanium-, aluminium-, iron-, and manganese-oxide contents show exact opposite proportional values to these highest sulphur-trioxide contents by having their lowest values in stratigraphic unit 2.

One can deduce from the conclusions in the chapter on the mineralogical composition that the increased concentrations of authigenic minerals (sulphates, authigenic calcites) in the lacustrine sediments result from multiplied inflow of aqueous solution via groundwater, whereas increased detrital contents (detrital carbonates, silicates, quartz) in the lacustrine sediment reflect relatively intensified erosion dynamics in the catchment. Therefore, the raised mean sulphur-trioxide contents in stratigraphic unit 2 conclude that the sediments of this unit were deposited in a wetter phase. Correspondingly, the sediments affected more by detritus in stratigraphic units 1 and 3 were deposited in an environment controlled by arid conditions (cf. chapter 5.1.1). The comparison of the mean chemical composition of the sediments of stratigraphic unit 3 with that of stratigraphic unit 1 indicates the greater importance of authigenic mineral formations (SO_3 factor 3) and lower importance of detrital minerals (SiO_2 factor 0.9) in stratigraphic unit 1. In this valuation one must also consider the growing land-use intensity with time which has led to magnified erosion processes ('soil erosion') in the most recent past (Stevenson et al. 1991; Faust, 1995). In the sediments of stratigraphic unit 3 these soil erosion processes cause an increase of the detrital components. Moreover, the increased gypsum resp. sulphur-trioxide contents in 50 to 60 cm depth and 260 to 270 cm

depth point to a short phase of equable water balance with increased groundwater inflow and, thereupon, proceeding increased rates of evaporite precipitation.

A syn- or postsedimentary change of the sediment chemistry by solution and displacement of silica containing sediments can largely be ruled out for lacustrine sediments with mean pH values of $\mu_{\text{pH}}=8.9$ (Fig. 2) because, in this environment, the solubility of silica and aluminium is only slightly higher than in a neutral environment (SiO_2 factor 1.5). The solubility of these substances only increases exponentially when basicity goes up (SiO_2 solubility at pH 9.5 factor 2.6, at pH 10 factor 5) (Krauskopf, 1956; Degens, 1962).

5.2.3 Statistics between the contents of selected elements

Chemical weathering and soil forming processes depend on the availability of water and both increase in intensity with growing precipitation-evaporation-ratios (Krauskopf, 1967; Chesworth, 1992). The resulting differentiation of the soil profile increases with the intensity of these processes. During phases of well-balanced water-budget the erosion rates are low due to denser vegetation (Rogers and Schumm, 1991). Regarding only gradual progress of erosion processes, the correlated lacustrine sediments show good statistics between the individual chemical substances owing to the differentiated soil profiles induced by chemical weathering and soil-formation processes in a humid to subhumid environment (Krauskopf, 1967).

Trend of statistics

In the three stratigraphic units defined the connections between the sulphur trioxide contents and the silica and titanium oxide contents are subject to a negative trend ($\alpha < 0.001$) as well as negative trends between aluminium and iron oxide contents to sulphur trioxide can be noticed in stratigraphic units 2 and 3 ($\alpha < 0.01$). This indicates the different process structures which led to the deposition of these substances. While the sulphur was dissolved by groundwater and precipitated, due to evaporation, in the Laguna de Jabonera basin after being transported there, the silica, titanium, aluminium and iron in the lacustrine sediments, predominantly detritically linked, were washed into the basin as a result of surface erosion in the catchment (Sanchez Navarro et al., 1991).

Quality of statistics

In stratigraphic unit 2 the concentrations of the silica, titanium, aluminium, iron, manganese, potassium, and sodium oxide contents are positively correlated with each other ($\alpha < 0.01$) which points towards the common origin of these substances from the weathering and erosion of the outcropping Miocene claystrata and Pliocene paleochannel fillings in the catchments. Comparatively, in stratigraphic units 1 and 3 the graphs of the silica, titanium, aluminium and iron oxide contents are also positively correlated ($\alpha < 0.05$). Yet, further statistically significant connections

with other component contents in the sediment are missing. Under semiarid conditions the weathering and soil-formation processes, and with that the chemical soil-profile differentiation, are limited (Krauskopf, 1967, 81). The simultaneously high erosion rates (Dunne et al., 1991) result in the correlated lacustrine sediments in 'random' chemical properties, that means statistics are incidental and are not subject to any regularities. The quality of statistics between the contents of different chemical substances is influenced by the mobility of the individual chemical parameters. The decreasing ionic potential of a substance makes the quality of its statistics with the concentrations of more stable substances go down. In addition, in stratigraphic unit 3, an intensified influence of phyllosilicates, occurring here as a minor component, particularly on the varying K_2O - and Na_2O contents must be taken into consideration due to the tying of the K^+ -ions into the crystal lattice or ionic absorption (Heim, 1990).

Trend of regression line

Apart from the quality of the statistics (correlation coefficients in the appendix, Table A1), also the character of the relationship between the different component concentrations in the lacustrine sediment is affected by the prevailing synsedimentary environmental conditions. If, during the examination of the statistical relationships between two chemical substances, the component with the higher ionic potential is used as the dependent variable, the slope of the regression line steepens when the weathering intensity of the eroded matter goes up (Fig. 7). Regarding the statistical connection $\text{Al}_2\text{O}_3 = f(\text{Fe}_2\text{O}_3)$, for stratigraphic unit 2, this is expressed in the steepening of the slope of the regression line by factor 1.15 compared with the counterpart relationship in unit 1 and by factor 1.58 compared with stratigraphic unit 3 (eq. 2-4). The same examination for the connection $\text{Fe}_2\text{O}_3 = f(\text{K}_2\text{O})$ establishes, for stratigraphic unit 2, a steepening of the slope of the

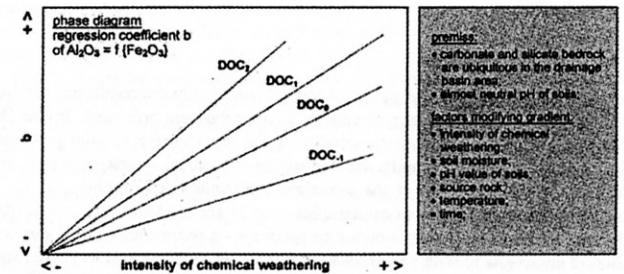


Fig. 7. Gradient of regression line of linear relation between Al_2O_3 and Fe_2O_3 contents of lacustrine sediments as paleoenvironment indicator

regression line by factor 1.28 compared with the corresponding relationship in unit 1 and by factor 1.43 compared with the same relationship in unit 3 (eq. 5-7). Proceeding from this comparison, allowing the same weathering and soil-formation processes the slope of the regression line is determined by the ionic potential of dependent and independent variables (ionic potentials: $IP_{K^+}=0.75$, $IP_{Fe^{3+}}=4.7$, $IP_{Al^{3+}}=5.9$).

Because element mobility is due to the element's ionic potential, gaps between oxide concentrations in soils increase with weathering intensity (Krauskopf, 1967). While soils get eroded and form soil sediments, the steepness of the regression line's slope between oxide concentrations in these deposits reflects the weathering intensity in the initial material.

5.2.4 Traces

The positively correlated connections between the heavy metals copper, chrome, nickel, and zinc and the silica, titanium, aluminium, and iron oxide contents of the lacustrine sediments ($\alpha < 0.001$) point towards the common origin of both substance groups from weathering and erosion of outcropping bedrock in the catchment of the Laguna de Jabonera. Due to the relatively high phyllosilicate contents in the lacustrine sediments of the Laguna de Jabonera, one can assume that the heavy metals are tied to the phyllosilicates – chiefly existing as illites – as exchangeable cations (Malle, 1990; Förstner et al., 1990; Schindler, 1991; Kühnel, 1992).

The positively correlated connections between the strontium and the sulphur-trioxide contents in the lacustrine sediments ($\alpha < 0.001$) in one respect follow from the common origin of these substances from the solution of the underlying Miocene evaporites in which strontium exists as strontium sulphate (Herrmann, 1961; for varying strontium concentrations of stratigraphic units see chapter 5.1.3).

6 Conclusions

During the Holocene alternating subarid and subhumid climatic conditions resulted in the alternating predominance of various geomorphologic processes. In the Desierto de Calanda subarid climatic conditions led to extensive erosion processes and, thus, caused predominantly the deposition of detrital quartz, silicates, and carbonates in the basal part of the lacustrine sediments (stratigraphic unit 1). In opposite, overlying sediments (stratigraphic unit 2) are predominantly evaporitic, with quartz and silicates only as minor components - a sedimentary fabric due to a subhumid environment with processes of groundwater recharge and increased subsurface influx of aqueous solution. In the most recent sediments (stratigraphic unit 3) concentrations of silica and metal oxides again increase, and precipitation of sulphates is secondary. This change of decomposition is once more attributed to a change in the process system: As already pointed out, sedimentation of stratigraphic unit 2 was mainly influenced by subsurface inflow and reduced surface

runoff, and so detrital deposits are only of secondary importance. In opposite, during deposition of the upper layer (stratigraphic unit 3) erosion dominated geomorphic process system occurred, possibly due to a sparse vegetation cover and to ephemeral to periodic heavy rains, corresponding to environmental conditions which altogether supported deposition of detrital sediments while the same time subsurface input of aqueous solution was reduced. At all, various chemical sediment characters (cf., strontium concentrations, quality of statistics) point out that environmental conditions during deposition of stratigraphic unit 1 were distinctly dryer than during deposition of stratigraphic unit 3. But, in general, comparison between stratigraphic units 1 and 3 is limited as for the most recent lacustrine sediments human impact has to be considered causing increased erosion rates (Stevenson et al., 1991). Increased detritals in the uppermost sediments are a result of these soil erosion processes (Faust and Diaz del Olmo, 1997).

Sediments in the depth of 50 to 60 cm, as well as in the depth of 260 to 270 cm indicate a short subhumid phase during the altogether subarid climatic conditions throughout deposition of stratigraphic units 1 and 3. As pointed out by sediment chemistry, especially the deflection of the sulphur graph, these brief wetter phases resulted in a short-term increasing input of solutions by subsurface flow and, thus, in increased precipitation of evaporites.

For the lacustrine sediments of the Laguna de Jabonera investigated there are no data yet available. Comparison with investigations from neighbouring playa-type lakes, predominantly based on pollen analyses, allows to put Holocene environmental history of the Laguna de Jabonera into a preliminary time scale. The subhumid environmental conditions as reconstructed for the depositional phase of stratigraphic unit 2 correspond with the *late Subboreal*, while oldest lacustrine sediments are possibly from the *Atlantic-Subboreal* transition (Macklin et al., 1994; Davis, 1994). Based on this preliminary time-scale it also can be assumed that the short phase of increased humidity which caused deposition of high sulphate contents in 50 to 60 cm depth might be due to the *Modern Times* climatic pessimum of the *Little Ice Age*. A similar climatic trend in the most recent past was also found out by various authors investigating the sediments from the Laguna de Gallocanta, an endorheic basin c. 150 west of the Desierto de Calanda (Davis, 1994; Burjachs Casas et al., 1996; Schütt, 1998b).

Finally, it can be concluded that the chemical characteristics of lacustrine sediments yields valuable information about environmental conditions in the watershed. They indicate predominantly intensity of weathering and soil forming processes, but also give clues to intensity of erosion processes and input of solutes. These information supplement knowledge about the limnic environment during sedimentation which is derived from the mineralogical character of the sediment. The comparison with the results from other drainage basin areas shows that in order to interpret the chemical and mineralogical sediment features the individual petrographic, hydrologic, and geomorphic features of the drainage basin area must always be considered. By doing this, information about environmental change is gained which is as valuable as information derived from analysing pollen or microfossils.

Table 3. Laguna Jabonera/1: Summary of reconstruction of environmental conditions during deposition of lacustrine sediments (subdivided by core sections 1-3)

Limnic Environment	Drainage Basin Environment	Depth	Stratigr. Unit
ephemeral lake with hypersaline to saline environment	subarid climate with low precipitation and high evaporation, low groundwater inflow and small input rates of aqueous solution, high rates of erosional processes cause predominance of detrital sediments, soil erosion processes	0 cm	3
		50 cm 60 cm	
perennial or periodical lake with a saline to brackish environment	subhumid climate with relative high precipitation and reduced evaporation, groundwater recharge and high input rates of aqueous solution, relatively dense vegetation cover prevents erosional processes, intensified soil forming processes	165 cm	2
		166 cm	
ephemeral lake with hypersaline environment	subarid climate with low precipitation and high evaporation, low groundwater inflow and small input rates of aqueous solution, high rates of erosional processes cause predominance of detrital sediments	240 cm	1
		241 cm	
bedrock		310 cm	
		311 cm	

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