

Large ^{13}C enrichment in primary carbonates from Andean Altiplano lakes, northwest Argentina

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Abstract

We report here extreme ^{13}C enrichments up to +13‰ PDB in primary calcite and aragonite precipitates in saline, well oxygenated waters from high-altitude lakes in the southern Andean Altiplano, northwestern Argentina. Biological effects, as well as variations in carbon source inputs, and in the exchange rate with atmospheric CO_2 , are commonly considered the main controls on the carbon isotope values of authigenic lacustrine carbonate. We present sedimentological and geochemical evidence that favors physical processes — evaporation effects and CO_2 -degassing — as major controls on ^{13}C enrichment. We propose that large enrichments may result from the non-equilibrium gas-transfer isotope fractionation during CO_2 -degassing from thermal springs and evaporation effects in arid environments. The dilution effect by large quantities of ^{14}C -free CO_2 hinders accurate ^{14}C chronology of these lake records based on lacustrine organic matter and aquatic plants. Our results indicate that geothermal and volcanic CO_2 sources in lake basins located in volcanic settings, and physical fractionation may have a greater significance than commonly accepted to explain lacustrine carbon isotope records. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The carbon isotopic compositions of primary precipitated lacustrine carbonates have been used as proxies for biological productivity, groundwater input, changes in vegetation cover of the watersheds and in the limnological conditions (exchange with atmospheric CO_2 , residence time) [1–3]. The $\delta^{13}\text{C}$

of primary carbonate phases is relatively insensitive to changes in temperature (e.g. $0.035\text{‰ } ^\circ\text{C}^{-1}$), and precipitation of carbonate minerals involves a small fractionation of carbon isotopes relative to the TIDC (Total Inorganic Dissolved Carbon) [4,5]. Consequently, such minerals can be used to monitor changes in the $\delta^{13}\text{C}$ of the lake waters. The main controls on the $\delta^{13}\text{C}$ of TIDC in most lake waters are [6]: (i) CO_2 contributed by degradation of organic matter (generally ca. -25‰); (ii) dissolution of pre-existing carbonate rocks (carbonate generally heavier,

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about +1–2‰); (iii) equilibration with atmospheric CO₂ (carbonate values up to +2‰); and (iv) photosynthetic sequestering of ¹²C into organic carbon. Carbon isotopic analyses on lacustrine sediments are a common tool to produce paleorecords of climate and environmental change [7–9]. However, the large range of hydrological, hydrochemical and limnological conditions in lakes makes our understanding of the carbon cycle difficult and our knowledge is imperfect. An increasing number of isotopic records illustrates examples of carbon budget in lakes not driven exclusively by organic productivity, and equilibrium with atmospheric CO₂ [3,10]. In this paper we present data that favor a significant role for physical processes in lake carbon budgets.

Most lake waters δ¹³C range from values similar to rivers and groundwaters (–10‰ PDB), to values close to equilibration with atmospheric CO₂ (+2‰) [2,6]. Primary carbonates from freshwater environments are often characterized by δ¹³C values of –6 to –12‰; saline environments show values of up to +5‰, the maximum value for equilibrium with the atmospheric CO₂. Lacustrine carbonates with high δ¹³C values have been reported from very concentrated evaporating brines [11], anoxic sediments [12,13], freshwater carbonates with methane output [14], travertines [15,16], and some Andean [10,17,18] and African saline lakes [19]. In this paper we report δ¹³C values up to +13‰ for authigenic aragonite and calcite from Andean Altiplano lakes located in active geothermal areas. These values are among the most positive values reported for surface water lacustrine calcite and aragonite described in the literature. We also present evidence for degassing of carbon dioxide and residence time evolution as the main mechanisms responsible for ¹³C enrichment.

2. Geologic and geographic setting

The study area belongs to the active Ojos del Salado volcanic region, in the Central Andean Volcanic Province that coincides with a major morphological, seismic and volcanic discontinuity [20]. The active magmatic arc encompasses the Western Cordillera and the Altiplano, a high ignimbrite plateau (average altitude 3800 m a.s.l.) of some 100,000 km².

Large, fault-bounded topographically closed basins developed in the Altiplano during the Tertiary, and were filled with siliciclastic, carbonate and evaporite sediments [21]. The San Francisco and El Peinado basins, located in the southernmost Altiplano (Cataamarca province, NW Argentina) (Fig. 1A), were formed by tectonic and volcanic activity during the Plio–Pleistocene and they belong to a chain of tectonic depressions bounded by N–S to NNE–SSW trending faults and active volcanoes (Fig. 1B) [20,22].

The climate is dry and cold, characterized by larger daily (up to 40°C) than seasonal temperature variations, and very low precipitation. The rainfall in the nearby Laguna del Negro Francisco area (27°28'S, 4125 m a.s.l.) has been estimated around 250 mm yr^{–1}, and evapotranspiration as more than 1500 mm yr^{–1} [23].

3. Methods

During a field work expedition in November 1996, sediment cores were collected with a square-rod piston corer, and surface sediments and waters sampled. Organic matter and carbonate contents were measured by loss on ignition. Mineralogy was determined using X-ray diffraction techniques. Calcite was the only carbonate in El Peinado samples; aragonite was dominant in the San Francisco samples, with minor amounts of calcite. The δ¹⁸O and δ²H lake water values were determined for the El Peinado lake and the largest playa-lake in the San Francisco Basin. Oxygen and carbon isotope analyses were performed on bulk-sediment and carbonate-coated macrophyte samples using standard techniques [24]. Previously, the samples were roasted in vacuum at 375°C. The isotopic ratios were measured with a Finnigan MAT 251 mass spectrometer, and the results are expressed in δ-notation with respect to the international standards PDB and SMOW. After carbonate removal with 1:1 HCl, the δ¹³C values of organic matter were measured in selected samples by means of an EA-IRMS elemental analyser connected to a Finnigan MAT 251 mass spectrometer. The standard deviations are 0.1‰ for δ¹⁸O and δ¹³C in carbonates, organic matter and water, and 2‰ for δ²H in water. Bulk sediment samples (0.5 g) were di-

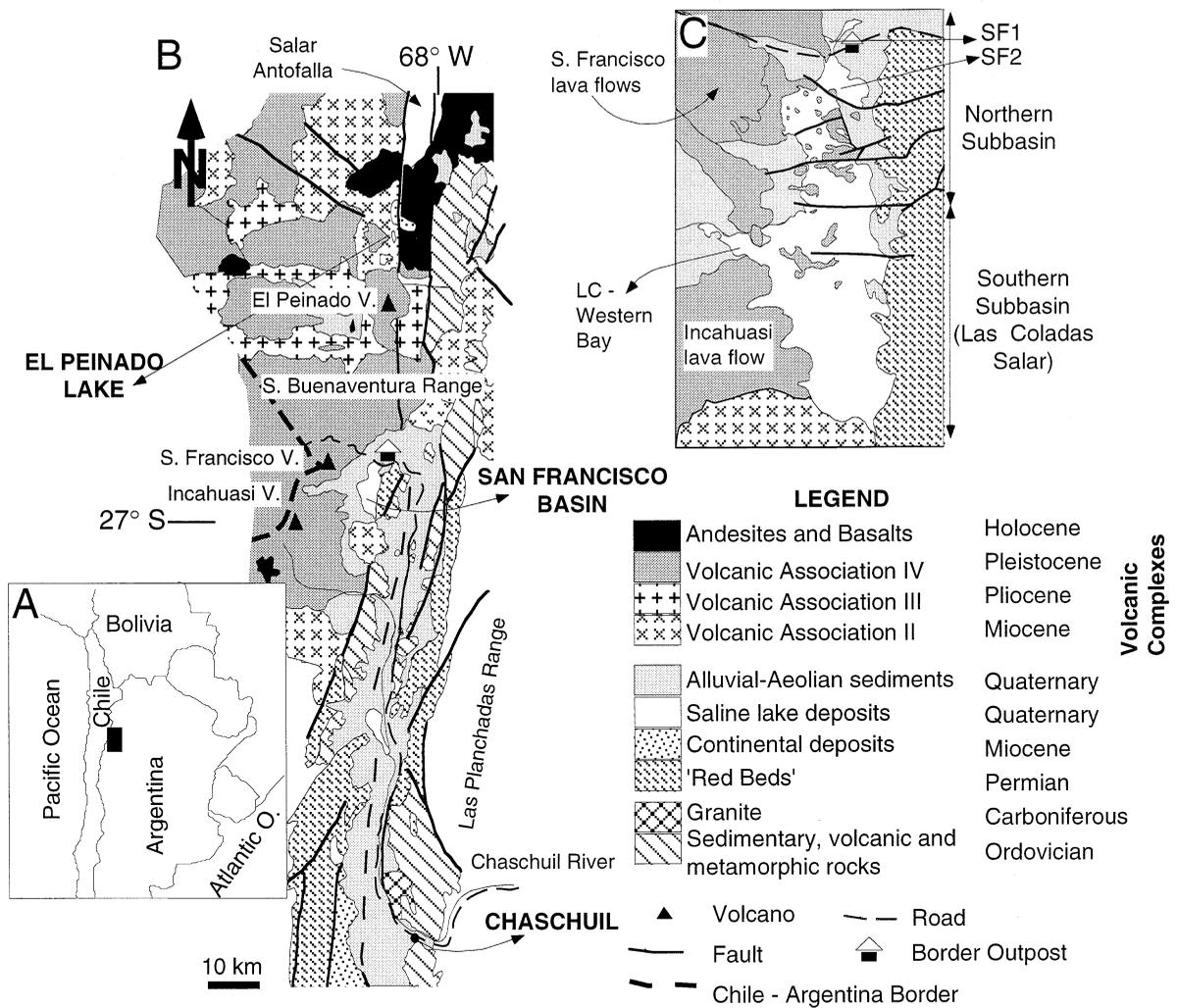


Fig. 1. Location of the El Peinado and San Francisco basins: (A) geographic location of the study area in the Central Andes; (B) geologic map; (C) the San Francisco Basin.

gested with a heated mixture of HCl and HNO₃ acids (3:1 ratio), filtered, and analyzed for main element composition with a JY 98 ICP spectrometer. Aquatic macrorests from organic-rich levels in El Peinado core and a peat sample from San Francisco were selected for AMS ¹⁴C analyses, and measured at the Woods Hole Laboratory (USA). The ²¹⁰Pb content was measured in eight samples from the El Peinado core at the St. Croix Watershed Research Station (Minnesota, USA), and a constant flux:constant sedimentation model [25] was used to reconstruct a chronology for the upper sediments.

4. Depositional environments of ¹³C-enriched primary carbonates

4.1. El Peinado Basin

The El Peinado Lake (26°29'59"S, 68°05'32"W, 3820 m a.s.l.) lies on an elongated N–S trending, topographically closed basin, north of El Peinado volcano (Fig. 1B). Waters are saline (electric conductivity: 55,500 μS cm⁻¹), alkaline (pH = 7.6), and the chemistry is dominated by SO₄²⁻, Cl⁻, Ca²⁺ and Na⁺, with relatively high content of strontium (58

ppm) and boron (135 ppm). Snowmelt and ground-water are the main water input to the lake. Thermal springs occur as diffuse seepage in emerged and submerged shoreline areas.

Several cores were retrieved in the littoral zone, at about 2 m water depth. The El Peinado core sediments consist of calcitic crusts (unit 3), overlaid by laminated muds (unit 2), and topped by travertine facies (unit 1) (Fig. 2). The calcitic crusts represent littoral facies cemented and indurated with low-magnesium calcite during low lake levels and subaerial exposure. Unit 2 groups six sequences composed of light-colored, carbonate-rich muds (facies 2a), dark-colored, with lower carbonate content (facies 2b), and grey-greenish, organic matter-rich muds (facies 2c). The carbonate fraction of the laminated muds is composed of fragmented travertine tubes reworked by wave action in the sublittoral zone. Unit 1 is composed of in-situ travertine deposits formed around the submerged vegetation in the littoral–shoreline zone (facies 1a) and reworked deposits with large travertine fragments included in a sandy matrix. The El Peinado sedimentary sequence records the evolution from a low lake level stage with subaerial exposure (unit 3) to a 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. Accurate dating of this sediment sequence has been hindered by the scarcity of terrestrial organic macrorests, and the large reservoir effects detected in the lake waters (Fig. 3). In current conditions, travertines are also found above the lake level, near the seepage areas along the shoreline. Fossil stromatolites occur in the lowest lacustrine terrace.

4.2. The San Francisco Basin

The San Francisco Basin can be subdivided into two subbasins (Fig. 1C). The northern one is a mosaic of shallow lakes, areas with halophytic and Andean grass vegetation, and small hills. Two of these small playa lakes were sampled (SF-1 and SF-2, 26°55′42″S; 68°07′21″W, 3980 m a.s.l.). There are no thermal springs directly feeding the lake, and, in current conditions, diffuse groundwater seepage dominates the water input. Modern sediments are massive carbonate and diatomaceous-rich muds. A

peat layer underneath the modern carbonate sediments in SF-2 core has given a modern ^{14}C AMS age, indicating that carbonate deposition is recent in the northern subbasin.

The southern subbasin is occupied by a large, flat-bottomed, shallow (up to 25 cm deep) playa lake bounded to the west by lava flows from the Incahuasi and San Francisco volcanoes and here designated as Las Coladas Salar (26°57′47″S, 68°10′16″W, 4000 m a.s.l.). Las Coladas waters are saline (E.C. = 41,900 $\mu\text{S cm}^{-1}$), 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 0.24). A number of seasonal creeks and thermal springs discharge in the area. Modern carbonate precipitation in Las Coladas is dominated by aragonite, due to the higher Mg/Ca ratio of the waters. Most of the surface of the western bay shows a patchy distribution of laminated aragonite speleothemic crust.

5. The $\delta^{13}\text{C}$ record

Carbon isotopic ratios of bulk organic matter provide information about sediment organic-matter sources, lake paleoproductivity, CO_2 concentration and availability, and changes in vegetation and catchment hydrology [7,26–28]. Changes in the $\delta^{13}\text{C}$ of authigenic lacustrine carbonate and lacustrine organic matter reflect variations in the dissolved inorganic carbon (DIC) pool, controlled by input, biological (mainly respiration and photosynthesis), and physical processes (evaporation, residence time) [1,9].

The $\delta^{13}\text{C}_{\text{organic matter}}$ record from El Peinado core (Figs. 2 and 4B) shows lower and decreasing values in the calcitic crust facies from unit 3 ($< -14\%$ PDB), and two sharp and large (up to 8‰ PDB) positive shifts in the banded facies of subunits 3c and 3a. The banded and laminated facies of units 2 and 1 also show heavier $\delta^{13}\text{C}_{\text{organic matter}}$ values and a smaller range (-14 to -10% PDB). The heavier $\delta^{13}\text{C}_{\text{organic matter}}$ values could be explained by a combination of factors [9,26,27]. Increased productivity could cause an accelerated carbon demand that could result in a positive shift of $\delta^{13}\text{C}_{\text{organic matter}}$. A change in the carbon source for phytoplankton photosynthesis from CO_2 to bicarbonate would also have en-

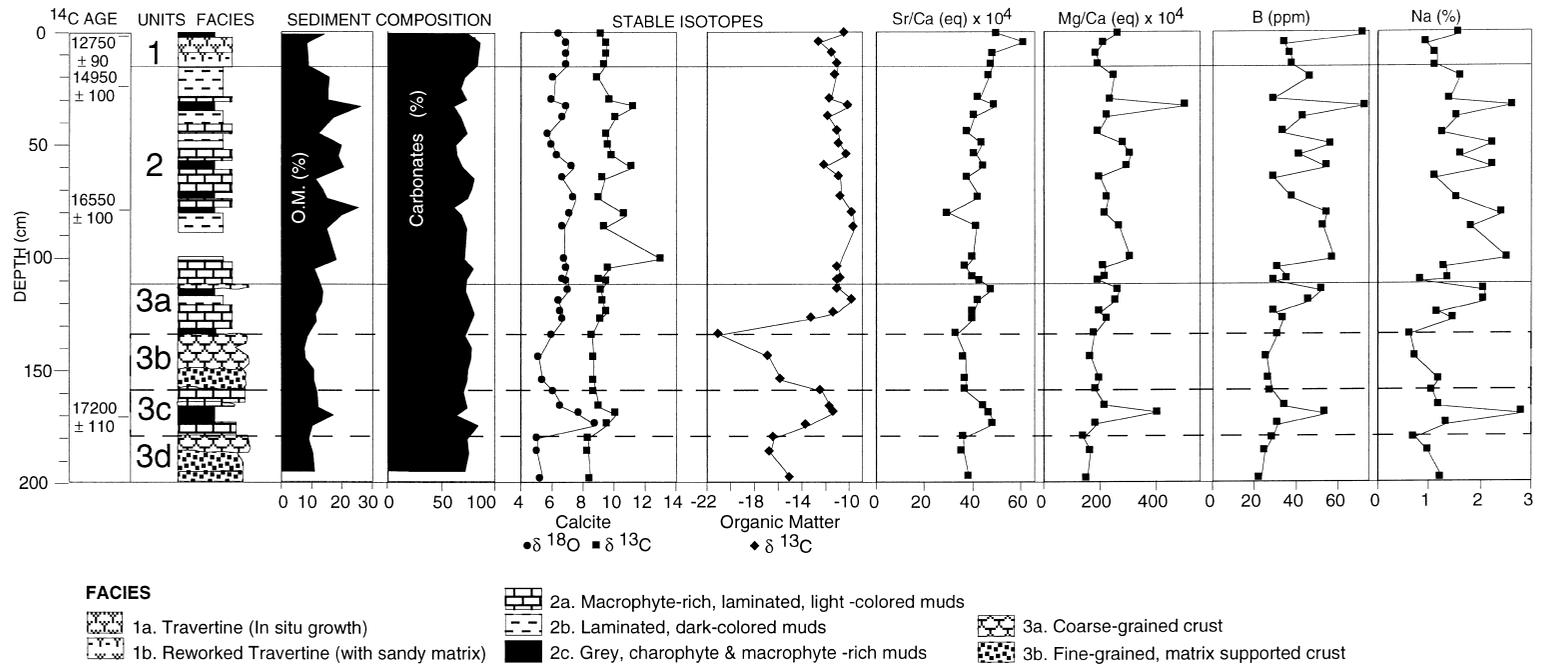


Fig. 2. Sedimentary facies, sediment composition, stable isotopes and geochemistry of the El Peinado core. Dates are un-corrected AMS ¹⁴C ages (years B.P.). All isotopic measurements are reported as δ values vs. the PDB standard.

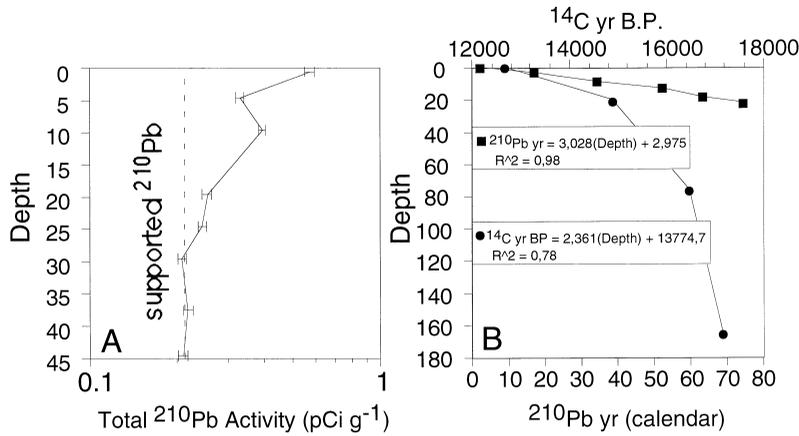


Fig. 3. The ^{210}Pb chronology for El Peinado Core based on a supported ^{210}Pb activity of 0.21 pCi g^{-1} and a constant flux:constant sedimentation model (A) shows a large reservoir effect (up to 12,000 yr) on ^{14}C dates (B).

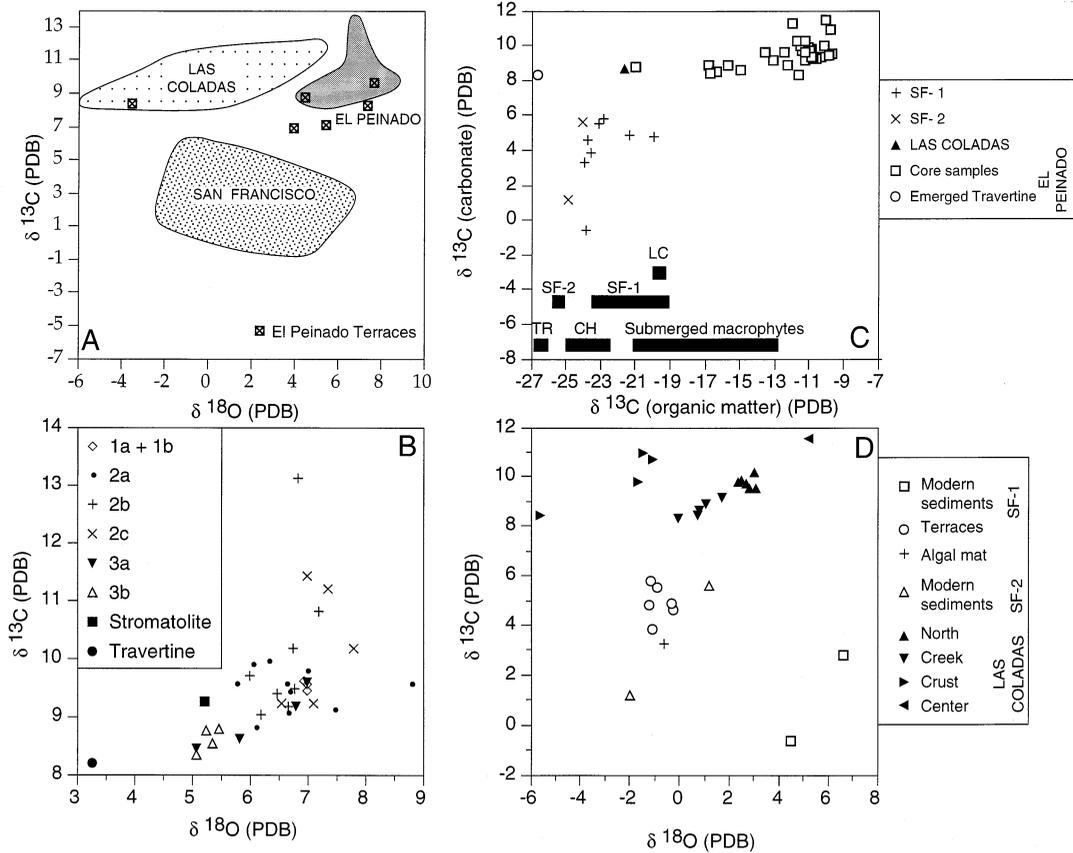


Fig. 4. Isotopic composition of carbonates and organic matter in Andean lakes. (A) Oxygen and carbon isotope compositions of primary carbonates from the three sites. (B) Isotopic composition of the different carbonate facies in El Peinado. (C) Carbon isotope compositions for organic matter and carbonates and for bulk organic matter and plants from several locations in the area (*SF* = San Francisco North; *LC* = Las Coladas; *TR* = emerged plants in the shoreline of El Peinado; *CH* = organic matter from the Chaschuil River banks). (D) Oxygen and carbon isotope composition of primary carbonates from the San Francisco Basin.

riched the carbon isotope composition of the organic matter. However, the clear correspondence between shoreline and littoral facies and $\delta^{13}\text{C}_{\text{organic matter}}$ values (lighter and heavier, respectively) indicates that the depositional environment is the main factor controlling the isotopic composition of organic matter.

The carbon isotope data for authigenic calcite and aragonite are shown in Figs. 2 and 4. Most of El Peinado and Las Coladas values were higher than 8‰ PDB; the northern San Francisco subbasin samples show lower compositions (5.7 to -0.7% PDB). The two striking features are the $\delta^{13}\text{C}$ values much higher than atmospheric equilibrium, and the large differences between lakes in the same San Francisco Basin (Fig. 4A). The El Peinado core shows lighter and less fluctuating $\delta^{13}\text{C}$ values in the lower unit dominated by calcitic crust facies, and generally heavier values and a larger range in the laminated facies (Figs. 2 and 4B). The heaviest $\delta^{13}\text{C}$ values correspond to organic-rich facies (2c and 2b), interpreted as deposition during high lake levels and saline conditions. The small positive shifts in $\delta^{13}\text{C}_{\text{calcite}}$ in units 3c and 3a, and in facies 2c in unit 2 also suggest a relative increase in organic productivity. The carbon isotope values of the El Peinado terraces were among the lowest of the El Peinado sequence indicating that the contribution of heavier TIDC waters was relatively smaller during high lake level stages.

Las Coladas carbonate samples show similar high isotopic values (between 8 and 12‰ PDB) as the El Peinado ones, and they display increasing isotopic values and higher Sr/Ca ratios from the margin to the center of the lake (Fig. 4D and Fig. 5). In the northern San Francisco subbasin (SF-1), modern aragonite sediments have similar heavy oxygen values (+5‰ PDB), but the carbon isotope compositions are the lowest of the San Francisco Basin samples (<3‰ PDB), suggesting that the bacterial mats occurring in the lake plays a major role in the carbon budget.

6. Carbon sources and carbon enrichment processes

The most conspicuous feature of the isotopic data is the unusually enriched ^{13}C content of these primary carbonates, which indicates a high $\delta^{13}\text{C}$ value

for the total dissolved inorganic carbon (TDIC) in the El Peinado and Las Coladas Salar waters. Equilibrium fractionation equations predict that CaCO_3 is about 1‰ PDB enriched in ^{13}C relative to the HCO_3^- [4], which would indicate values between +7 and +12‰ PDB for DIC in El Peinado. The estimated values for DIC in equilibrium with atmospheric CO_2 (-7% PDB) at lake water temperatures between 0°C and 30°C should be in the range of +4.0 to 0.4‰ PDB, according to the equations for the isotopic enrichment factor between HCO_3^- and atmospheric CO_2 [4,29]. In this section we discuss the possible heavy carbon sources and the physical and biological processes that can generate ^{13}C enrichment in the Andean surface waters over those values.

6.1. Biological processes and sources

6.1.1. Diagenetic CO_2 related to methanogenesis

Organic matter modified during diagenesis by acetate fermentation processes produces CO_2 characterized by its heavy carbon isotope composition (+15‰ PDB; [12,13,30]). Carbonate precipitation is common during the diagenesis of organic matter-rich marine and lacustrine sediments [8]. CO_2 of such origin is unlikely to occur in a region with no organic-rich geologic formations. Besides, carbonate phases formed in these Altiplano lakes are undoubtedly of primary origin, and although we lack any data on methane production, it is very unlikely that methanogenesis occurs to any extent in these lake basins. Las Coladas, a playa lake with a hypersaline, high SO_4^{2-} brine and very low organic-matter accumulation should be more conducive to sulfate reduction processes. Maximum water depth, organic-matter content, and pore brine chemistry of El Peinado are unknown. However, the well oxidized nature of the core sediments, the absence of any indication of anoxic bottom sediments, and the high sulfate content of the lake waters suggest that organic-matter degradation would be dominated by oxic processes. Should any anoxic environment develop, sulfate reduction would be the most likely process to destroy organic matter.

6.1.2. Biogenic sources and processes

The vegetation cover in both watersheds is scarce, dominated by steppe grasses. In saline soils around

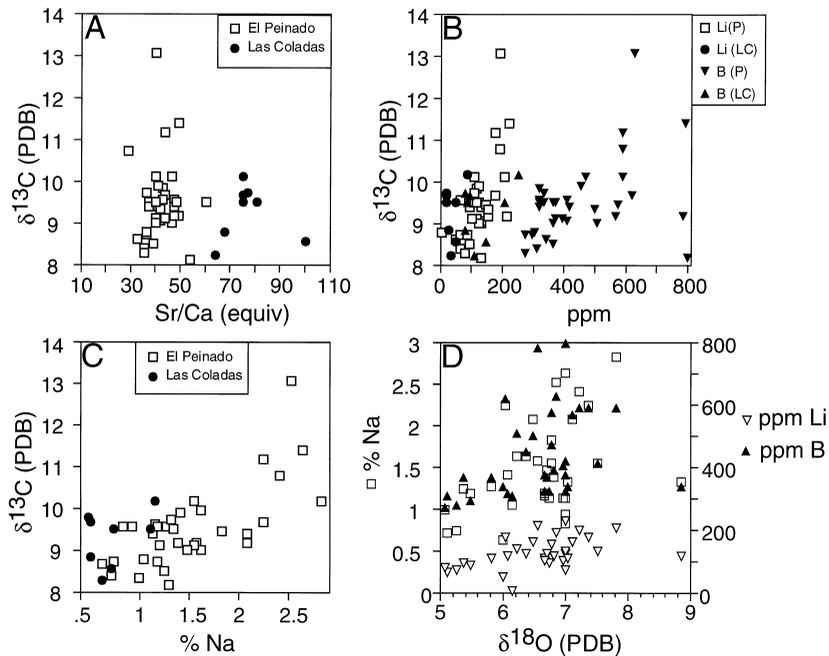


Fig. 5. Isotopic compositions and geochemical salinity indicators for El Peinado (P) and Las Coladas (LC) samples. Carbon isotope compositions and $\text{Sr}/\text{Ca} \times 10^4$ ratios (A), lithium and boron (B), and sodium (C) contents. Oxygen isotope compositions and the same geochemical salinity indicators for El Peinado core samples (D).

lakes and depressions halophytic communities develop. Steppe grasses at these high altitudes should follow the C_3 photosynthetic cycle because C_4 plants only occur in areas where lower temperatures are higher than 8°C , and consequently C_4 plants disappear at high altitudes [31]. The soil CO_2 generated by these plants is about 4.5‰ PDB heavier than the plant biomass [32], and it would be characterized by $\delta^{13}\text{C}$ values between -18‰ and -22‰ PDB [33]. The $\delta^{13}\text{C}$ values of bulk lacustrine organic matter and peat from the San Francisco Basin (-27 to -19‰ PDB), the modern emerged aquatic vegetation around El Peinado Lake (-26.6‰ PDB), and organic matter deposited in the banks of the Chaschuil River (-25 and -23.5‰ PDB) (Fig. 4B) were within the expected range for terrestrial plants following C_3 photosynthetic cycle (-24 to -30‰ PDB) [34]. Most of the $\delta^{13}\text{C}_{\text{organic matter}}$ values from the El Peinado core samples show heavier values (-8.4 to -11‰ PDB) than those from submerged plants in hard water lakes (-12 to -20‰ PDB), and similar to samples of organic matter from other

Andean saline lakes with heavy carbon-enriched primary carbonates (about -7‰ PDB, [18]). These $\delta^{13}\text{C}$ values indicate that submerged macrophytes are the main organic contributors in the littoral areas of El Peinado lake and that terrestrial and emerged aquatic plants dominate the San Francisco Basin. The correspondence between ^{13}C -enriched carbonates and submerged plants suggests a common source of heavy CO_2 for photosynthesis and carbonate precipitation in Andean saline lakes. A change in dominant biota from emerged shoreline plants during deposition of the calcitic crusts to submerged macrophytes could account from the sharp $\delta^{13}\text{C}_{\text{organic matter}}$ increases and the heavier values of the upper two units. The enriched $\delta^{13}\text{C}_{\text{organic matter}}$ intervals are interpreted as periods of relatively higher lake levels. Some of the peak $\delta^{13}\text{C}$ values in facies 2c occur without increasing the oxygen isotope composition. These ^{13}C -enrichments could be related to increased biologic activity, as these facies have the highest organic-matter content.

6.2. Physical processes

The absence of heavy carbon sources and biologic or diagenetic ^{13}C -enrichment processes able to explain the heavy $\delta^{13}\text{C}$ values suggest that abiotic processes play a major role on the carbon budget.

6.2.1. Old carbon inventories

Carbonate formations are absent in both basins, dominated by volcanic rocks. Their presence in the subsurface geological formations is too restricted [22] to explain any large isotope enrichment due to decarbonation reactions during metamorphism [35]. However, the anomalously old AMS ^{14}C dates for the El Peinado core provide a clear proof for a large contribution of ^{14}C -free CO_2 to these lake systems (Figs. 2 and 3). Terrestrial organic-matter samples from the study area did not show this effect: the peat sample from the San Francisco Basin yields a modern AMS ^{14}C age in SF-2, and the fluvial–lacustrine organic-rich sediments deposited in the Chaschuil River yield mid- to late-Holocene conventional ^{14}C ages [36] coherent with regional chronologies. Old radiocarbon ages are common in calcareous terrain affected by old carbon inventories [27], but are not expected in areas devoid of carbonate rocks. The contribution of old groundwaters recharged during more humid periods (late Glacial–early Holocene) could be significant in this arid environment [17,18]. In volcanic regions ^{14}C -free CO_2 emanations may introduce a dating effect of more than 1000 years [25]. Both sedimentologic evidence and a ^{210}Pb -based chronology indicated a much larger reservoir effect in El Peinado. Travertines are currently being formed at the coring site, and, consequently the radiocarbon age of the uppermost sediments should be modern. Although the values of total ^{210}Pb activity were very low (less than 0.6 pCi g^{-1} , Fig. 3A), they were within the range of other Altiplano ^{210}Pb profiles (0.31 in Laguna Miscanti, [18]). The calculated fluxes of ^{210}Pb to these core sites were extremely low ($0.5\text{--}0.6 \text{ pCi cm}^{-2} \text{ yr}^{-1}$) and this could be a reflection of low atmospheric ^{210}Pb deposition rates in a region like the Altiplano with very low rainfall. The large reservoir effect for ^{14}C ($>12,000 \text{ yr}$, Fig. 4B) indicates a large input of old carbon to the lake waters, either as old groundwaters or as ^{14}C -free volcanic CO_2 .

6.2.2. Geothermal and volcanic CO_2

Geothermal activity is widespread in the San Francisco and El Peinado basins. Seepage areas occur along the shoreline of El Peinado lake and Las Coladas Salar. Although we lack any compositional data, carbon dioxide is likely one of the main components of geothermal gases, as occur in most geothermal areas, and particularly in El Tatio where CO_2 is 99.5% of the total gases [33]. The $\delta^{13}\text{C}$ values for geothermal CO_2 range between -1.0 and -6.6% PDB [33,35]. Volcanic CO_2 is free of ^{14}C and typically has $\delta^{13}\text{C}$ values between -3.2 and -7.1% PDB [33]. Heavy carbonates have been reported in geothermal springs with $\delta^{13}\text{C}$ between 6 and 12% PDB (Italy), and 3 and 8% PDB (Yellowstone) [15], and related to the presence of carbonate rocks in the substrate. A regional volcanic source for dissolved CO_2 in groundwaters has been proposed in northern Chile to explain some relatively heavy $\delta^{13}\text{C}$ values (up to $+7.3\%$ PDB) in the Loa and Salado river waters [33]. Saline lakes in the Atacama Altiplano [17,18] also showed heavy $\delta^{13}\text{C}$ values (up to $+14\%$ PDB), and a large reservoir effect in ^{14}C dates (up to 8000 years) explained as a result of volcanic–hydrothermal CO_2 and old water reservoirs contributions [18]. $\delta^{13}\text{C}$ values consistently above atmospheric equilibrium, and up to 10% PDB were found in authigenic carbonates and ostracods from Laguna Seca ($18^\circ 11'\text{S}$, $69^\circ 14'\text{W}$, 4500 m a.s.l.) in northern Chile [10]. Laguna Seca depositional environment shows striking similarities with El Peinado Lake: (1) both are ground-fed lakes, with a number of geothermal springs occurring along the shoreline; (2) they are located in a young geothermal field, close to active volcanoes; and (3) the sediments are characterized by abundant travertine deposits. A strong kinetic fractionation during volcanic CO_2 evasion is a suitable mechanism for ^{13}C enrichment in the lake waters.

Both evaporation effects and degassing of carbon dioxide have been proposed as ^{13}C enrichment processes in saline lakes [7,10,11,19,37]. Degassing of CO_2 -rich hot-spring could adequately explain the heavy $\delta^{13}\text{C}$ values and the high proportion of dead carbon. CO_2 degassing occurs when groundwaters with high CO_2 content reach the surface; a preferential loss of ^{12}C atoms to the atmosphere results in ^{13}C enrichment of surface waters [38]. Playa lakes

as SF-1 and SF-2 without thermal springs do not show large ^{13}C enrichments (Fig. 4A,D). The $\delta^{13}\text{C}$ value for emerged travertine carbonate in El Peinado (8.2‰ PDB) is similar to the lowest values from Las Coladas (speleothemic crust) and these could indicate that emerging groundwaters in both basins are characterized by minimum TDIC $\delta^{13}\text{C}$ values of about 5‰ PDB. Further isotope enrichment would be achieved by non-equilibrium processes such as CO_2 degassing. Degassing of carbon dioxide plays a major role in the formation of travertines [16] and this process must exert some control on the $\delta^{13}\text{C}$ values of the El Peinado Lake. However, the absence of travertine facies in Las Coladas clearly indicates that carbonate formation during degassing of CO_2 -rich groundwaters occurs without biomediation.

6.2.3. Evaporation processes and residence time evolution

The isotopic composition of El Peinado and Las Coladas waters ($\delta^{18}\text{O} = 4.34\text{‰}$, $\delta^2\text{H} = -6.8\text{‰}$ and $\delta^{18}\text{O} = 7.34\text{‰}$, $\delta^2\text{H} = 29\text{‰}$, respectively SMOW) indicate large evaporative enrichments, stronger in Las Coladas, as expected in a playa lake with a large surface/depth ratio. These large evaporation rates are responsible for the heavy $\delta^{18}\text{O}$ values in carbonates from these high-altitude lakes (Fig. 4A and Fig. 5D). The $\delta^{18}\text{O}$ carbonate curve cannot be interpreted as a function of simple evaporation from a closed system that would be related to salinity. The oxygen-isotopic composition of lake water is controlled by (1) the isotopic composition of the rainfall, its seasonality, and the relative humidity, (2) temperature at the time of precipitation, (3) potential evaporation, and (4) groundwater inflow [7,39,40]. The $\delta^{18}\text{O}$ of precipitating carbonates depends on the temperature of formation, and the isotopic composition of the water. The $\delta^{18}\text{O}$ values from El Peinado lacustrine terraces show a large range (-3.4 to $+7.5\text{‰}$ PDB; Fig. 3A and Tables 1 and 2) which indicates that different water sources were involved during more positive water balance periods. There is a general positive correlation between $\delta^{18}\text{O}$, and salinity proxies (Na, Li and B content), although the scatter in the data shown in Fig. 5D indicates that other factors besides evaporation effects — most likely groundwater influx, and redissolution of previously precipitated salts — control both chemical and isotope concentration.

Degassing of carbon dioxide during evaporation could be responsible for increasing $\delta^{13}\text{C}$ trends and the covariance with $\delta^{18}\text{O}$ values. Geochemical proxy indicators of salinity such as the Sr/Ca ratio (Fig. 5A), Li, B (Fig. 5B) and Na (Fig. 5C) content in sediments show a general good correlation with the $\delta^{13}\text{C}$ values in both El Peinado and Las Coladas. The extreme $\delta^{13}\text{C}$ values of El Peinado ($>10.5\text{‰}$ PDB) show the highest Na contents, but the Sr/Ca ratio range is large and the high Li and B contents are similar to other samples with lower carbon isotope compositions. The development of some calcitic crusts in El Peinado (top of unit 3a and 3b, for example) is marked by a relative increase in some salinity indicator ($\delta^{18}\text{O}$, Sr/Ca, B, and Na values), suggesting increased evaporation during those periods (Fig. 2). However, the $\delta^{13}\text{C}$ values remain similar or slightly decrease. Similarly, during periods of higher lake levels indicated by deposition of banded facies the $\delta^{13}\text{C}$ values increased (subunit 3c) or remained similar (subunit 3a). In unit 2, heavier oxygen and carbon values corresponded with Sr/Ca and Na peaks in laminated, organic-rich facies. Therefore, large ^{13}C enrichments are not directly related to decreasing water balance in the lake.

Emerged travertines formed at the shoreline springs in El Peinado show lighter oxygen and carbon isotope composition than the stromatolites in the lower lacustrine terrace and than the submerged travertine at the top of the core (Fig. 4B). These compositions are coherent with isotope enrichment in the lake due to evaporation and increased residence time. Coupling between ^{18}O and ^{13}C enrichments occurs in the units dominated by laminated facies (1, 2 and 3c). This covariant pattern has been considered as an indication of a long residence time of water in hydrologically closed basins [7].

Las Coladas isotope values also displayed a clear covariant trend, with increasing $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and higher Sr/Ca ratios from the margin (-1 to $+1\text{‰}$ PDB) to the center of the lake ($+5\text{‰}$ PDB) (Fig. 4D), suggesting that evaporation-related effects played a major role in isotope enrichment. However, the $\delta^{13}\text{C}$ values of the speleothemic crust and the aragonite muds are similar ($>8\text{‰}$ PDB) suggesting that the TDIC of the waters before the evaporation was already ^{13}C -enriched. In the nearby northern San Francisco subbasin, modern aragonite sediments

Table 1
Chemical and isotopic composition of El Peinado and Las Coladas carbonate samples

Sample	Mg/Ca (equiv.) ($\times 10,000$)	Sr/Ca (equiv.) ($\times 10,000$)	Li (equiv.)	Na (equiv.)	B (ppm)	$\delta^{13}\text{C}_{\text{cal.}}$	$\delta^{18}\text{O}_{\text{cal.}}$	$\delta^{13}\text{C}_{\text{O.M.}}$
El Peinado Core								
1	262	50.36	31.28	686.25	787.84	9.19	6.59	−10.29
5	212	61.50	18.64	411.07	379.46	9.53	7.03	−12.39
10	188	48.65	15.60	502.36	411.33	9.59	6.97	−11.40
15	197	48.37	19.50	498.21	421.51	9.42	7.02	−10.93
20	253	47.18	20.23	710.00	513.72	9.00	6.24	−11.13
23						8.72	4.71	−10.82
30	239	43.14	17.34	617.35	321.51	9.87	6.11	−11.47
33	506	49.93	32.87	1152.95	797.88	11.39	7.03	−9.93
38	224	41.13	16.78	681.80	476.05	10.15	6.79	−11.63
45	194	38.41	16.66	554.64	370.48	9.53	5.84	−10.92
50	285	44.08	25.88	979.35	623.25	9.68	6.05	−10.78
55	309	41.53	18.57	709.36	456.46	9.92	6.38	−10.1
60	294	44.74	25.87	982.88	596.96	11.18	7.38	−11.95
65	199	38.09	13.81	492.55	324.39	9.39	6.75	−10.76
74	228	42.96	19.50	673.58	417.42	9.09	7.52	−10.55
79						8.42	5.86	−8.35
81	221	30.03	28.75	1052.42	596.61	10.77	7.24	−9.73
87	270	42.15	22.22	795.62	578.10	9.44	6.81	−9.59
101	307	40.48	28.19	1100.13	630.94	13.08	6.87	−10.98
105	215	37.44	16.48	578.37	342.69	9.74	7.06	−10.67
110	219	40.65	17.35	602.90	395.87	9.15	6.83	−10.92
111	193	43.45	10.58	366.31	327.37	9.57	7.03	−10.84
115	266	48.33	23.43	905.00	571.26	9.19	7.13	−9.74
120	258	42.77	23.18	913.19	503.01	9.36	6.5	−11.14
125	198	40.85	16.47	514.66	327.33	9.54	6.7	−13.07
128	227	40.67	18.51	646.80	372.75	9.02	6.73	
130						8.64	6.02	
135	181	33.66	7.50	278.68	343.69	8.64	6.02	−20.92
145	167	37.10	10.46	325.19	282.45	8.73	5.27	−16.71
155	201	37.30	12.87	521.67	300.08	8.74	5.49	−15.61
160	188	37.48	1.29	457.11	308.56	8.79	6.15	−12.24
167	219	44.90	15.32	523.24	378.61	9.13	6.70	−11.56
168						8.23	6.10	−11.05
170	404	47.25	30.21	1234.44	594.47	10.14	7.84	−11.17
175	191	49.08	17.46	584.93	342.93	9.52	8.86	−13.45
181	142	36.43	9.47	318.57	316.25	8.41	5.12	−16.30
187	168	36.20	11.74	433.67	276.44	8.32	5.10	−16.60
199	188	39.70	14.11	547.42	368.74	8.51	5.39	−14.86
El Peinado Terrace #2								
	510.63	54.66	19.96	565.96	807.94	8.16	7.5	
Las Coladas								
LC-3 A-1	336.27	75.66	13.14	505.10	259.38	10.16	3.09	
LC-3 A-2	293.12	76.41	8.03	482.58	213.09	9.51	2.87	
LC-3 A-3	185.43	81.18	3.92	325.95	94.78	9.51	3.13	
LC-3 A-4	105.35	77.68	3.49	215.97	84.85	9.75	2.44	
LC-3 A-5	87.27	76.31	3.20	221.05	97.32	9.69	2.72	
LCV-2	198.28	68.27	5.03	227.05	88.01	8.83	1.13	
LCV-7	355.42	65.29	6.24	273.46	115.88	8.26	0.03	

Table 2

Isotope data for the Las Coladas subbasin and the northern San Francisco subbasin (SF-1 and SF-2 sites), El Peinado lacustrine terraces, and Chaschuil

Sample	$\delta^{13}\text{C}_{\text{carb.}}$	$\delta^{18}\text{O}_{\text{carb.}}$	$\delta^{13}\text{C}_{\text{O.M.}}$
Las Coladas			
<i>North:</i>			
LC-3 A-1	10.16	3.09	
LC-3 A-2	9.51	2.87	
LC-3 A-3	9.51	3.13	
LC-3 A-3	9.8	2.53	
LC-3 A-4	9.75	2.44	
LC-North			−19.71
LC-3 A-5A	9.69	2.72	
<i>Creek:</i>			
LCV-2	8.83	1.13	
LCV-3	8.58	0.86	−21.55
LCV-5	8.39	0.81	
LCV-7	8.26	0.03	
LCV-8	9.12	1.75	
LCV-A			−19.87
LCV-B			−20.51
<i>Center:</i>			
LCC-1	11.52	5.28	
<i>Crust:</i>			
LC-1	9.74	−1.63	
LC-2	10.67	−1.02	
LC-3	8.38	−5.57	
LC-4	10.89	−1.43	
Chaschuil			
CH-1			−24.98
CH-2			−23.54
El Peinado (Terraces)			
Middle T-2	8.16	7.5	
Base T-2	6.85	4.1	
Top T-3	8.23	−3.41	
Emerged travertine	8.17	3.31	−26.56
Stromatolite	9.22	5.26	
T-1	7.01	5.57	
Top T-4	9.55	7.74	
Base T-4	8.69	4.57	
San Francisco			
<i>San Francisco-1:</i>			
SF-1 (salt crust)	−0.67	4.58	−23.69
SF-2 (0 cm)	4.54	−0.15	−23.59
SF-3 (4 cm)	5.74	−1.09	−22.72
SF-4 (6 cm)	4.79	−0.21	−21.27
SF-5 (12 cm)	4.73	−1.12	−19.87
SF-6 (22 cm)	5.44	−0.8	−22.96
SF-7 (29 cm)	3.8	−1.01	−23.46
SF-9 (algal mat)	3.21	−0.53	−23.86
SF-0 (salt crust)	2.71	6.69	

Table 2 (continued)

Sample	$\delta^{13}\text{C}_{\text{carb.}}$	$\delta^{18}\text{O}_{\text{carb.}}$	$\delta^{13}\text{C}_{\text{O.M.}}$
<i>San Francisco-2:</i>			
SF-2-1	5.5	1.26	−23.98
SF-2-2	1.1	−1.89	−24.8
SF-2, o.m., surface			−25.52
SF-2 (peat, 10 cm)			−26.06

display similar heavy oxygen values (+5‰ PDB), but the carbon isotope composition is the lowest of the whole San Francisco Basin samples, suggesting a modern carbon budget dominated by biological sources (microbial and biogenic). The sediments from the lacustrine terraces at SF-1 show lower oxygen isotope values and a smaller range (about 1‰ PDB), indicating a different hydrologic regime in the past, with higher lake levels and smaller evaporite effects. Carbon isotope compositions, however, are heavier than the modern values. Therefore, evaporation has to be ruled out as the main carbon-enrichment process in the northern San Francisco subbasin. The deposition of ^{13}C -enriched carbonates during relatively higher lake levels suggests a greater input of heavy carbon associated to increased water balance. More positive water balance and TDIC compositions could be achieved by increasing input of waters with heavier TDIC, as thermal springs.

7. Conclusions

The degassing of geothermal CO_2 during groundwater discharge can best explain the enriched $\delta^{13}\text{C}$ values for primary calcite and aragonite precipitated in El Peinado and San Francisco lakes, northwestern Argentina. Further degassing of carbon dioxide during lake water evaporation also contributes to increasing $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ trends. Physical rather than biological processes control the carbon budget in these high-altitude, saline lakes. We present evidence of a large contribution of old carbon inventories in lake basins located in a geologic setting without carbonate or carbonaceous rocks. The radiocarbon dates of lake sediments are not only controlled by the lithologic composition of the watershed and the biological and hydrological history of the basin, but also by the dilution effect of large quantities of

^{14}C -free CO_2 introduced by geothermal activity or old groundwaters. In active volcanic areas, accurate ^{14}C chronology based on lacustrine organic matter or aquatic plants is hindered unless the input of geothermal CO_2 is evaluated. The dominance of abiotic processes in the carbon budget of some lakes has implications for the global carbon cycle in surface environments. Besides, our results contribute to better understand the carbon cycle in lakes and the reliability of paleoclimatic and paleoenvironmental records inferred from $\delta^{13}\text{C}$ values.

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