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Characteristics of sediments in an altitudinal sequence of lakes in the Venezuelan Andes: Climatic implications

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Abstract—Analyses of water and sediments from lake basins along an altitudinal transect in the Central Andes of Venezuela (elevation range 1100 to 3700 m) suggest that some geochemical and clay mineral characteristics follow distinct altitudinal patterns. The distribution of extractable sedimentary iron shows that organically-bound iron dominates in the sediments of high-elevation lake basins in the Tierra Helada climatic zone (cold and humid, alpine). In the Tierra Templada zone (warm and wet, temperate), amorphous iron is most abundant and the concentration of organic matter is at a maximum. In the lowest lake basin, located in the Tierra Caliente zone (hot and semi-dry, subtropical), amorphous and crystalline iron show similar abundances. Illite and chlorite dominate the clay mineral assemblage of the high elevation (>3400 m) lake sediments. At lower elevations (around 2000 m), gibbsite and kaolinite become the primary constituents of the clay mineral fraction, but in the lowest lake basin, at 1100 m, illite reappears as the main clay mineral. The observed variations in lake sediments and water chemistry can be only partially explained by the bedrock composition and other physical properties of the lake basins. It is suggested that, to a great extent, these characteristics are controlled by weathering processes in the drainage basins.

Resumen—Análisis del agua y sedimentos de cuencas lacustres, a lo largo de un trayecto altitudinal en los Andes Centrales de Venezuela (alturas de 1100 a 3700 m), sugieren que los minerales de arcilla y algunas características geoquímicas siguen patrones altitudinales definidos. La distribución de hierro extraible contenido en los sedimentos, indica que los complejos orgánicos de hierro dominan en sedimentos de cuencas lacustres en la Tierra Helada (clima frío y húmedo, alpino). En la Tierra Templada (clima húmedo, templado) el hierro amorfo es el más abundante y la concentración de materia orgánica es máxima. En la cuenca más baja, dentro de la Tierra Caliente (clima caliente, semi-seco, subtropical), el hierro amorfo y el cristalino son los más abundantes. Ilita y clorita dominan el conjunto mineralógico de arcillas en los sedimentos lacustres encima de los 3400 m. En alturas más bajas, (alrededor de 2000 m), gibsita y kaolinita son los constituyentes más importantes, mientras que en la cuenca más baja (1100 m), la ilita reaparece como la arcilla principal. Las variaciones litológicas en las formaciones geológicas y las características físicas de las cuencas lacustres solo permiten una explicación parcial de los cambios observados en las aguas y en los sedimentos. Se sugiere que estas características estan principalmente controladas por los procesos de meteorizacion en las cuencas de drenaje.

INTRODUCTION

THE VENEZUELAN ANDES are an elongated mountain chain extending SW-NE for over 450 km across northwestern Venezuela (Fig. 1). The central and highest portion of the Venezuelan Andes, the Sierra Nevada de Mérida, reaches elevations of up to about 5000 meters (Pico Bolivar, 5007 m above sea level).

Of the two glacial advances documented in the Venezuelan Andes (Schubert, 1974), the older advance descended to elevations of approximately 2600 meters, but morphological evidence is sparse and obscure. In the last, and extensively documented, glaciation (the Mérida), glaciers extended down to 3400 meters. Consequently, lakes are more abundant at elevations above 3400 meters, most occupying cirques and other glacially scoured depressions. Lower elevation lake basins do not possess clear evidence suggesting their origin, except for a faulted basin within the Chama River Valley.

Only a few lakes in the Venezuelan Andes have been studied, mostly in the Tierra Fría (Lewis and Weibezahn, 1976; Weibezahn *et al.*, 1970). Intensive pollen studies in Venezuela were initiated in the late 1970's (*e.g.*, Salgado-Labouriau and Schubert, 1976, 1977; Salgado-Labouriau *et al.*, 1977; Salgado-Labouriau, 1979, 1980, 1984), but these were done on peat bog and exposed lacustrine sediments.

Here, we report analyses of lake waters and lake sediments (clay minerals and extractable iron in short cores 44–108 cm long) of nine lakes in different elevational groups ranging from 1100 to 3700 meters.

GEOLOGIC AND TOPOGRAPHIC SETTING

The regional geologic history of the Venezuelan Andes has been discussed by several authors, but here we refer to studies by Shagam (1972a,b). Three rock formations crop out in the study area: the Precambrian(?) Sierra Nevada, the Paleozoic Mucuchachí, and the Mesozoic La Quinta Formations. Metamorphosed and complexly deformed schists,

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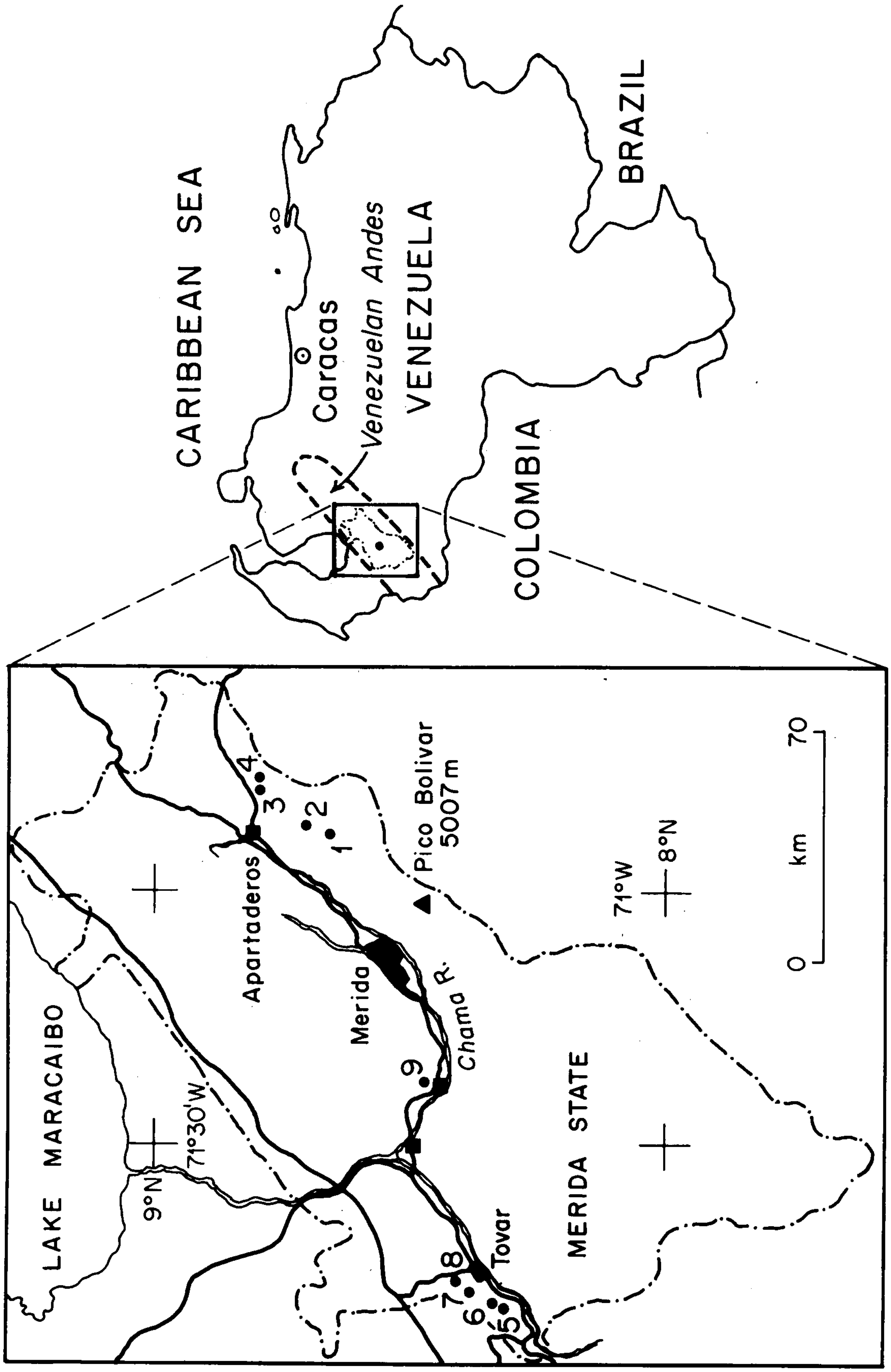


Fig. 1. Index map of the study area and lake locations: 1, Montón, 2, Saisay, 3, Mucubají, 4, Negra (A), 5, Brava, 6, Los Lirios, 7, Negra (M), 8, Blanca, 9, Urao.

gneisses, and amphibolites are the principal rocks of the Sierra Nevada Formation. The schists and gneisses are dominated by quartz and plagioclase, with variable amounts of microcline, muscovite, and biotite; the amphibolites contain plagioclase, clinozoisite, and hornblende (Kovisars, 1971).

The Mucuchachí Formation consists of metamorphosed marine deposits of late Paleozoic age and is dominated by laminated slates intercalated with beds of quartzite. The slates are carbonaceous and, in part, phyllitic. The metaquartzites are composed of quartz and plagioclase, with muscovite, chlorite, quartz, microcline, and plagioclase in the matrix. The Jurassic La Quinta Formation is dominantly a non-marine sandstone containing quartz, microcline, plagioclase, muscovite, chlorite, and rock fragments — all embedded in a red stained clayey matrix which is locally calcareous.

Topographically, the Venezuelan Andes bear the imprint of a late Tertiary orogenic event that uplifted this mountain range to its present elevation (Giegengack, 1984). Discontinuous central depressions of variable width, enclosed within two parallel sub-ranges, result in a topographic configuration that has been interpreted as a series of grabens (Giegengack and Grauch, 1972) or pull-apart basins (Schubert, 1980). Subsequently, the topography was modified by erosion and glaciation.

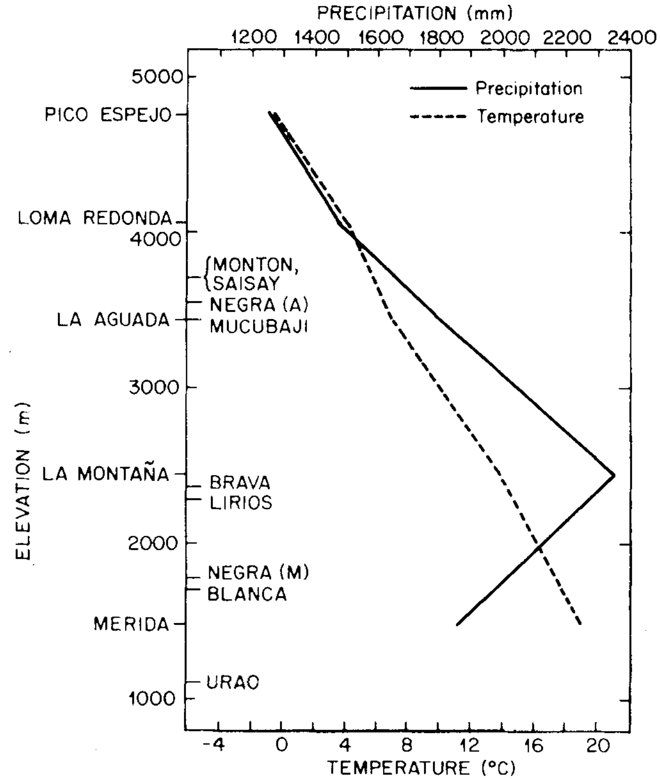


Fig. 2. Variations in temperature and precipitation along an altitudinal NW-SE transect Mérida-Pico Espejo (after Gonzáles-Vivas, 1971). According to Andressen and Ponte (1973), a similar trend persists in a SW-NE direction.

LAKE BASINS AND CLIMATE

The lakes occur at various elevations between 1100 and 3700 meters above sea level. The altitudinal variation of mean annual precipitation (MAP; data for the last 20 years) and mean annual temperature (MAT) are shown in Fig. 2 (Gonzáles Vivas, 1971). Walter (1977) studied the climate of the Venezuelan Andes and defined four altitudinal zones based on temperature: Tierra Helada, Tierra Fría, Tierra Templada, and Tierra Caliente. We have used this altitudinal subdivision of the Venezuelan Andes, as did Lauer (1979), although some researchers consider the "Tierra Helada" an inappropriate zone for the Venezuelan Andes (Schubert, personal communication, 1989). Approximate boundaries for each zone (as used in this paper) are shown in Fig. 3.

Of the nine lakes studied, four are located in the Tierra Helada zone: Montón, Saisay, Mucubají, and Negra (A). Lake Mucubají is confined in a terminal moraine, the other three are cirque lakes. The Tierra Helada zone extends between Pico Bolivar (5007 m) and 3200 meters, with respective MAT's between −1.5°C and 8°C. The Tierra Helada is further subdivided into five zones based on type of vegetation (Lauer, 1979).

Altitudinally, the Tierra Fría extends between 3200 and 2400 meters, with MAT's ranging from 8°C to 13°C. The Tierra Templada zone lies below the Tierra Fría, extends between 2400 and 1000 meters, and has a MAT range of 13°C to 21°C. Lakes Brava (elevation 2380 m) and Los Lirios (2300 m) lie within the Tierra Templada zone but close to the upper limit of the Tierra Fría. Lake Urao (at 1100 m) is considered part of the Tierra Caliente zone (elevations below 1000 m) with a MAT of 25°C, although it lies close to the lowest part of the Tierra Templada zone.

The morphometric data in Table 1, particularly lake area and drainage area, should be regarded as estimates only. Clearly, the high-elevation lakes are deeper than the rest of the lakes due to glacial excavation. The other two parameters — lake area and size of drainage basin — do not exhibit a particular grouping.

SCOPE OF STUDY

Recent studies indicate the existence of a sensitive response of both clay minerals and geochemical properties of sediments to climate-induced changes (Barshad, 1966; Ismail, 1969; Dean and Gorham, 1976; Jones and Bowser, 1978; Kelts, 1978; Singer, 1980, 1984; Bradbury *et al.*, 1981; Lewis and Weibezahn, 1981; Yuretich, 1982). These studies have led to two important conclusions: *(i)* environmental signatures are generally imprinted upon the geochemical and clay mineral properties of sediments while they are still exposed in the catchment area; and *(ii)* in freshwater lake systems, post-depositional modifications of the previously acquired environmental signature are selective and limited.

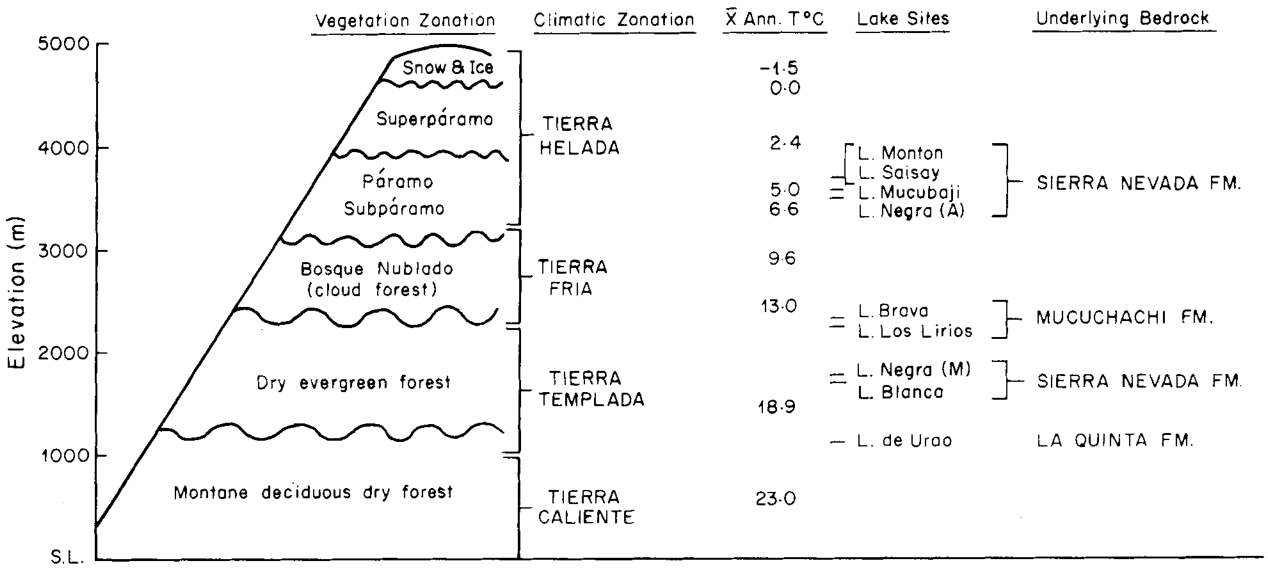


Fig. 3. Schemtic altitudinal cross-section through the Venezuelan Andes displaying the altitudinal distribution of climatic and vegetation zones.

In this study, interbasinal variations in extractable forms of crystalline and amorphous sedimentary iron, as well as clay mineral assemblages, were examined as a function of altitudinal changes in climate in order to gauge the extent to which these two sedimentary iron forms and clay minerals preserve an environmentally induced signature. The observed historical variations in clay mineral abundance within each lake basin are not discussed here because of their limited influence on the outcome of this study.

METHODS

Four sediment cores were collected from each of the nine lakes using a Davis-Doyle piston corer. Water samples were collected from the surface, middle, and bottom of the water column using a Kemmerer water sampler. Four water samples from equally spaced depths were collected in the two deeper lakes, Montón and Saisay.

Field measurements of water temperature, salinity, and electrical conductivity values were obtained using a YSI Model 33 S-C-T meter. Additionally, dissolved oxygen and temperature readings were recorded using a YSI Model 51 B dissolved oxygen meter. A portable digital pH meter was employed to record water pH.

Nine sediment cores, one core from the deepest part of each lake, were subdivided into 5 cm intervals (unless otherwise specified), resulting in a total of 127 samples. All samples were analyzed for organic matter content by loss on ignition (LOI) at 450°C. Organic, amorphous, and crystalline phases of iron and manganese were determined quantitatively. This was done on one sub-sample, rather than the common practice of three sub-samples, using the following sequence of extractions: the pyrophosphate method was employed first, to extract the organically bound iron (McKeague, 1968), followed by the oxalate-extractable amorphous iron (McKeague and Day, 1966); finally, the citrate-bicarbonate-dithionite (CBD) method (Mehra and

Table 1. Morphometric characteristics of the drainage basins.

Lake	Elevation in meters asl	Maximum Depth (m)	Area Drained (ha)	Lake Area (ha)	D/L
Montón	3700	38.1	387.9	20.8	18.6
Saisay	3700	43.5	713.3	23.1	30.9
Mucubají	3540	15.7	1279.7	43.4	29.5
Negra (A)	3460	24.0	330.4	19.1	17.3
Brava	2380	14.6	516.2	38.5	13.4
Lirios	2300	8.7	323.5	20.2	16.0
Negra (M)	1700	3.9	213.7	10.4	20.5
Blanca	1620	4.8	274.2	22.0	12.5

Jackson, 1960) was used to extract crystalline iron oxides.

Clay minerals were determined qualitatively and semi-quantitatively. Qualitative analysis of the clay minerals was performed on the clay-size fraction (<2 μm) of untreated sediment samples which were analyzed on a Siemens X-ray diffractometer using Cu Kα radiation with a Ni filter. Semi-quantitative estimates of clay minerals in a sample were obtained by measuring the area under the (001) reflection. Subsequently, the percentage of the area under each (001) peak was calculated as part of all the (001) peaks measured in each sample.

Water samples were analyzed for major cations (Ca^{++}, Mg^{++}, Na^{+}, K^{+}), anions (NO_3^-, $SO_4^=$, Cl^-), and silica (SiO_2). Cation concentrations were determined by atomic absorption using an IL AA/AE 357 spectrophotometer. The anions NO_3^- and $SO_4^=$ were analyzed on a WESCAN Model 1 A ion chromatograph employing a resin column. Electrode techniques were used to determine Cl^- concentrations, and silica concentrations were achieved employing the Heteropoly-Blue method (Greenberg *et al.*, 1980) with a Bausch and Lomb Spectronic 20 transmittance/absorbance spectrophotometer. Additional measurements included pH and alkalinity using an Orion Research Model 601 A/Digital ion analyzer.

RESULTS

Lake Waters

Mean total dissolved solids (TDS) are given in Table 2. The data show very low and similar mean TDS for the four high-elevation lakes of the Tierra Helada zone. The large differences in TDS among the mid-elevation, Tierra Templada, lakes may be attributed to three principal factors: *(i)* different bedrock underlying the drainage basins — Mucuchachí slates and phyllites in Lakes Brava and Lirios versus the gneissic Sierra Nevada in Lakes Negra-Mariño [Negra (M)] and Blanca; *(ii)* the apparent anthropogenic disturbance which varies from lake to lake (most pronounced in Lake Blanca); and *(iii)* variation of hydrologic factors among the basins — for example, the observed changes in the volume of water in Lakes Brava and Lirios is apparently controlled by strong fluctuations in groundwater level. The processes that control these fluctuations, and their possible influence on lake water chemistry are discussed elsewhere (Ludlam and Weingarten, in preparation).

Estimates of the intensity of chemical weathering can be achieved from concentration ratios of the different cations to Cl^-. The reasons for this are the conservative nature of the Cl^- ion and the fact that the principal source of Cl^- is from the atmosphere rather than from the bedrock itself. The apparent differences in concentration ratios of cations to Cl^- (Table 3) in the high-elevation lakes can be attributed to the variability in the lithology of the Sierra Nevada Formation (Kovisars, 1971). The higher concentration ratios in the four mid-elevation lakes suggest significantly higher chemical weathering rates for the mid-elevation lake basins compared with the high-elevation basins. However, lithologic differences between the two higher and the two lower mid-elevation lake basins [the Mucuchachí Formation in Lakes Brava and Lirios versus the Sierra Nevada Formation in Lakes Negra (M) and Blanca] are not reflected in the concentration ratios. Consequently, water quality may reflect the environmental conditions of the lake basins.

Lake Urao water shows uniform and unusually high salinities throughout the water column. The high silica content is expected because of the high alkalinity (pH >10). The very low Ca^{++}/Cl^- ratio (Table 3) and the high concentration of chloride suggest that Ca^{++} is being preferentially removed through the formation of evaporite minerals (gaylussite is abundant in Lake Urao sediments; Sievers, 1885-1886; Weingarten, 1988). Because of this saline-alkaline water chemistry, post-depositional changes are more likely to occur in the original sediments of Lake Urao than in the other basins.

Lake Sediments

The bottom section of each analyzed sediment core was radiocarbon dated (Table 4) and the dates were used to calculate accumulation rates. Comparisons among lakes are based on average geo-

Table 2. Mean ionic concentrations (ppm) and calculated TDS of the lake waters.

Lake	N	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	SiO_2	Cl^-	$SO_4^=$	TDS
Montón	4	0.9	0.2	0.7	0.2	4.7	1.0	1.1	10.4
Saisay	4	0.6	0.1	0.6	0.2	2.6	0.9	1.2	9.3
Mucubají	3	0.6	0.2	0.7	0.3	4.8	0.9	1.9	11.6
Negra (A)	3	0.9	0.2	0.8	0.4	5.0	0.8	1.6	11.7
Brava	3	1.8	1.2	3.9	2.8	13.4	1.4	4.1	43.2
Lirios	3	1.8	1.5	4.4	5.1	1.5	3.6	8.4	45.6
Negra (M)	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Table 3. Concentration ratios of K^+, Na^+, Mg^{++}, and Ca^{++} to Cl^-.

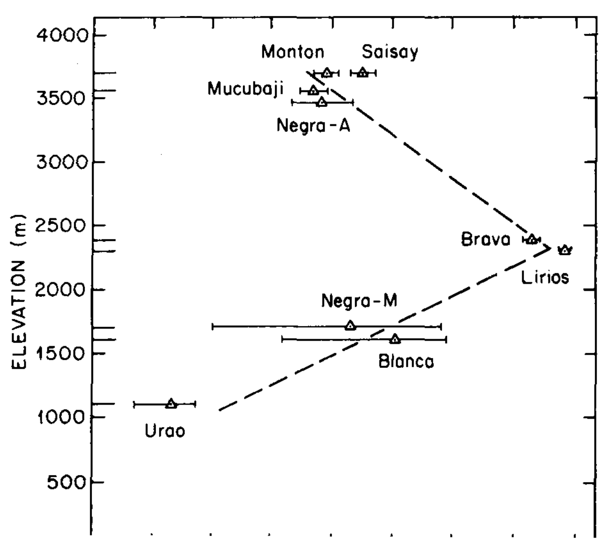
Lake	Elevation (m)	K^+/Cl^-	Na^+/Cl^-	Mg^{++}/Cl^-	Ca^{++}/Cl^-
Montón	3700	0.19	0.59	0.17	0.89
Saisay	3700	0.20	0.61	0.19	0.72
Mucubají	3540	0.38	0.83	0.25	0.64
Negra (A)	3460	0.36	0.92	0.27	1.00
Brava	2380	2.01	2.83	0.89	1.58
Lirios	2300	1.40	1.21	0.42	0.48
Negra (M)	1700	1.18	1.04	0.67	1.41
Blanca	1620	1.67	1.33	0.52	0.98
Urao	1100	0.22	4.58	0.04	0.05

Table 4. ^{14}C dates of the basal portion of the sediment cores.

Lake	Depth (m)	^{14}C YBP	$\delta^{13}C_{PDB}$	Lab ID
Montón	0.89	1595 ± 275	−25.9 ‰	GX-10798
Saisay	0.98	1745 ± 300	−26.5 ‰	GX-10796
Mucubají	0.82	1550 ± 245	−26.7 ‰	GX-10800
Negra (A)	1.01	3165 ± 330	−27.3 ‰	GX-10799
Brava	1.08	2010 ± 180	−29.0 ‰	GX-10795
Lirios	0.57	3395 ± 195	−33.3 ‰	GX-10801
Negra (M)	1.04	1675 ± 190	−30.9 ‰	GX-10794
Blanca	0.52	1035 ± 170	−27.8 ‰	GX-10797
Urao	0.44	990 ± 170	−21.5 ‰	GX-10793

chemical and clay mineral data for the last 1000 years of the sedimentary record from each lake.

Organic Matter. Plots of LOI data suggest that the highest abundance of organic matter is found at about 2400 meters above sea level, diminishing toward lower and higher elevations (Fig. 4). Although the data are too sparse to be certain, an altitudinal trend may be inferred — with a reversal at about 2400 meters.



Iron and Manganese. Analytical data for the three iron extractions show substantial variations in concentration of total iron among the basins (Fig. 5). Because of these variations, we have compared the relative abundance of iron species as a percentage of total iron. Data in Table 5 demonstrate that, except for Lake Negra (A), organically bound iron is the most abundant form in high-elevation lake sediments.

In the Tierra Templada climatic zone, with the exception of Lake Negra (M), lake sediments contain a greater percentage of amorphous than of crystalline iron. The relative abundances of iron species in the sediments of Lakes Negra (M) and Blanca are similar to those found in the Tierra Helada zone, which may be a function of similar bedrock (Sierra Nevada Formation). Crystalline and amorphous iron are the dominant forms in Lake Urao, located in the Tierra Caliente climatic zone (Table 5).

Compared to iron, manganese species in the lake sediments display greater variations in relative abundance (Table 5), due to the greater suscep-

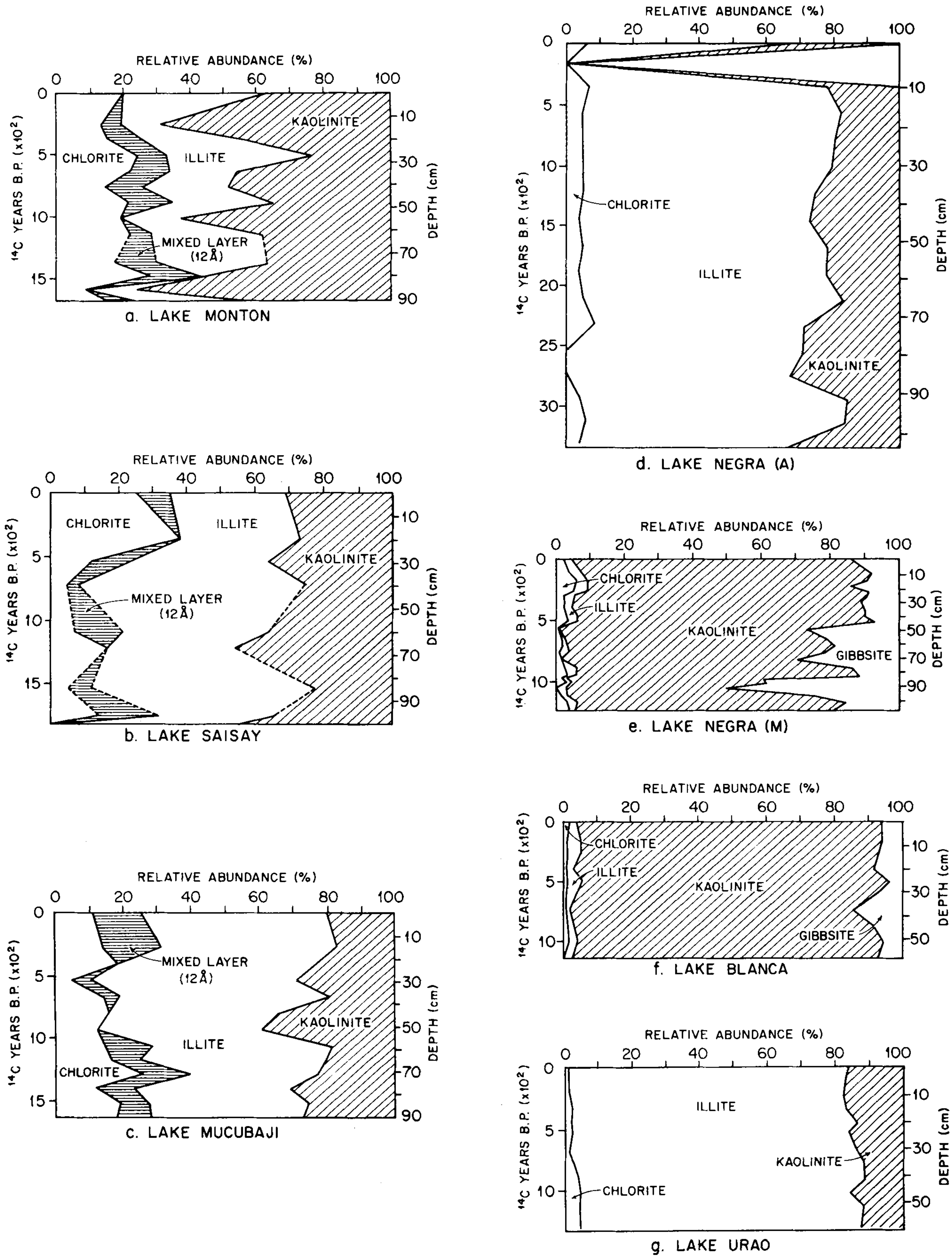


Fig. 6. Abundance trends of clay minerals in sediments from the various lakes: a. Lake Monton; b. Saisay; c. Lake Mucubají;

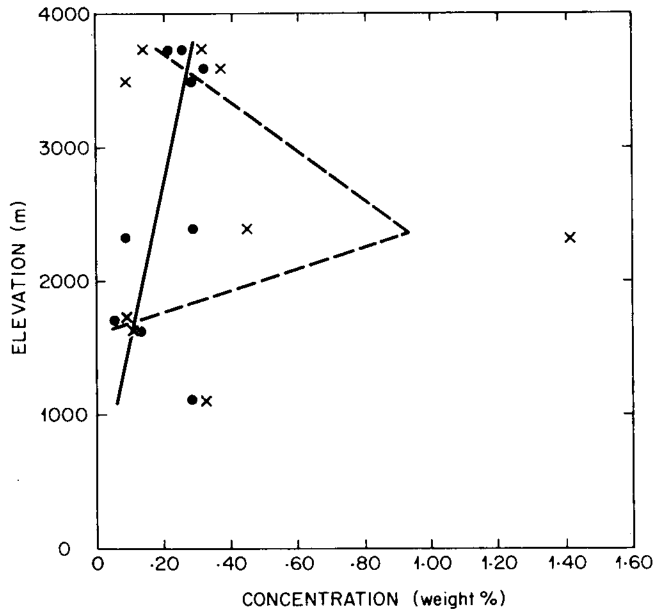


Fig. 5. Changes in concentration (ppm) of crystalline and amorphous iron as a function of elevation. The resulting trends (solid line, cFe; dashed line, aFe) are based on means (cFe, X; aFe, dot) calculated from absolute concentrations. The number of cases used is the same shown in Table 5.

Clay Minerals. X-ray diffraction analysis of the clay fraction (<2 μm) in the sediment cores from the high-elevation lake basins [Montón, Saisay, Mucubají, and Negra (A)] reveals the presence of chlorite, illite, kaolinite, and a mixed-layer clay (Fig. 6). In addition, gypsum was identified in the clay fraction from Lakes Montón and Saisay. The clay fraction of sediments in Lakes Brava and Lirios (mid-elevation basins) is almost entirely amorphous to X-ray diffraction, although highly crystalline gypsum and traces of gibbsite are present occasionally. In the two lower basins of the Tierra Templada climatic zone, Negra (M) and Blanca, kaolinite is the most abundant clay, followed by gibbsite with subordinate illite and degraded chlorite (Fig. 6e,f). Illite is the primary clay mineral in Lake Urao (Fig. 6g).

Mean values of illite crystallinity in sediments from all lake basins (except for Brava and Lirios) follow a similar altitudinal trend, as suggested by the organic matter (Fig. 4; Weingarten *et al.*, 1990).

DISCUSSION

Clay Minerals

Bedrock plays an important role in determining the products of weathering (Barshad, 1966; Loughnan, 1969). The Sierra Nevada Formation that underlies the four high-elevation lake basins is not entirely uniform (the principal composition is gneissic; Shagam, personal communication, 1986), but this variability does not appreciably affect clay mineral assemblages. Clay mineral assemblages in sediments from mid-elevation (Tierra Templada) lake basins underlain by the Sierra Nevada Formation (Lakes Negra (M) and Blanca) also resemble each other but differ from those of the high-elevation lakes as well as from Lakes Brava and Lirios higher in the Tierra Templada. Lack of clay mineral assemblages in the sediments of two higher lakes in the Tierra Templada climatic zone, Lakes Brava and Lirios, may result from a different weathering pattern of the slates and phyllites of the Paleozoic Mucuchachí Formation, which underlie these drainage basins. A different clay mineral assemblage is expected in Lake Urao (Tierra Caliente), which receives most of its sedimentary influx from Jurassic red beds of the La Quinta Formation.

An apparent association between climate and clay minerals was initially recognized in deep sea sediments of the South and North Atlantic Ocean (Biscaye, 1965; Jacobs, 1970). Latitudinal belts of clay minerals were observed on the ocean floor, and the location of these provinces assisted in tracing their provenance back to the continental masses. The close association with climate differences worldwide indicates that there is a climatic signal stored in those sediments inherited from continental environments (Singer, 1984). The application of this relationship between climate and clay mineralogy may also be extended to altitudinal climatic zones because of the close analogy between latitudinal and altitudinal climatic gradients (Lauer, 1979).

Clay mineral analyses of lake sediments from the Tierra Helada climatic zone (analogous to high-latitude cold and dry climates) show similar pat-

Table 5. Mean relative abundances (as percentage of total iron and of total manganese) of the three extracted iron and manganese forms.

Lake	N	Iron			Manganese		
		Organic	Amorphous	Crystalline	Organic	Amorphous	Crystalline
Montón	7	50.3	24.9	24.8	82.7	9.1	9.2
Saisay	6	60.8	16.2	22.0	78.0	9.9	12.1
Mucubají	8	71.6	15.3	13.1	72.3	15.9	11.8
Negra (A)	6	38.6	14.6	46.8	60.9	14.4	24.7
Brava	5	29.1	59.5	11.4	46.3	19.5	34.4
Lirios	3	45.9	45.1	9.0	0.0	40.0	60.0
Negra (M)	19	48.5	21.4	30.1	58.5	17.0	25.5
Blanca	9	56.4	28.3	15.3	83.9	8.5	7.6
Urao	9	18.4	40.5	41.1	15.9	45.8	38.3

terns of abundance and distribution. Illite is the dominant clay mineral, although some exceptions are observed — the most conspicuous being the predominance of kaolinite over illite in sediments of Lake Montón. Bockheim (1982) interpreted the presence of illite and chlorite in the Antarctic soils and sediments as indicators of weak weathering intensities, typical for cold climatic conditions with a predominance of mechanical weathering. The high abundance of illite in the high elevation lakes is in good agreement with these observations.

Chlorite can be interpreted in a similar way to illite, but the presence of degraded-chlorite (d-Ch) requires additional clarification. Degraded-chlorite was identified in the sediments of the two lower lake basins of the Tierra Helada climatic zone — Mucubají and Negra (A). The increasing abundance of d-Ch may indicate a relative increase in weathering intensity (Barshad, 1966) caused by an increase in temperature and precipitation. The total absence of a mixed-layer clay mineral phase from the clay mineral assemblage of Lake Mucubají, and the low abundance of this clay mineral phase in Lake Negra (A), supports such an assumption as abundances of mixed-layer clays often show inverse correlations with weathering intensities (Millot, 1970). However, these changes could be related to variations in the mineralogic composition of the Sierra Nevada Formation (Kovisars, 1971).

The presence of kaolinite in the clay assemblages of these high-elevation lake basins may be anomalous. According to Singer (1984), kaolinite forms and remains highly stable under conditions of increasing hydrolysis. Thus, the presence of kaolinite contradicts the inference of reduced hydrolysis under Tierra Helada climatic conditions. Malagon (1982) discarded the possibility of kaolinite formation in present Tierra Helada soils. Kaolinite in these lake sediments was probably inherited from a paleosol known to be present in other parts of the Venezuelan Andes (Weingarten, 1977). This anomaly does indicate the caution that must be exercised in interpreting climate from clay mineral assemblages.

In the four lake basins in the Tierra Templada climatic zone, X-ray diffraction analysis of the sediments in Lakes Brava and Lirios demonstrates an abundance of gypsum and a faint indication for a possible presence of gibbsite and kaolinite. Gypsum was found to be present in the soil surrounding the lake basin, suggesting that the gypsum in the lake sediments is probably derived from the drainage basin. A lacustrine source is unlikely as calcium and sulfate in the lake water are undersaturated with respect to gypsum.

Clay mineral assemblages are identical in the two lower lake basins, Negra (M) and Blanca, consisting primarily of kaolinite and gibbsite, with minor amounts of degraded chlorite (d-Ch), chlorite, precipitation as compared to the Tierra Helada climatic zone, resulting in intense hydrolysis and chemical weathering.

The high abundance of illite in Lake Urao sediments may be the result of decreased hydrolysis due to the hot and semi-arid climate that prevails in the Urao lake basin. On the other hand, the unusual tectonic setting and unusually alkaline water mass of Urao lake water could lead to post-depositional diagenetic variations that may mask the original sedimentary characteristics (Yuretich, 1983).

Organic Matter

Current studies of organic matter (OM) in sediments tend to concentrate on specific organic components rather than on the more common bulk analysis by LOI (Cranwell, 1984). The reason for this is the strong tie to environmental and climatic factors suggested by certain organic components (Schwertmann *et al.*, 1986). Fractional analyses of organic matter were not available for this study, but preliminary microscopic identification indicated that the organic matter in the lake sediments is predominantly derived from terrestrial vegetation.

In the lake sediments from the Venezuelan Andes, OM trends are complicated. The highest OM concentration is found in lakes at around 2200-2300 meters above sea level, decreasing in both higher and lower elevation lakes (Weingarten, 1988). Rainfall is most abundant between 2000 and 2500 meters (see Fig. 2); so is the density of vegetation, which decreases toward higher and lower elevations. Judging from the apparent high correlation between precipitation (Fig. 2) and LOI (Fig. 4) data, it would appear that rainfall is significantly important in controlling the abundance of organic matter in these lake sediments.

Iron

Iron is transported to lake basins by three general mechanisms: true solution; organic-iron complexes; and oxyhydroxide sols (Stumm and Morgan, 1981). Although groundwater can be occasionally high in dissolved iron, the first process is negligible under most natural settings, and the distribution of iron between the two other phases will depend upon the weathering conditions and vegetative cover. Thus, the type and distribution of iron in lake sediments may have climatic significance.

According to Burns and Nriagu (1976), iron oxyhydroxides are the dominant forms in cold-temperature climatic conditions, as in the glacial lakes of North America. Contrary to these findings, results in this study show that, in the Tierra Helada climatic zone, organically bound iron is the most abundant phase. This discrepancy could be a result of the different sequence of iron extraction employed separate sub-samples. In this study, all three extractions were performed on a single sub-sample. The pyrophosphate extraction (organically bound iron) was performed first, followed by the oxalate extraction (amorphous hydrous iron oxides), and culminating with the citrate-bicarbonate-dithionite extraction (well crystallized iron oxides). Since this sequence begins with the weakest and terminates with the most intense extraction, three exclusive iron phases are separated. Consequently, the CBD (citrate-bicarbonate-dithionite) extraction contains the extracted "crystalline iron" only, while in the common mode of extraction the CBD also includes the "amorphous" and "organic" iron fractions and results are computed by subtraction.

The abundance of organically bound iron in the Tierra Helada lake sediments suggests that the binding of iron by organic matter predominates over the oxidation of the ferrous iron released from the primary silicate phase upon weathering. The principal reason for this is the diminished rate of decomposition of organic matter under cold and humid climatic conditions (Schwertmann *et al.*, 1986), such as those that prevail in the Tierra Helada climatic zone. Consequently, the greater availability of non-decomposed organic matter may enhance complexation and the formation of organically bound iron.

Following the sequence of iron extractions in this study, Zielinski (1987) analyzed sediment cores from three cirque lakes in the Wind River Range of west-central Wyoming. That study area is characterized by a high-alpine, continental climatic setting with estimated mean annual (minimum and maximum) temperatures of approximately $-15°C$ and $-3°C$. His results show that organically bound iron (pyrophosphate extraction) is most abundant, followed by crystalline (citrate-bicarbonate-dithionite) and, finally amorphous, oxalate-extracted iron.

Amorphous iron is the most abundant form in mid-elevation, Tierra Templada lakes. The predominance of amorphous iron at these elevations is probably and primarily due to favorable temperatures and abundant precipitation, and, consequently, enhanced hydrolysis compared to levels of hydrolysis in the higher elevation climatic settings. In a recent study of soils in Hawaii, Parfitt *et al.* (1988) suggested that the abundance of amorphous iron is directly related to rainfall. According to Schwertmann and Fisher (1973), ferrihydrite (amorphous iron) will form by fast hydrolysis of inorganic ferric iron and by oxidation of organically bound ferric iron. The climatic conditions required for these reactions can be inferred from experimental studies by Torrent *et al.* (1982), who showed that ferrihydrate abundance in soils increases with decreasing relative humidity. The climatic and environmental settings suggest that, although precipitation in the Tierra Templada is significantly higher compared to Tierra Helada, the higher temperatures in Tierra

Manganese

The behavior of manganese resembles that of iron except for one significant characteristic — under similar environmental conditions, manganese is more readily dissolved than iron (Mn^{2+} is more susceptible to reduction than Fe^{3+}). In a recent study, Weingarten, (1988) compared the abundances of total iron (the sum of pyrophosphate, oxalate, and CBD extractions) and total manganese in a 17,000-year sedimentary record from Lake Lirios and found a close resemblance between the trends of total iron (TFe) and the TFe/TMn ratio. Consequently, it was suggested that post-depositional reduction and resolution of Fe^{3+} in these lakes is insignificant.

SUMMARY

Sediments in the studied lakes form compositional groups that seem to reflect the climatic conditions at their respective locations. The Tierra Helada zone is characterized by low temperatures and, consequently, a positive precipitation/evaporation ratio. The resultant cold and moist environment sustains strong physical weathering conditions that are reflected in the high abundance of crystalline, CBD-extracted, iron compared to amorphous, oxalate-extracted, iron. The high abundance of organic iron is probably caused by the minimal decomposition of organic complexes under cold climatic conditions.

In the intermediate elevations, Tierra Templada, the relative abundance of amorphous iron is greatest. This is probably caused by an increase in the intensity of chemical weathering, as indicated by water quality data — particularly hydrolysis, which is due to the high annual precipitation and higher temperatures. The high abundance of organic matter at these elevations does not contrast with the relatively low concentrations of organically bound iron because reduced soil moisture conditions (due to high evaporation) will enhance the transformation of organically bound to amorphous iron.

Finally, the semi-arid climatic setting of Lake Urao, within the Tierra Caliente zone, may reduce the hydrolysis of minerals, promoting the formation of crystalline iron. Some of this crystalline iron may be hydrolyzed to amorphous iron in the alkaline lake waters, giving rise to an almost equal abundance of crystalline and amorphous iron.

The types of clay minerals and their relative abundances in the lake sediments are strongly influenced by climatic factors. Illite and chlorite are most abundant in sediments of the high-elevation lakes. The decreasing abundance of chlorite with decreasing elevation is accompanied by a qualitative change within the 14Å-mineral phase, which indicates a relative increase in the abundance of but an increasing portion of the remaining chlorite degrades to a low-crystallinity clay (d-Ch). Despite complications from inherited sources, kaolinite generally increases with decreasing elevations (Weingarten, 1988).

Quantitative variations in the abundance of clay minerals in lake sediments representing the last 1000 years are most probably controlled by variations in climate, bedrock composition, local hydrologic factors (*e.g.*, groundwater fluctuations), and anthropogenic input. However, the distinctive altitudinal grouping of clay mineral assemblages and the observed altitudinal distribution pattern of organic matter and iron species point to the overriding influence of climate.

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