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Paleohydrology of Andean saline lakes from sedimentological and isotopic records, Northwestern Argentina

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Abstract

The paleohydrological evolution of several high altitude, saline lakes located in the southernmost Altiplano (El Peinado and San Francisco basins, Catamarca province, NW Argentina) was reconstructed applying sedimentological, geochemical and isotopic techniques. Several playa lakes from the San Francisco basin (26 ° 56′ S; 68 ° 08′ W, 3800–3900 m a.s.l.) show evidence of a recent raise in the watertable that led to modern deposition of carbonate and diatomaceous muds. A 2 m – long core from El Peinado Lake (26 ° 29′ 59″ S, 68 ° 05′ 32″ W, 3820 m a.s.l.) consists of calcitic crusts (unit 3), overlaid by an alternation of macrophyte-rich and travertine clast- rich, laminated muds (unit 2), and topped by travertine facies (unit 1). This sedimentary sequence illustrates a paleohydrological evolution from a subaerial exposure (unit 3) to a high lake stand (unit 2), and a subsequent smaller decrease in lake level (unit 1). The $\delta^{13}C_{\text{organic matter}}$record also reflects the lake transgression between units 3 and 2. Although there is a general positive correlation between $\delta^{18}O_{\text{carbonate}}$ and salinity proxies (Na, Li and B content), the large data dispersion indicates that other factors besides evaporation effects control chemical and isotopic composition of lakewater. Consequently, the oxygen isotopic composition cannot be interpreted exclusively as an indicator of salinity or evaporation ratio. The degassing of CO_2 during groundwater discharge can explain the enriched $\delta^{13}C$ values for primary carbonates precipitated. The carbon budget in these high altitude, saline lakes seems to be controlled by physical rather than biological processes.

The Altiplano saline lakes contain records of environmental and climatic change, although accurate ^{14}C dating of these lacustrine sediments is hindered by the scarcity of terrestrial organic material, and the large reservoir effects. Sedimentologic evidence, a ^{210}Pb-based chronology, and a preliminary U/Th chronology indicate a very large reservoir effect in El Peinado, likely as a result of old groundwaters and large contributions of volcanic and geothermal ^{14}C-free CO_2 to the lake system. Alternative chronologies are needed to place these paleorecords in a reliable chronological framework. A period of increased water balance in the San Francisco basin ended at about 1660 ± 82 yr B.P. (calendar yr U/Th age), and would correlates with the humid phase between 3000 and 1800 yr B.P detected in other sites of the southern Altiplano. Both, ^{210}Pb and preliminary U/Th dating favor a younger age for the paleohydrological changes in El Peinado. The arid period reflected by subaerial exposure and low lake levels in unit 3 would have ended with a large increase in effective moisture during the late 17th century. The increased lake level during deposition of unit 2 would represent the period between A.D.1650–1900, synchronous to the Little Ice Age. This chronological framework is coherent with other regional records that show an abrupt transition from more arid to more humid conditions in the early 17th century, and a change to modern conditions in the late 19th century. Although there are local differences, the Little Ice Age stands as a significant climatic event in the Andean Altiplano.

Introduction

The Altiplano is a N-S trending high volcanic plateau that spans from tropical to subtropical latitudes of South America, and includes areas with tropical summer precipitation in the northeast to areas dominated by the extratropical winter rainfall in the south``west (Schwerdtfeger, 1976). The location of the Altiplano in the dry transition between these two climatic regimes, makes the region very susceptible to changes in effective moisture (Grosjean, 1998). The current climate in the Altiplano is dry (Kull & Grosjean, 1998), but numerous paleorecords have shown large fluctuations in effective moisture during the Last Glacial Cycle (seeeferences in Clapperton, 1993; Wirrmann & Mourguiart, 1995; Abbot et al., 1997; Grosjean, 1998; Thompson et al., 1998; Sylvestre et al., 1999). In the southern Altiplano (the Atacama region), annual precipitation increased to > 500 mm during the Tauca phase (12000–8000 yr B.P.), dropped below 200 mm during the mid Holocene arid phase (8000–3600 yr B.P.), and reached modern levels of 200 mm around 3000 yr B.P. (Grosjean, 1998).

In many Altiplano lakes, accurate dating of the paleohydrological changes has been hindered by the scarcity of adequate terrestrial organic matter, and by the contamination by old carbon (reservoir effect) (Grosjean et al., 1995; Geyh et al., 1998). Closed-basin lakes are among the best sensors of past environmental changes because of their sensibility to small fluctuations in the effective moisture budget (Valero-Garcés et al., 1996: Abbot et al., 1997; Grosjean et al., 1997). In this paper we apply sedimentological, geochemical, and isotopic techniques to recent saline lake sediment from the southernmost part of the Altiplano (Catamarca province, northwestern Argentina). Our data illustrate the complexities of the relationship between geochemical and isotopic records and past lake water salinity and hydrological budget fluctuations. Our results reveal that sedimentary facies analyses provide reconstructions of the paleohydrological evolution that can be related to large-scale atmospheric changes. We combined ^{14}C AMS, with ^{210}Pb and U/Th dating techniques to evaluate the reservoir effect and construct a preliminary chronological framework for the recent large hydrological changes in these saline lakes.

Geographic setting

Geology

The San Francisco and El Peinado basins are located in the southernmost Altiplano (Catamarca province, NW Argentina) and were formed by tectonic and volcanic activity during the Plio – Pleistocene (Figure 1A). The Altiplano is a high volcanic plateau of some 100,000 km^2 from about 15 °S to 28 °S at an average altitude of 3800 m a.s.l.. The southern end of the Altiplano belongs to the active Ojos del Salado volcanic region in the Central Andean Volcanic Province (Baker et al., 1987). The Ojos del Salado area is characterized by major volcanic structures such as calderas, stratovolcanoes, ignimbrites and compound volcanoes. A number of large, fault-bounded, topographically – closed basins occur in the Andean Altiplano and they are filled with siliciclastic, carbonate and evaporite sediments. Miocene clastic rocks occur in the Bolsón de Fiambalá, East of Las Planchadas Range, and in the Antofalla Salar basins (Martínez, 1995). The Quaternary El Peinado and San Francisco basins belong to a chain of tectonic depressions bounded by N-S to NNE-SSW faults (Figure 1B).

El Peinado Lake, north of the San Buenaventura Cordillera, belongs to the same structural basin that the large Antofalla Salar to the north (Martínez, 1995). The Quaternary San Francisco basin, south of the San Buenaventura Range, is bounded on the East by Permian red beds outcrops and on the west by the San Francisco and Incahuasi volcanoes (Figure 1C). The San Francisco Basin is the northermost part of a large N-S tectonic valley bounded by Carboniferous – Permian continental and marine siliciclastic rocks and Ordovician dacites and filled with Quaternary alluvial and aeolian sediments.

Climate

The climate in the southern regions of the Altiplano is mostly influenced by the subtropical high pressure systems of the south-eastern Pacific and the south-western Atlantic (Schwerdtfegen, 1976; Vuille et al., 1998; Kull & Grosjean, 1998). The Atlantic moisture does not reach the eastern side of the Altiplano because the effective blocking effect of the Subandean Sierras, although convective activity over the Altiplano produces precipitation in the high elevation areas during the summer. The climate is dry and cold, characterized

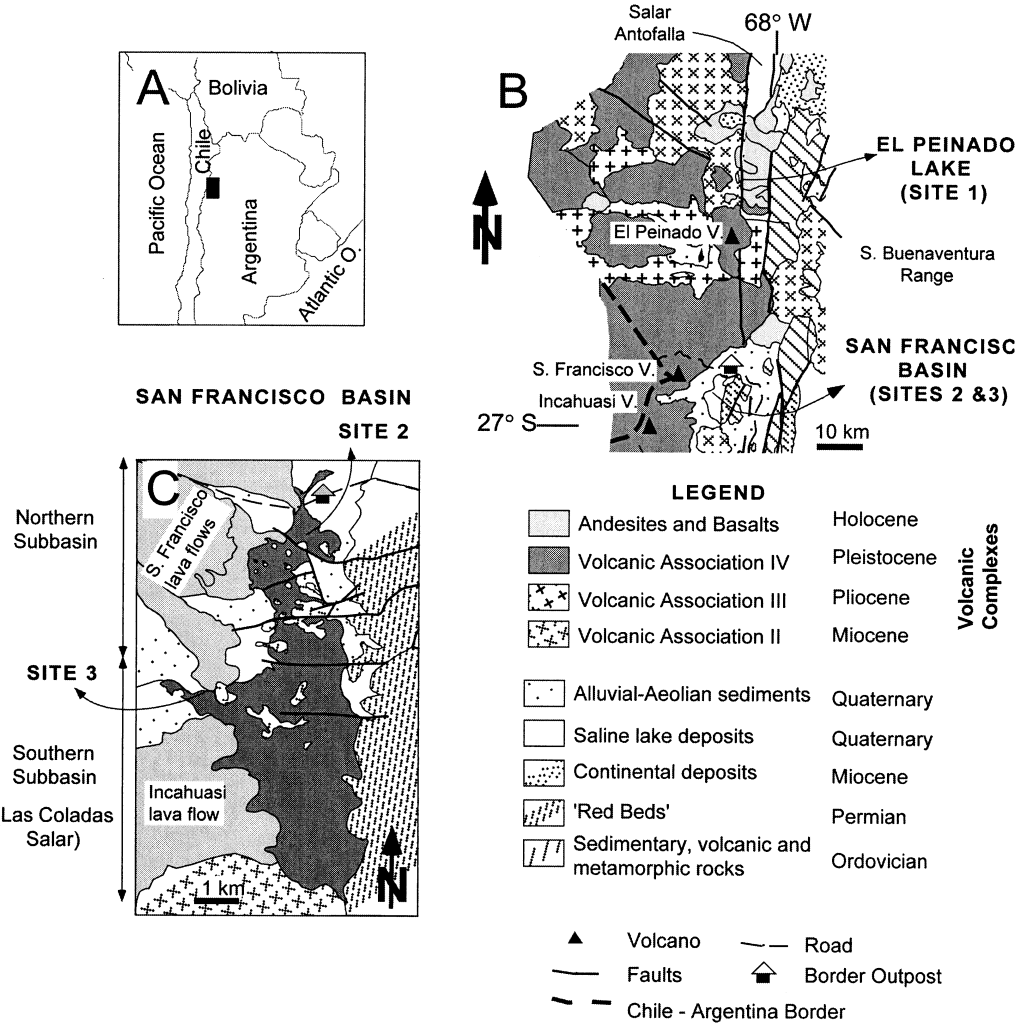

Figure 1. (A) Location of the study sites in the Catamarca province, northwestern Argentina, Central Andes; (B) Geological map of the El Peinado (site 1) and San Francisco Basin (sites 2 and 3); (C) Location of the study sites in the San Francisco Basin: site 2 (northern subbasin) and site 3 (Las Coladas salar, southern subbasin).

by larger daily (up to 40 °C) than seasonal temperature variations. Grosjean et al. (1997) estimated precipitation on the western side of the Andes in the nearby Laguna del Negro Francisco area (27 ° 28′ S, 4125 m a.s.l.) to be about 250 mm yr^{-1}, occurring mostly during the winter months. Potential evaporation (> 1500 m yr^{-1}) greatly exceeds precipitation.

Winter precipitation as snowfall is the dominant source of moisture in the southern Altiplano (Vuille & Ammann, 1996). They distinguished two synoptic mechanisms for winter precipitation in the high arid Andes: cold fronts from the Pacific, often associated to blocking episodes in the South Pacific, and isolated cells of cold polar air that migrate far north and collide with tropical moist air masses. The subtropical latitudes (north of 30 °S) are under the influence of the subtropical high pressure systems of the south-eastern Pacific and south-western Atlantic, which also show seasonal shifts. The heat -induced low pressure cell that forms over the center of South America during the Austral summer draws moisture from the South Atlantic to the Altiplano, particularly east of the Andes (Kull & Grosjean, 1998). At the same time, convective activity over the Altiplano produces precipitation in the high elevation areas during the summer. The contribution of this summer precipitation is unknown due to the absence of weather stations at high altitude.

Another major component of the climate dynamics in the Altiplano is the El Niño – Southern Oscillation. Under the present climate regime, coastal Peru and Ecuador suffer from heavy rains during El Niño events, while the Altiplano often experience drought conditions (Thompson et al., 1984; Thompson et al., 1992). During the warm ENSO mode (El Niño), the subtropical highs are weaker and farther equatorward and, consequently, the subtropical areas of Chile and Argentina also experience increased precipitation and higher temperatures. In higher latitudes, El Niño events produce dry phases during the normal wet season (Thompson et al., 1984; Villalba, 1994a). During El Niño events, lower rainfall in the Altiplano leads to a decrease in lake Titicaca water levels (Francou & Pizarro, 1985; Martin et al., 1993), and substantially reduces snow accumulation in the tropical Quelccaya ice cap (Thompson et al., 1984). Conversely, during La Niña years (cold phase of the Southern Oscillation), rainfall is enhanced and the lake Titicaca level is consistently higher.

Methods

The sediment cores from El Peinado Lake (Site 1) were retrieved with a square-rod piston corer from the littoral zone (Z = 2 m) in November 1996. Samples from surface sediment, short cores and exposed paleo-sediments were collected in several small playa lakes and a large salar in the San Francisco basin (Site 2). Organic matter and carbonate contents were measured by weight loss on ignition. Mineralogy was determined using a Siemens D-500 difractometer. Calcite was the only carbonate in El Peinado samples; aragonite was dominant in the San Francisco samples, with minor amounts of calcite. Oxygen and carbon isotopic compositions were measured on bulk-sediment samples following standard procedures, (McCrea, 1950) and the isotopic values reported in the conventional delta notation relative to the PDB standard. The $\delta^{13}C$ values of organic matter were measured in selected samples from both basins after carbonate removal with HCl 1:1. The $\delta^{18}O$ and $\delta^{2}H$ lakewater values were also determined. Analytical precision was better than 0.1 ‰ for $\delta^{18}O$ and $\delta^{13}C$ in carbonates, organic matter and water, and better than 2 ‰ for $\delta^{2}H$ in water. All the isotope work was performed at the Estación Experimental de El Zaidín (Consejo Superior de Investigaciones Científicas, CSIC, Granada, Spain).

Geochemical analyses were run at the Estación Experimental de Aula Dei (CSIC, Zaragoza, Spain). Bulk sediment samples (0.5 g) were digested with a heated mixture of HCl and HNO3 (3:1 ratio), filtered, and analysed for main elements (Ca, Mg, Na, Al, Sr, Fe, Mn, B and Li) composition with a JY 98 Inductively Coupled Plasma spectrometer. Potassium content was measured with a Perkin Elmer/Coleman 51-Ca photometer. Aquatic remains from organic-rich levels in El Peinado core and a peat sample from the San Francisco Basin were selected for AMS ^{14}C analyses, and measured at the Woods Hole Laboratory (USA). The ^{210}Pb content was measured in eight samples from the El Peinado core at the St. Croix Watershed Research Station (Minnesota, USA). Pure carbonate samples were selected for U/Th dating and analyzed at the Minnesota Isotope Lab (University of Minnesota, USA) and the Institut Jaume Almera (CSIC, Barcelona, Spain).

Results

Sedimentology and geochemistry

El Peinado Lake

El Peinado Lake (26 ° 29′ 59″ S, 68 ° 05′ 32″ W, 3820 m a.s.l.) lies on an N-S elongated, topographically-closed basin, north of El Peinado volcano and at the southern end of the Salar de Antofalla (Site 1, Figure 1B). Waters are saline (Electric conductivity: 55,500 µS/cm) and alkaline (pH = 7.6), and dominated by sulfate-chloride-carbonate anions, and calcium and sodium cations. Other minor elements are in high concentrations (strontium, 58 ppm; boron,135 ppm). The isotopic composition of lake waters ($\delta^{18}O = 4.34$ ‰, $\delta D = –6.8$ ‰ SMOW) indicate strong evaporite effects.

The El Peinado core sediments consists of indurated calcite crusts (unit 3), overlain by banded to laminated muds (unit 2), and topped by travertine (unit 1) (Figure 2). We have identified seven sedimentary facies. The sediments are carbonate-rich (up to 85%). Low magnesium calcite is the only carbonate phase present. Macrophyte remains make up most of the organic-matter fraction. Unit 3 is composed of indurated calcite crusts (facies 3a and 3b) with some intercalated banded muddy sediments (facies 2). The calcitic crusts are composed of cm-sized travertine clasts within a sandy matrix. The crusts contain lower organic matter, Na, K, Al, and B than the banded facies (Figure 3). The crusts are composed of a bottom layer made of smaller clasts with higher matrix content (facies 3b) topped by a coarser, more indurated layer with larger and more

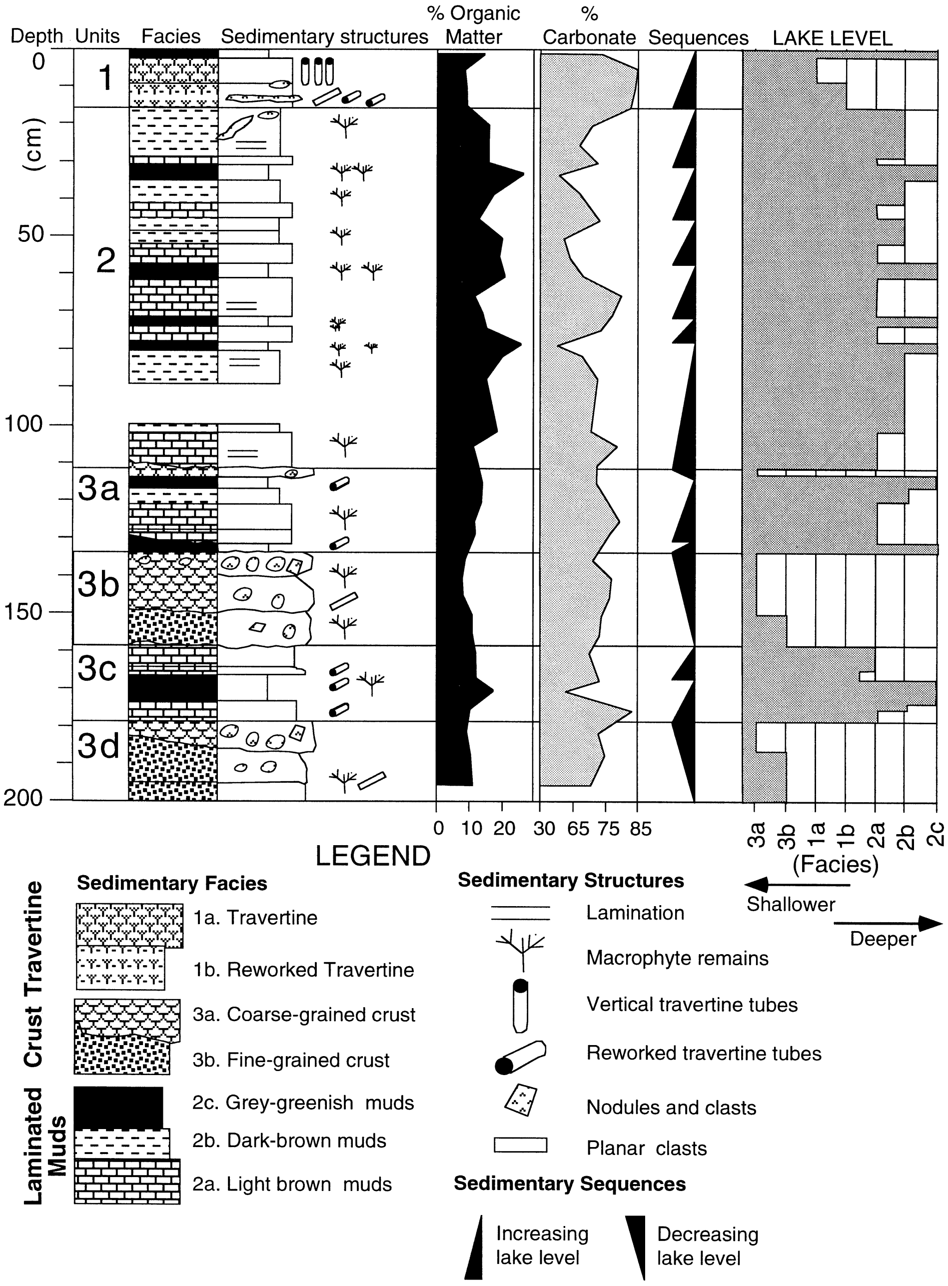

Figure 2. The El Peinado sediment core. From left to right: Depth (cm), sedimentary units, sedimentary facies, sedimentary structures, organic matter content, carbonate content, sequences, and paleohydrological evolution.

numerous clasts (facies 3a). They represent shoreline deposits cemented with low magnesium calcite during periods of low lake levels and subaerial exposure. During relatively higher lake levels muddy facies were deposited (units 3c and 3a). The lower carbonate content of these muddy intervals is also marked by peaks in cation content related to detrital input (Al, K, Fe, Mn) and saline minerals (Na, Li, and B) (Figure 3).

Unit 2 groups laminated, muddy sediments with higher organic-matter content and generally lower carbonate content than the calcitic crusts. Three sedimentary facies are defined: i) massive to banded, light brown muds with high carbonate content (facies 2a); ii) dark brown muds with increasing content of macrophyte remains (facies 2b); and iii) laminated, dark gray-greenish, carbonate-poor and macrophyte-

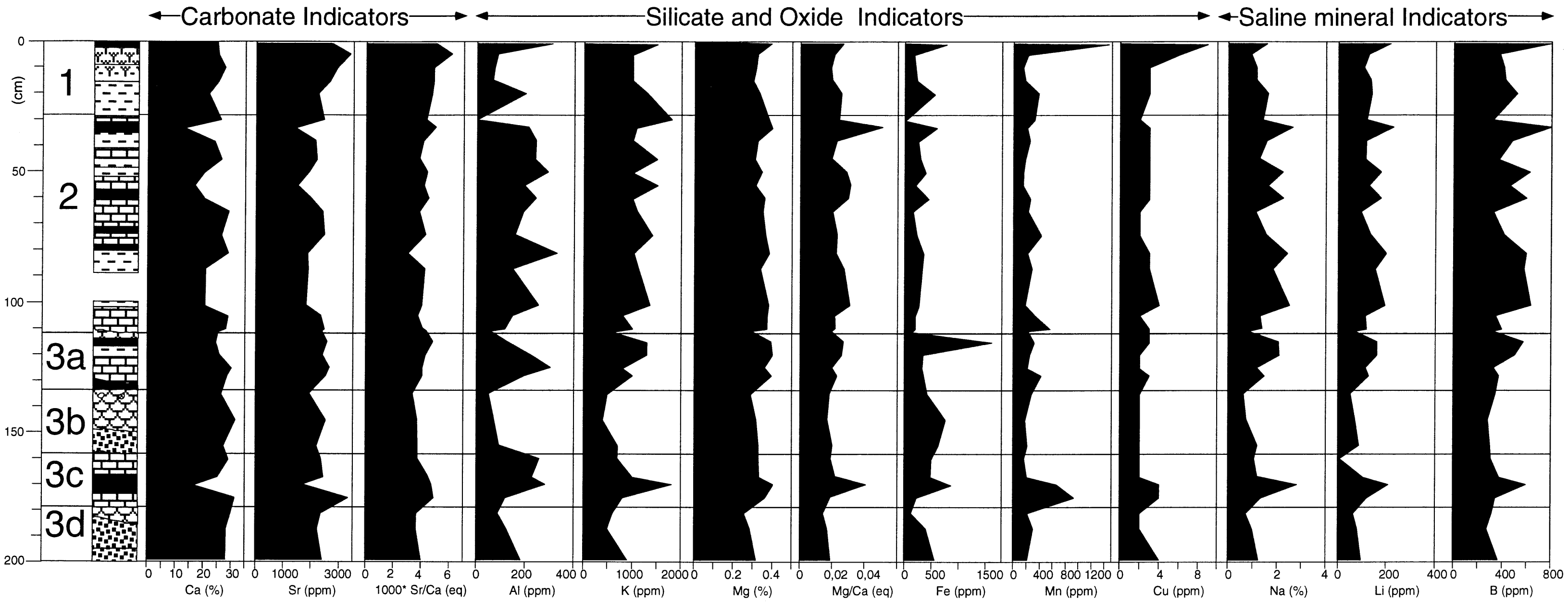

Figure 3. Geochemical composition of El Peinado sediments. The profiles are arranged according with the geochemical affinities of the elements. Ca and Sr are related to the calcite, and have higher contents in unit 3. The Sr/Ca ratio shows constant values in unit 3 and a slightly increasing trend in units 2 and 1. Aluminum and potassium are provided by the silicates and have higher contents in the upper units 2 and 1. The Mg profile shows similar pattern to silicates-related elements. The Fe, Mn and Cu profiles show relatively higher contents in unit 3, when subaerial exposure and oxic conditions were frequent. The Na, Li and B contents are higher in the upper units 2 and 1, interpreted as littoral saline lake deposits.

rich muds (facies 2c). These facies are arranged in sedimentary sequences 2a-2b-2c, that are interpreted as representing deposition dominated by silt-sized particles of travertine carbonates originated by wave action (facies 2a) that gradually changed to lower energy sedimentation, with a higher input of organic matter derived from macrophytes with no carbonate coatings that colonized the lake floor (facies 2c). These fining – upward, energy decreasing sequences can be related to fluctuations in lake level of a few meters from littoral to sublittoral conditions, and changes in some limnological parameters as wave intensity.

The lower calcite content of sediments in unit 2 is responsible for lower strontium values, and an increase in the Mg/Ca ratios compared to unit 3 (Figure 3). Magnesium content is relatively constant in unit 2. The values of salinity indicators such as Na, Li and B, peak in this unit. A higher detrital input is also marked by higher values of Al and K.

Sedimentological and geochemical evidence suggests that sediments of unit 2 were deposited in the littoral-sublittoral realm of a shallow saline lake. Lamination, better organic matter preservation, and finer grain size indicate a relative deeper deposition environment for facies 2c compared to facies 2a. However, several chemical indicators (higher B, Na, Li, and K contents and Mg/Ca ratios) point to increased salinity during deposition of facies 2c. An alternative explanation could be that these elements are preferentially adsorbed to the finer grain size and the organic matter fractions. Higher salinities during higher lake levels are frequent in lacustrine systems where previously precipitated salts in the littoral areas are re-dissolved during periods of increased lake level (Chivas et al., 1993; Valero-Garcés et al., 1999a,b), or where high salinity water sources are available (geothermal springs, for example).

Unit 1 is composed of reworked and *in situ* travertine deposits. The highest carbonate and very low organic-matter content are indicative of the dominance of calcite precipitation processes in these facies. Facies 1a is interpreted as *in situ* travertine formation around the submerged vegetation in the littoral-shoreline zone. Travertine facies with more matrix and including broken travertine fragments (facies 1b) is interpreted as reworked deposits. In current conditions, travertine also occur above the lake level, near the geothermal springs along the shoreline. They show similar fabrics to facies 1a, although the vegetation involved is not the same. A general trend to slightly higher salinity is suggested by the Sr/Ca ratio trends in units 2 and 1 relative to that in unit 3 (Figure 3). Unit 1 represents lower lake levels than unit 2, but without reaching subaerial exposure conditions as during unit 3.

The El Peinado sedimentary sequence records the evolution from a low-lake level stage with subaerial exposure (unit 3) to higher lake level environment (unit 2), and a subsequent smaller lake-level decrease during deposition of unit 1. Minor lake level fluctuations are reflected in both sedimentary environments by facies alternation.

The San Francisco Basin

The San Francisco Basin can be subdivided into two sub-basins. In the northern subbasin, a hummocky topography of small hills and shallow depressions forms a landscape dotted with shallow, small playa lakes (site 2); two of these small playa lakes were cored (26 ° 55′ 42″ S; 68 ° 07′ 21″ W, 3980 m a.s.l.). The southern sub-basin contains a larger playa lake (26 ° 57′ 47″ S, 68 ° 10′ 16″ W, 4000 m a.s.l.), named Las Coladas Salar (site 3, Figure 1C).

The Las Coladas Salar (site 3) is bounded to the west by lava flows from the Incahuasi and San Francisco volcanoes (Figure 1C). The large surface, flat bottom, and small water depth (up to 25 cm) identified this laguna as a Salar, with a hydrologic behaviour similar to a ground-discharge playa-lake. Las Coladas waters are saline (E.C. = 41,900 µS/cm), alkaline (pH = 8.5), Ca – poor (73 ppm versus 2653 ppm in El Peinado), with lower Boron (47 ppm) and Strontium (1 ppm) values and much higher Mg/Ca ratio than El Peinado (11 versus 0.25). The isotopic compositions of lakewaters indicate that evaporite processes are stronger than in El Peinado Lake ($\delta^{18}O = 7.34$ ‰, $\delta D = 29$ ‰), as expected in a playa lake with a large surface/depth ratio. Most of the salar surface sediments are gravels composed of volcanic clasts and covered by a thin (few cm) layer or aragonite muds (Figure 4A). A volcanic lapilli layer intercalates in some areas. Carbonate precipitation in Las Coladas is dominated by aragonite, due to the higher Mg/Ca ratio of the waters. In the western margin, a small creek enters the lake, and the alluvial gravel unit and the carbonate units are overlaid by silts and sands deposited by the creek prograding into the salar.

In the western bay, a lake terrace less than 1 m above current lake level is composed of carbonate-cemented gravels (Figure 4A). In other areas, particularly along the southern shoreline, large blocks of the terrace have been reworked due to wave action and cemented with aragonite. The lake floor in the western bay shows

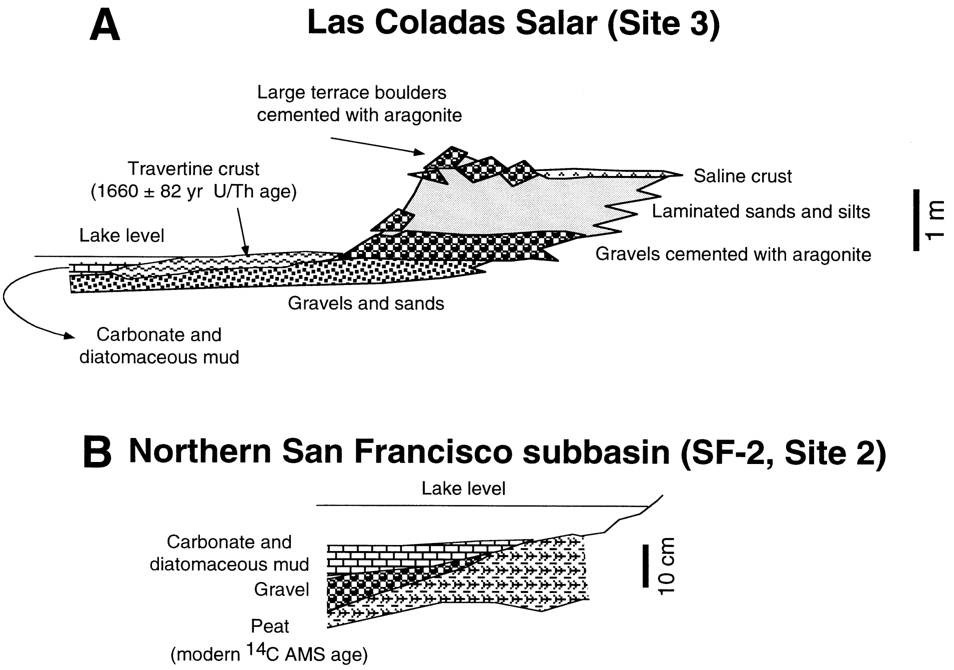

Figure 4. The San Francisco Basin playa lakes. (A) Lacustrine terrace, travertine crust and modern sediments in Las Coladas Salar; (B) The sediment sequence in one of the shallow playa-lakes in the northern San Francisco subbasin.

patches of laminated aragonite speleothemic crusts. All these features suggest a period of aragonite crust generation at the lake bottom and cementation in the shoreline zone. Increased discharge of the thermal springs that feed the western creek could be responsible for higher lake levels and increased precipitation of aragonite. Although U/Th series are not commonly used to date recent materials, the high ^{238}U content (55 ppm) of the carbonate allowed to use this methodology which provided a 1660 ± 82 yr B.P. age for the speleothemic hardground development at Las Coladas salar.

The north subbasin is a mosaic of shallow lakes at about 3980 m a.s.l., wetlands with hallophytic vegetation and relatively higher areas with Andean grass vegetation. Topography and water table fluctuations control the evolution of these discharge-playas. Two playa lakes were cored (SF-1 and SF-2) and both show similar stratigraphy: an upper lacustrine unit composed of aragonite and diatom-rich muds, and a bottom alluvial unit composed of gravels and sands (Figure 4B). A peat layer underneath the alluvial gravel unit in the SF2 has given a modern (< 200 yr) ^{14}C AMS age, which suggest that carbonate lacustrine deposition in these playa lakes is recent (Figure 4B). A volcanic lapilli layer, similar to the one found in Las Coladas, intercalates between the lacustrine and gravel units in SF1, but it has not been identified in the SF2 core. The same white lapilli layer appears intercalated between aeolian deposits and cultural horizons in a rock shelter located a few meters from the SF1 shoreline. In this archeological site, the cultural horizons have been dated between 1000 and 500 yr B.P. (N. Ratto, unpublished data). The lapilli layer also occurs in another archeological site in the San Francisco Basin, an Inca *tambo* with multiple human occupation levels.

To sum up, water tables above the topographic surface have allowed deposition of aragonite and diatomaceous muds in the shallow playa lakes of the San Francisco basin only during the last few centuries. The period of speleothemic crust formation and aragonite cementation of the terrace in Las Coladas Salar marks an older period of higher spring discharge in the basin.

Stable isotopes

Oxygen isotopes

The δ^{18}O of precipitating carbonates depends on the temperature of formation, and the isotopic composition of the water (Talbot, 1990; Chivas et al., 1993). In these Andean lakes subjected to strong evaporation, the oxygen stable-isotope compositions of authigenic carbonate mostly reflect changes in the oxygen-isotopic composition of the lake water. Consequently, they are, potentially, very sensitive paleohydrological indicators. The isotopic composition of the waters in high altitude, saline lakes in the Altiplano is mainly controlled by the composition of the input waters (snowfall and groundwater) and by the large evaporation effects. In the Altiplano the maximum of precipitation during the austral summer (November– March) is characterized by depleted $\delta^{18}O$ values that can be as low as -20 ‰ (Aravena et al., 1999). Spatial distribution of $\delta^{18}O$ and δH composition in precipitation over the Andean region is governed by the influence of different moisture sources (mostly Atlantic and Amazon origin), the seasonal movement of the Intertropical Convergence Zone, and the altitudinal effect of the Andes (Rozanski & Araguas-Araguas, 1995; Aravena et al., 1999). The Andes block free air flow and lead to enhanced condensation of moisture along the slopes due to orographic uplift of air masses and the associated depletion in the heavy isotopes. The compilation of $\delta^{18}O$ values of precipitation, springs and small rivers across the Andes at ca. 33 °S (Vogel et al., 1975; Rozanski & Araguas-Araguas, 1995) shows that up to an elevation of approximately 1500 m, $\delta^{18}O$ decreases with an average of 0.6 ‰ /100 m elevation, whereas substantially smaller slope (0.2 ‰ / 100 m) is observed at higher altitudes. Both El Peinado and San Francisco basins are fed by thermal springs and the contribution and isotopic composition of groundwaters has not been quantified.

Figure 5A shows a $\delta^{18}O$-$\delta^{13}C$ crossplot of values of authigenic carbonates in the three study sites. The high evaporation rates in the Altiplano are responsible for the heavy $\delta^{18}O$ and δH compositions of lake waters in El Peinado and Las Coladas basins, particularly if compared with the light values of rainfall in the Altiplano ($\delta^{18}O$ values as low as –20 ‰, Aravena et al., 1999). However, although evaporation is the main responsible for oxygen isotopic evolution of the lake waters, and consequently, the carbonates precipitated in the lakes, the $\delta^{18}O_{carbonate}$ record cannot be interpreted exclusively as an evaporation or salinity ratio indicator (Kelts & Talbot, 1990; Talbot, 1990). Although there is a general positive correlation between increasing $\delta^{18}O$ values and increasing Na, Li and B contents, the large data dispersion (Figures 5C and 5D) indicate that other factors besides evaporite effects control both chemical and isotope concentration. There is no correlation between increasing Sr contents and $\delta^{18}O$ values (Figure 5C) Sedimentological evidence also warns against a simplistic interpretation of the $\delta^{18}O$ record. For example, samples from the calcitic crusts (subunits 3d and 3b) interpreted as deposition during low lake levels show the lowest $\delta^{18}O$ value of the whole core (Figure 6), and relatively low Sr and Na contents (Figures 3 and 5B). Oxygen isotope values during deposition of relatively deeper facies (unit 2) show generally heavier values and a smaller range (Figures 6A and 6B). However, the development of calcitic crusts at the base of unit 3d, and at the top of units 3b and 3a are marked by higher $\delta^{18}O$ values, suggesting increased evaporation during those periods (Figure 6A). Crust formation at the top of subunit 3a corresponded with increased salinity, as indicated by higher Sr/Ca and Na, Li, and B content. Higher lake level during the deposition of the upper part of subunit 3c, indicated by deposition of muddy, laminated facies, corresponds to a large negative shift in $\delta^{18}O$. However, the lake level increase during subunit 3a corresponds to an increasing $\delta^{18}O$ trend. These discrepancies suggest that waters of different isotopic and chemical compositions and sources were involved in the lake water balance. Different mechanisms for chemical and isotopic enrichment and depletion would also contribute to the development of uncoupled chemical and isotopic trends.

In unit 2, some, but not all, $\delta^{18}O$ increasing trends correspond to the defined fining-upwards and deeping-upwards sedimentary sequences. The gray-greenish, laminated, organic-rich facies 2c show heavier oxygen values and they correspond to Sr/Ca and Na, Li and B peaks (Figures 3, 5B and 6). However, the general increasing trend in salinity deduced from the Sr/Ca ratio does not show up in the isotope record. The $\delta^{18}O$ values for unit 1 are slightly heavier. Emerged travertines formed at the shoreline springs show lighter oxygen isotope composition than the submerged travertine at the top of the core (Figure 6B). These compositions are coherent with isotope enrichment in the lake due to evaporation.

Carbon isotopes

The carbon isotope data for authigenic calcite and aragonite are presented in Figures 5A and 6. Most of El Peinado and Las Coladas values were higher than 8 ‰, while samples from the northern San Francisco subbasin showed lower values (6 to 3 ‰). A detailed study of the carbon isotopic composition of carbonate phases from these basins can be found in Valero-Garcés et al. (1999a). Here we will summarize some of the environmental implications.

The $\delta^{13}C_{organic\ matter}$ record from El Peinado core (Figure 6A) shows lower values in the calcitic crust facies from

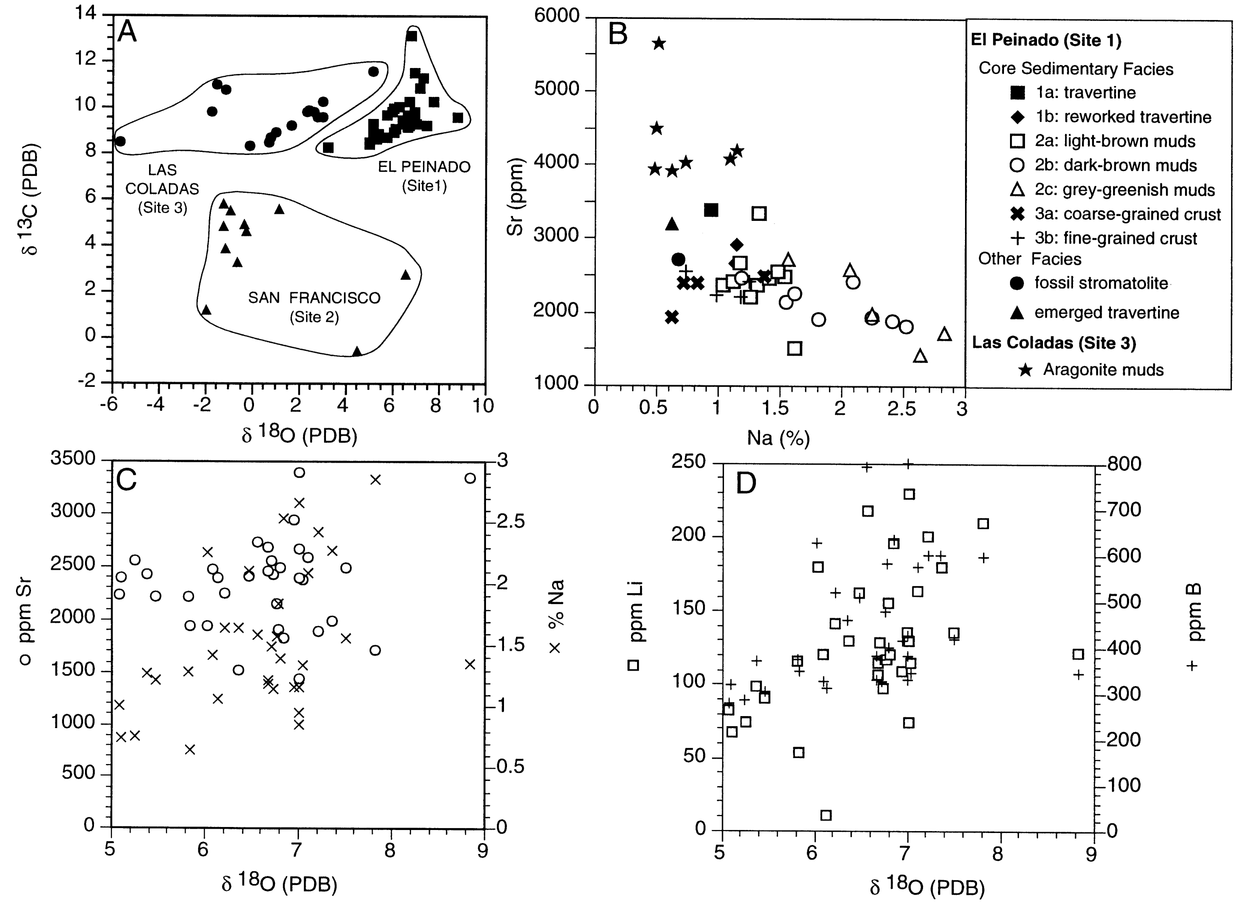

Figure 5. Geochemistry and stable isotopes of El Peinado (Site 1) and San Francisco (Sites 2 and 3) samples. (A) Crossplot of $\delta^{18}O$ and $\delta^{13}C$ values for carbonate samples from the three sites; (B) Sedimentary facies and salinity indicators (Sr and Na content) for carbonate samples from El Peinado and Las Coladas. The sedimentary facies for El Peinado core are defined in Figure 2. The Na and Sr contents for fossil stromatolites and emerged travertines for El Peinado are also shown. The higher Sr contents for Las Coladas salar samples reflect the presence of aragonite; (C) Crossplot of Sr and Na contents versus $\delta^{18}O$ values for calcite samples from El Peinado core (Site 1); (D) Crossplot of Li and B contents versus $\delta^{18}O$ values for calcite samples from El Peinado core (Site 1).

unit 3 (< -14 ‰ PDB) and heavier $\delta^{13}C_{\text{organic matter}}$ values in the littoral and travertine facies of subunits 3c and 3a, 2 and 1. This correlation with sedimentary facies indicates that changes in the biological assemblages are likely the main factor controlling the isotopic composition of the organic matter. The modern emerged aquatic vegetation around El Peinado Lake has lighter $\delta^{13}C_{\text{organic matter}}$ values (–26.6 ‰ PDB) than the submerged vegetation (–8.4 to –11 ‰, PDB). A change in dominant biota from emerged macrophytic plants in the shoreline during periods of subaerial exposure to submerged macrophyte could account from the sharp $\delta^{13}C_{\text{organic matter}}$ positive shifts in units 3c and 3a and the heavier values of the upper two units.

Changes in the $\delta^{13}C_{\text{carbonate}}$ reflect variations in the dissolved inorganic carbon (DIC) pool from which the carbonate precipitated (Hakänsson, 1985; Talbot, 1990). The carbon isotope budget in lakes is mostly controlled by fluctuations in the input values (surface and groundwaters), and changes in the limnological and biological parameters of the lake (Kelts, 1988). The $\delta^{13}C_{\text{calcite}}$ curve in El Peinado core follows the $\delta^{18}O$ curve (Figure 6A). The covariance between all $\delta^{13}C$ and $\delta^{18}O$ values (Figure 6B) is a reflection of a hydrollogically-closed dynamics where residence time evolution plays a significant role in the carbon isotope budget (Talbot,1990; Li and Ku, 1997). In El Peinado, the $\delta^{13}C_{\text{calcite}}$ values are lighter and less fluctuating in units 3 and 1, and generally heavier and with a larger

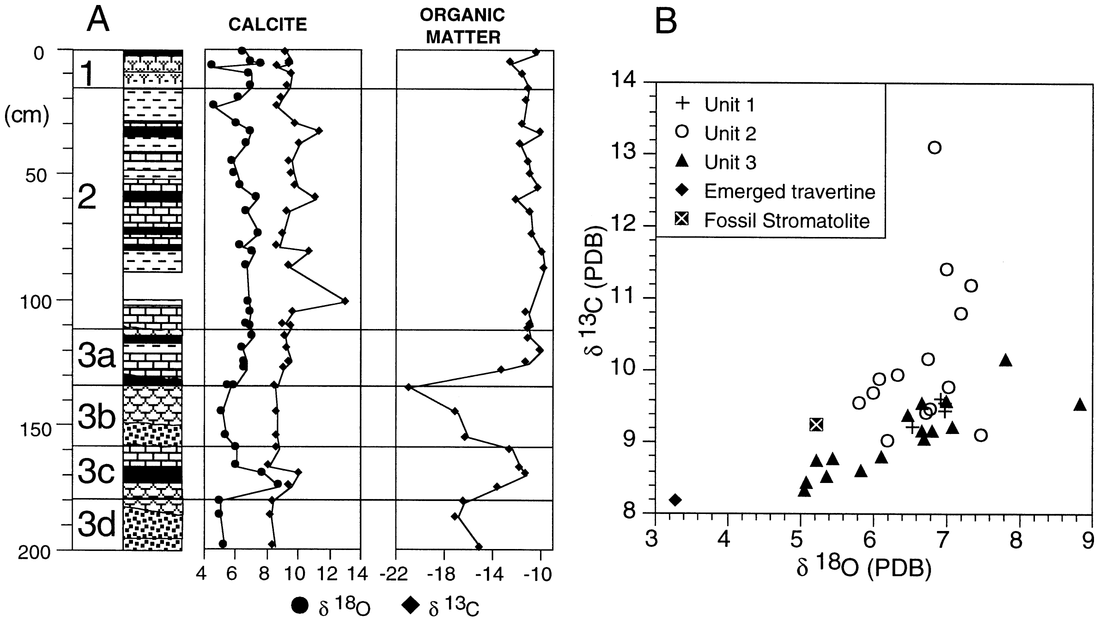

Figure 6. B. Isotope stratigraphy for El Peinado core samples. (A) Isotope composition of calcite and organic matter from El Peinado core samples. Note the heavy $\delta^{13}C_{calcite}$ values and the general covariance between $\delta^{13}C$ and $\delta^{18}O$. Lower $\delta^{13}C_{organic\ matter}$ reflect periods of frequent subaerial exposure with dominant emergent aquatic vegetation; higher $\delta^{13}C_{organic\ matter}$ values correlate with periods of higher lake levels and dominant submerged vegetation; (B) Crossplot of $\delta^{13}C$ and $\delta^{18}O$ values from El Peinado samples. The emerged travertine, close to the thermal springs, has the lighest $\delta^{18}O$ and $\delta^{13}C$ composition. The largest $\delta^{13}C$ enrichements occur in samples from unit 2.

range in the unit 2 (Figures 6A and 6B). The heaviest $\delta^{13}C$ values correspond to facies 2c, characterized by higher organic matter content and abundant macrophyte remains, suggesting periods of increased organic productivity in the lake (Hakänsson, 1985; Kelts & Talbot, 1990). Las Coladas samples show similar high values (between 8 and 12 ‰) as El Peinado, whereas the northern San Francisco subbasin samples (SF1 site) are much lower (Figure 5A). Modern $\delta^{13}C$ values in carbonate samples (aragonite and calcite) from the northern San Francisco subbasins (around 0 ‰) suggest a larger input of biogenic carbon (microbial) in this playa lake. Evaporation could also have an effect on the isotope carbon budget of the Altiplano lakes, because extreme ^{13}C enrichments (up to +16.5 ‰) have been reported in evaporating brines (Stiller et al., 1985). However, the large range of some salinity indicators suggest that large ^{13}C enrichments are not directly related to increased salinity.

The high $\delta^{13}C$ values reported here are a very conspicuous feature. Heavy $\delta^{13}C$ values for carbonates in the Andean Altiplano have been found in other saline lakes (Grosjean, 1994; Grosjean et al., 1995; Schwalb et al., 1999) and fluvial travertine deposits (Aravena & Suzuki, 1990). However, in one site (Laguna Seca, Schwalb et al., 1999) the values were comparable to El Peinado and San Francisco (up to +13 ‰). Valero-Garcés et al. (1999a) discuss the mechanisms that can generate ^{13}C enrichment in these lake waters over values in equilibrium with atmospheric CO_2. They conclude that the influence of geothermal and volcanic CO_2 and degassing during groundwater discharge can explain the enriched $\delta^{13}C$ values for primary calcite and aragonite precipitated in El Peinado and Las Coladas lakes.

Chronology

Accurate dating of lacustrine sediments in the Altiplano has been hindered by the scarcity of terrestrial organic materials, and the large reservoir effects detected in the lake waters (Grosjean et al., 1995; Geyh et al., 1998). The old AMS ^{14}C dates in the top of El Peinado core indicate a very large (> 12000 yr) reservoir effect (Table 1). Lacustrine sediments are being deposited currently at the core site and, consequently, the age of the uppermost sediments should be modern. Contamination by old carbon from carbonate or carbonaceous rocks can be ruled out since they are absent in the watershed. Influx of old groundwaters recharged during past humid periods has been identified in other saline lakes in the Altiplano (Grosjean et al., 1995) and it could account for some old carbon inventories. Valero-Garcés et al. (1999a) explained the large reservoir effect (> 12000 yr) as a dilution effect by large quantities of ^{14}C – free CO$_2$ introduced from thermal and volcanic CO$_2$. Assuming a 12000-yr constant reservoir effect, at least during the higher lake level phases (units 1 and 2), the period of lower lake levels with subaerial exposure would have ended around 4000 ^{14}C yr B.P. (Figure 7). The subsequent period of higher lake levels (unit 2) would span between 4000 and 2000 ^{14}C yr B.P. Finally, sedimentation rate would have greatly reduced during deposition of unit 1. However, an accurate ^{14}C – based chronology needs an evaluation of the old carbon inventories.

Radiometric techniques help to constrain the large effects of old carbon sources. The values of total ^{210}Pb activity are very low (less than 0.6 pCig^{-1}, similar to other ^{210}Pb profiles from the nearby Laguna del Negro Francisco (0.54; M. Grosjean, pers. commun.), and other Altiplano lakes (Laguna Miscanti: 0.31; Valero-Garcés et al., 1996). The calculated fluxes of ^{210}Pb to these cores sites are extremely low (0.5–0.6 pCi cm^{-2} yr^{-1}) and this could be a reflection of low atmospheric ^{210}Pb deposition rates in a region like the Altiplano with very low rainfall. If we assume a stable background activity of 0.21 pCi g^{-1} (Figure 7) and use a constant flux:constant sedimentation model (Olsson, 1986), the calculated mean sediment accumulation rate for the upper core is 0.25 g cm^{-2} yr^{-1} (3.3 mm yr^{-1}) (Figure 7). The sedimentation rate, according to the four AMS dates is about 10 times smaller (0.37 mm yr^{-1}), and considering only the two uppermost AMS dates is about thirty times smaller (0.01 cm yr^{-1}). The preliminary U/Th dates are also coherent with the ^{210}Pb chronology and give an age of 314 ± 9 calendar yr for the top of unit 3, and an average sedimentation rate of 4.3 mm yr^{-1} for unit 2. The onset of travertine deposition in unit 1 would correspond to the beginning of the 20th century.

Discussion

El Peinado and San Francisco sediment records show a similar pattern of paleohydrological evolution in both basins. A rise of the water table in the San Francisco basin has allowed deposition of lacustrine muds that overlay gravel sediments in most of the playa lakes. The El Peinado core record indicates an older period of lower lake levels and subaerial exposure followed by an increase in lake level during a second period.

Although the reservoir effect-corrected ^{14}C chronology for El Peinado would show a sequence of events coherent with the regional chronologies and paleoclimatic reconstructions, we consider the ^{210}Pb and U/Th chronologies to be more reliable. Based on the corrected ^{14}C dates, the increase in lake level in El Peinado during the late Holocene (4000–3000 yr BP) would be consistent with the general trend of increasing moisture documented in tropical and temperate South America: southern Argentina (Stine, 1994), the Pampa (Prieto, 1996), the Chilean Altiplano (Grosjean et al.,

Table 1. AMS ^{14}C and U/Th dates for El Peinado and San Francisco Basin

Sample	Lab Number	Material	^{14}C age (yr B.P.)	δ^{13}C	Fraction of Modern ^{14}C
El Peinado: 0–1 cm	WHOI 17536	Macrophyte	12750 ± 90	–25 ‰ (estimated)	0.2050
El Peinado: 22–24 cm	WHOI 17535	Macrophyte	14950 ± 100	–25 ‰ (estimated)	0.1558
El Peinado: 78–80 cm	WHOI 17534	Macrophyte	16550 ± 100	–25 ‰ (estimated)	0.1271
El Peinado: 166–168 cm	WHOI 17533	Macrophyte	17200 ± 110	–25 ‰ (estimated)	0.1176
SF-2: 10 cm	WHOI 17537	Peat	Modern	–26.06 ‰ (measured)	1.0583
Sample	Laboratory	Material	^{238}U (ppm)	^{230}Th age (Calendar year)	
PE–15	Minnesota Isotope Lab	Calcite travertine	41.50	91 ± 12	
PE–111	Minnesota isotope lab	Calcice travertine	38.45	314 ± 9	
LCV–6	Instituto Jaume Almera-CSIC, Spain	Aragonite travertine	55	1660 ± 82	

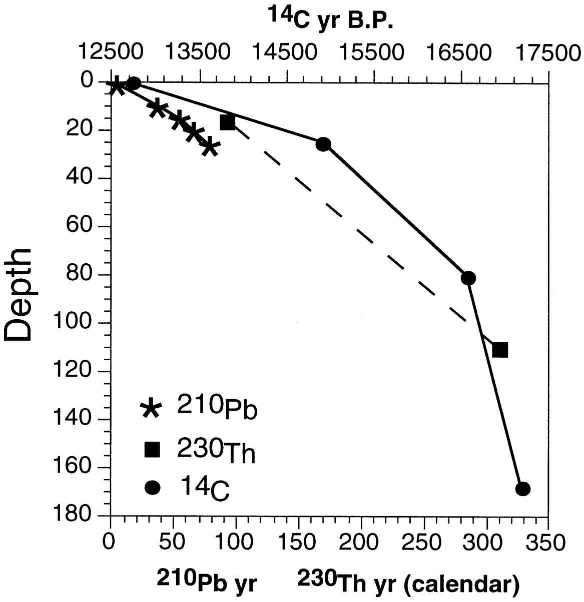

Figure 7. Radiometric chronologies for El Peinado core. The ^{210}Pb and ^{230}Th chronologies show similar accumulation rates for the upper units 2 and 1, and a basal age for unit 2 of about 300 yr B.P. Comparison with the ^{14}C dates indicates a very large reservoir effect for the upper sediments (about 12000 yrs).

1997), the Norte Chico (Veit, 1996), the coastal areas of central Chile (32–33 °S) (Villagrán & Varela, 1990), and the Andes at 29 °S (Grosjean et al., 1998). In the Argentinian Andes, there are also evidences of late Holocene increased humidity: neoglacial advances at the Río Atuel valley at 33 °S that ended before 4500 B.P. yr (Stingl & Garleff, 1985); the presence of lake deposits in the Chaschuil river at 3000 m a.s.l. dated between 6000 and 3000 yr B.P. (Garleff et al., 1992), the first agricultural practices in the Fiambalá Basin dated about 3000 yr B.P. (Rex Gonzales & Sempe, 1975). This late Holocene humid phase that has been explained as an intensification of moonsonal easterly flows on the subtropical zone (Garleff et al., 1992).

Although the ^{210}Pb and U/Th chronologies favor a much younger age for the lake level increase in El Peinado (< 300 yr B.P.), there is a paleohydrological change in the San Francisco basin that could be related to the older late Holocene trend (4000–3000 yr BP). The formation of a the crust and the cementation of terraces in Las Coladas marks a hydrological event that took place during the late Holocene. Assuming that the formation of the crust occurred when the water level decreased, the U/Th age of 1660 ± 82 yr B.P. would mark the end of the period of higher discharge to the lake. This chronology would also fit with the end of the period of relatively deeper saline lake deposition in Laguna del Negro Francisco (27 ° 30′ S) between 3600 –1800 yr B.P. (Grosjean et al., 1997), and the period of peat formation in the Encierro and Valeriana glacial valleys (29 °S) at about 2600 yr B.P. (Veit, 1996; Grosjean et al., 1998) B.P. The Laguna Miscanti record (23 ° 44′S) shows a general increase in precipitation during the late Holocene (Valero-Garcés et al., 1996), without any marked wetter phase around 3000–2000 yr B.P. Grosjean et al. (1997) suggested that the different moisture regimes were responsible for these different climatic evolutions between 23 ° and 27 °S. The southern shift of tropical moisture during the late Holocene would have a stronger impact in the northern and central Altiplano regions. The presence of the 3000–1800 yr B.P. humid phase only in the southern Altiplano favor an enhanced westerly precipitation as the main cause.

The lake level evolution recorded in El Peinado core, according with the ^{210}Pb and U/Th dates, reflects a large, but much younger paleohydrological evolution variability. The transition between unit 2 and 3 would have happened in the late 17th century (around 1650). Unit 2 would represent deposition between A.D. 1650–1900, a period that corresponds with the Little Ice Age as defined in the Quelccaya ice core (Thompson et al., 1986). At this moment we lack a reliable chronology to adscribe the lake level fluctuations in unit 3 to some of the recorded arid and humid periods in the Quelccaya ice core prior to the Little Ice Age. Comparison with other Altiplano late Holocene paleorecords indicates that the increase in effective moisture indicated by the abrupt transition between unit 3 and 2 is of regional significance.

The two main hydrological events in El Peinado core could correspond to the onset and termination of the Little Ice Age. The Little Ice Age, as recorded in the Quelccaya ice cap, set in at the end of the 15th century (A.D. 1490) and ended during the latter half of the 19th century (Thompson et al., 1986). It was a period characterized by cooler temperatures and increased wind activity, as indicated by lower δ^{18}O ice values and higher dust content in the ice. The relationship between ENSO and other lower frequency climatic variability is not conclusive (Enfield & Cid, 1991; Enfield, 1992; Villalba, 1994a). The ENSO phenomenon is fairly robust to large-scale climate changes, however, there is some evidence, albeit not conclusive, that there were more frequent and stronger El Niño events during the LIA, and fewer during the previous period (Little Climatic Optimum: A.D. 1000–1290)

(Quinn et al., 1982; Quinn, 1992; Anderson, 1992). The Quelccaya ice cap cores exhibit high particulate content during the LIA as a result of increased wind velocities across the high Altiplano of southern Peru, and high amplitude seasonal oxygen isotope variations, that suggest increased seasonality (Thompson et al., 1992). Precipitation, as deduced from the thickness of annual ice core layers, was higher during the period A.D. 1500–1750 and greatly reduced afterwards until 1860.

Historical sources (Prieto et al., 1998) document a dry period in northwestern Argentina since the arrival of the Spaniards (A.D. 1580) until A.D. 1641 and a marked humid period between A.D. 1663 and 1710. Dendrochronological and glaciological records in mid latitudes of South America (30–45 °S) show precipitation above the long-term mean from A.D. 1450–1550 and 1840–1900, extended droughts from A.D. 1570–1650 and 1770–1820 (Villalba, 1990; Lara & Villalba, 1993; Villalba, 1994a, b). The dry period in NW Argentina deduced from historical records (Prieto et al., 1998) between A.D. 1580 and 1641 is synchronous with the coldest period in Patagonia during the last 1000 yrs.

The transition from the LIA to the warmth of the current century occurred over a two to three year period centered on A.D. 1880 (Thompson et al., 1986), and it is one of the most abrupt changes detected in the Quelccaya ice cores. The last 100 years are characterized by reduced wind velocities, increased annual snow fall, and increased annual mean temperatures. In El Peinado, the termination of the LIA may correspond to the transition from unit 2 to 1, characterized by a small decrease in lake levels. Travertine deposition in unit 1 could also correspond to some climatic fluctuations during the 20th century. For example, the period of higher global temperatures in the northern hemisphere (A.D. 1920–1940), also is recorded in the Quelccaya ice core (Thompson et al.,1986).

The ^{210}Pb chronology for Laguna Miscanti (Valero-Garcés et al., 1996) also shows significant paleohydrological events during the last few centuries. As in El Peinado, modern conditions in Laguna Miscanti inaugurated at the end of the last century (around A.D. 1880). Sediments deposited during the previous period (A.D. 1600–1850) are characterized by lower organic content, higher carbonate content and the presence of gypsum. The highest organic content (up to 13%) occurs in sediments before A.D. 1600. The interval of increased organic content could correspond to a humid period prior to A.D. 1600; increased carbonate and gypsum occurrence would reflect a dry period between the mid 17th to the mid 20th centuries. Nevertheless the relationships between organic matter content, salinity, and water balance are not straightforward in saline lakes, but the ocurrence of sedimentological changes in both lakes points to a regional climatic cause for these synchronous hydrological events. The upper sediments from the Laguna del Negro Francisco core also reflect significant limnological changes with an earlier humid period followed by more arid conditions (Grosjean et al., 1997). The lack of reliable chronological control makes it difficult to assign these changes to the LIA or the Litlle Climatic Optimum. Although time resolution for the Miscanti and Negro Francisco chronologies is low, the interpreted climatic evolutions from these sites during the last centuries seems to be antiphase with climatic changes interpreted from El Peinado. These discrepancies could be another reflection of the different climatic regimes of the central and southern Altiplano regions and the western and eastern slopes of the Andes.

Conclusions

Sedimentological, geochemical an isotopic analyses of a 2 m long core from El Peinado lake illustrate the stepwise paleohydrological evolution from a low to a high stand, and a final smaller decrease in lake level that may correspond to the end of the Little Ice Age. Sedimentological and geomorphologic evidence also suggest a recent raise in water table in the San Francisco basin. Considering the ^{14}C based chronology, the general trend of increasing lake level interpreted from El Peinado core is coherent with the regional reconstructions of increasing effective moisture in tropical and temperate South America for the Late Holocene. However, the anomalously too old AMS ^{14}C dates for El Peinado indicate a large contribution of old carbon inventories that hinders accurate dating of these lacustrine sequences. The travertine crusts in Las Coladas salar allow U/Th dating of a period of increased water balance in the salar that ended at about 1660 ± 82 yr B.P. The occurrence of a period of increased effective moisture in other records at similar latitudes in the Argentinian and Chilean Andes favors the regional significance of the humid phase between about 3000 and 1800 yr B.P.

Both, ^{210}Pb and preliminary U/Th dating favor a much younger age for the paleohydrological changes in El Peinado. An arid period prior to the 17th century with several water balance fluctuations (unit 3), ended with a large increase in effective moisture during the late 17th century. The increased lake level during deposition of unit 2 would represent the period from the 17th to the 19th centuries, synchronous with the Little Ice Age. This chronological framework is coherent with other regional records that show an abrupt transition from more arid to more humid conditions in the early 17th century, and a change to modern conditions in the late 19th century. The Quelccaya Ice cap, historical documents, dendrochronological records, and lake records show abrupt paleohydrological and paleoclimatic changes synchronous to the onset and termination of the Little Ice Age. Although there are local differences, the Little Ice Age stands as a significant climatic event in the Altiplano and South America.

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