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Early–Mid Pleistocene environments in the Valsequillo Basin, Central Mexico: a reassessment

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ABSTRACT: The Valsequillo Basin in Central Mexico has been of interest due to the presence of megafaunal remains and evidence for early human occupation, but research has been controversial. It has been suggested that extensive and deep lakes characterized the Early Pleistocene environment but sediment exposure is highly fragmentary and reliable dating has been difficult. Here we report, for the first time, Early Pleistocene palaeoenvironmental reconstructions using stable isotopes, diatoms, tephra and pollen. We studied several stratigraphic sections of mainly non-volcanic rocks, containing the 1.3-Ma Xalnene Ash as a stratigraphic marker. The isotope and other proxy data show that topographically low points in the basin were occupied by spring-fed, shallow water lakes during the Early–Mid Pleistocene, with a trend to drier conditions. The basin was a dynamic volcaniclastic environment during this period, with the production of the Toluquilla volcanic sequence and other rhyolitic–dacitic volcanic ashes interbedded with the lake sediments at the sections studied. There is no evidence from the sections for extensive and deep lakes before or after deposition of the Xalnene Ash. Wetter conditions in the basin during the Early Pleistocene would have made it attractive for megafauna.

KEYWORDS: Early–Mid Pleistocene; lakes; Mexico; stable isotopes; volcanic ash.

Introduction

Here we report a palaeoenvironmental reconstruction from rare exposures of Early Pleistocene sediments from the Valsequillo Basin of Central Mexico, using multiple proxies to help identify the depositional environment (stable isotopes, sedimentology, diatoms, tephra and pollen). The stratigraphy of the basin is complex and comprises deposits of sedimentary (lacustrine and fluvial) and volcanic origin. Placing these deposits into a chronological sequence has been hampered by limited dating control. However, the Xalnene Ash marker is evident in sections throughout the basin and recent work (Renne *et al.*, 2005; Mark *et al.*, 2010) assigns this tephra to the period around 1.3 Ma and provides a robust geochronological marker for the sequences investigated in our study.

The Valsequillo Basin (18°55′N, 98°10′W) lies south of Puebla City in the highlands of the Trans-Mexican Volcanic Belt (TMVB) at an elevation of ca. 2000 m a.s.l. (Fig. 1). The area is dominated by the stratovolcanoes Popocatépetl and La Malinche, although there are also several small monogenetic volcanoes in the basin. The basin lies in the central sector of the TMVB, which is a magmatic arc developed by the interaction of the Pacific and North American plates between the Miocene and the present day (Garduño-Monroy *et al.*, 1993; Szynkaruk *et al.*, 2004; Gomez-Tuena *et al.*, 2005). This tectonism has created large volcanoes and basin extensions have resulted in tectonic grabens and depressions within which lakes developed. Since the Pliocene the development of monogenetic magmatism has occurred and there has been infilling of lacustrine basins, along with rapidly changing environmental conditions. The development of such lacustrine basins is relatively well known in the western sector of Mexico, especially during the Late Miocene and Pliocene, for example in the Lerma, Acambay, Guanajuato and Amajac basins (Ferrari *et al.*, 1994; Israde-Alcántara and Garduño-Monroy, 1999; Arellano-Gil *et al.*, 2005; Israde-Alcántara *et al.*, 2010). Large freshwater lakes developed during the Late Miocene in the region to the west, south and north of Lake Chapala along tectonic depressions (Fig. 1), whilst Pleistocene lakes occupied the E–W depressions of Ixtlahuaca and in the region of Acambay, Cuitzeo, Pátzcuaro and Zacapu.

In the Late Miocene the climate in the TMVB region was apparently more humid than today, and the lakes were generally shallow, turbid, alkaline and received both surficial drainage and groundwater inputs. Fluvial deposits that characterize the Pliocene to Pleistocene sequences indicate a reduction of previously existing, large lakes (Israde-Alcántara *et al.*, 2010). In the Valsequillo Basin, however, palaeoenvironmental reconstructions and a chronology for any such lake basins are almost non-existent and current interpretations are based on a detailed, unpublished geological report by Malde (1968) and papers on the diatom flora of selected samples collected by Malde [particularly focusing on those associated with the archaeological site of Hueyatlaco (see below) by VanLandingham (2004, 2006)]. This paper is the first to report on rare exposures of Early to Mid-Pleistocene lake sequences and to use the sediments to interpret the environmental conditions in the basin at this time amid substantial activity from both monogenetic and stratovolcanoes. We test Malde's (1968) hypothesis of the existence of two lake systems above and below the marker Xalnene Ash and provide palaeoenvironmental data for these lakes. Since the 1940s, a reservoir has filled the lower part of the basin (Steen-McIntyre *et al.*, 1981) and our interpretation keeps this restriction in mind.

Stratigraphy of the Valsequillo Basin

Geological mapping by Malde (1968) suggested the presence of thick, but undated, palaeolake deposits both below and

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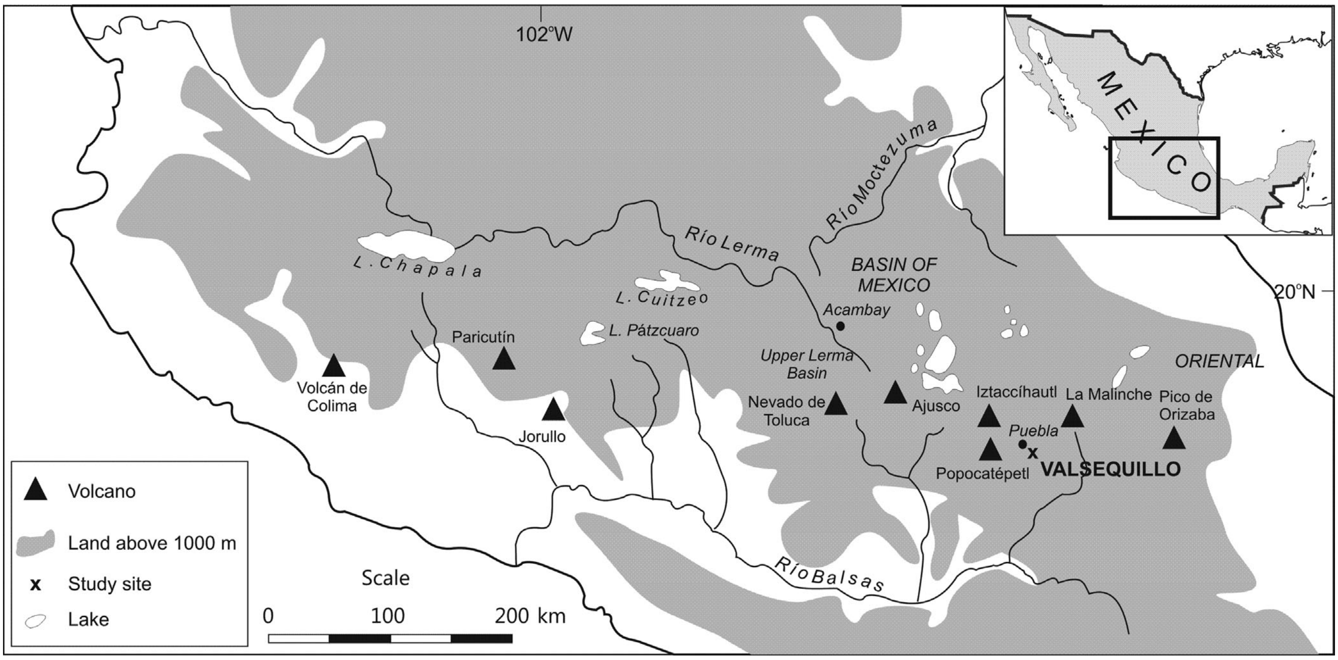

Figure 1. Location of the Valsequillo Basin in Central Mexico, showing major volcanoes and other sites referred to in the text.

above the distinctive Xalnene Ash (tuff) marker. He described a bedrock of folded Cretaceous limestone, overlain by a Tertiary limestone conglomerate with a matrix of red mudstone (Balsas Group). The overlying 'Pleistocene' deposits are around 70 m thick and comprise several major units: the Caulapan Tuff, the Ixcalo lava and the Amomoloc (or lower) lake beds (Fig. 2), which extend from below reservoir level to locations over 100 m higher. They are horizontal and thickest

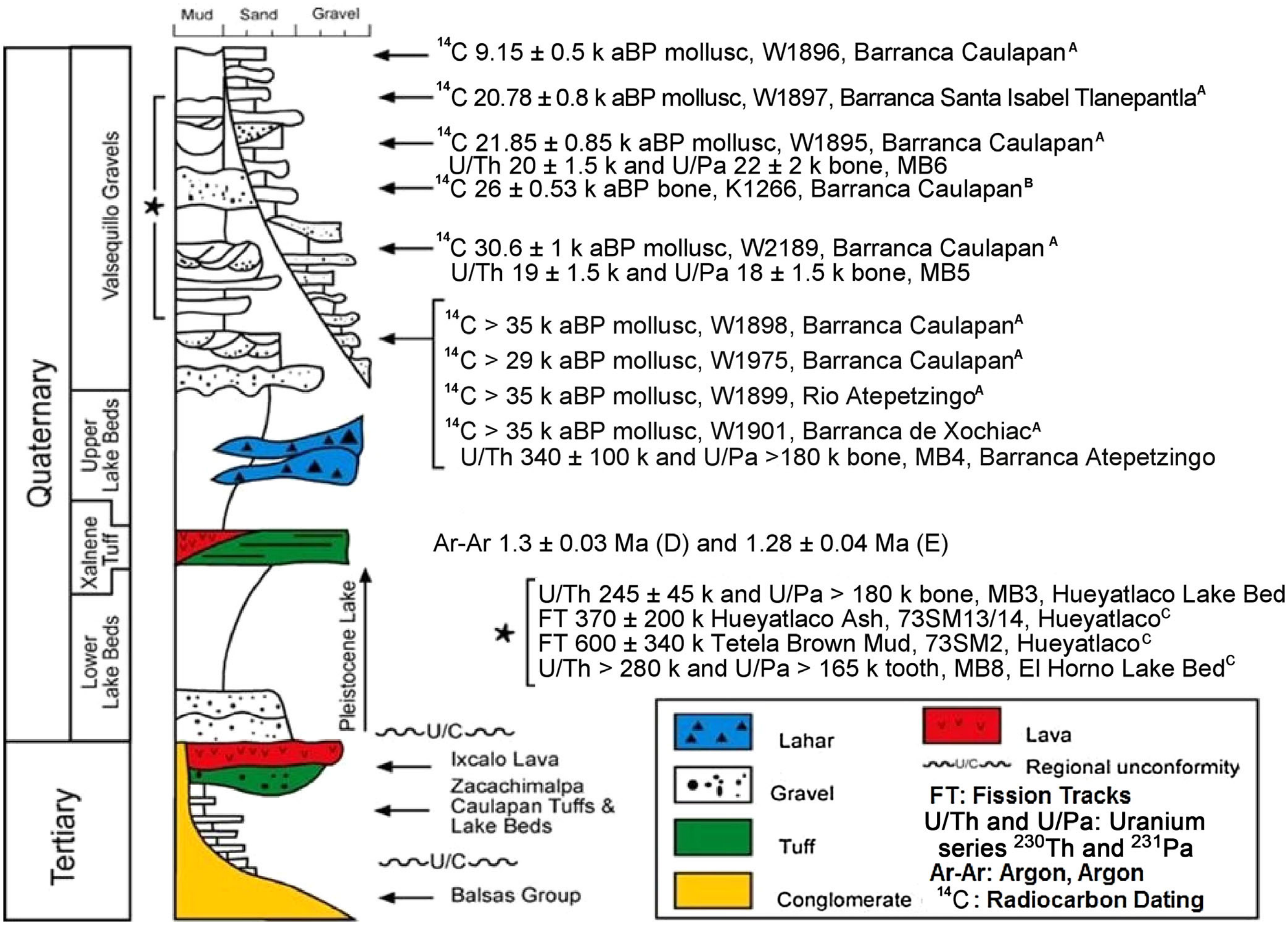

Figure 2. Composite stratigraphic sequence and dating in the Valsequillo Basin after: A, Szabo *et al.* (1969); B, Guenther *et al.* (1973); C, Steen-McIntyre *et al.* (1981); D, Renne *et al.* (2005); and E, Mark *et al.* (2010).

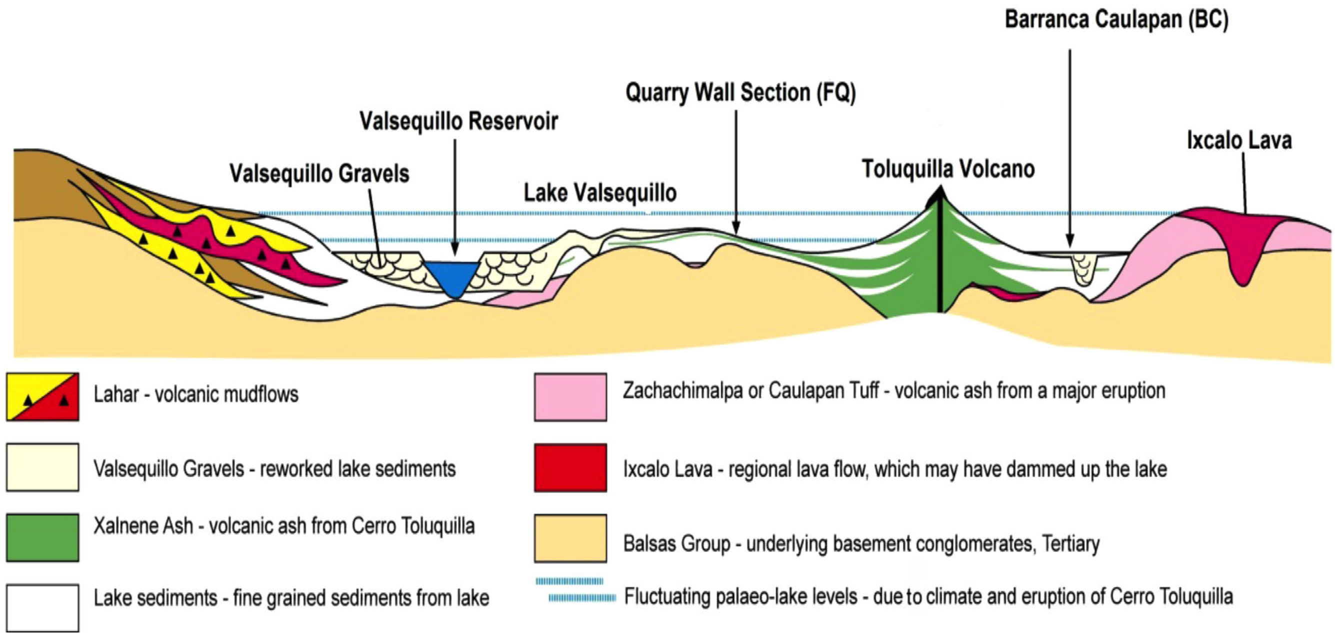

Figure 3. Profile across the Valsequillo Basin showing the main stratigraphic units.

in the lowlands (up to 30 m) but feather out against the uplands. The lower lake beds were described as red–brown, non-indurated clay, silt and fine sand, often with white limestone nodules. Locally these form limestone ledges, which show crenulated laminae that resemble algal structures and some contain *Chara*. There is a contact with the overlying Xalnene Ash as seen at the Barranca Amomoloc where there is 30.5 m of these lake sediments from a base at 2050 m a.s.l. and 17.5 m at Malde's described Section No. 30, near the mouth of the Rio Atepetzingo (see Stratigraphy, Results and Discussion). As they are rich in $CaCO_3$, Malde (1968) thought they indicated a closed basin system. In contrast, the Atoyatenco (or upper) lake beds, which overly the Xalnene Ash, were described as non-calcareous, massive, brown and grey clays, interbedded with silt and sand, up to 36.0 m thick. Malde thought they indicated exterior drainage, although there were locally mudcracks, suggesting a playa, and a white, siliceous volcanic ash up to 1 m thick. The Valsequillo Gravels, with megafauna (e.g. mammoth, ground sloth, horse) and some lithics, interdigitate and are eroded into the Atoyatenco lake beds. Mark *et al.* (2010) published Ar–Ar dates for volcanic materials in the basin, indicating Tertiary ages of 21.7 ± 0.31 Ma for the Caulapan Tuff (a rhyolitic tuff deposited into an extensive lake), approximately 20 Ma for the Ixcalo lava and 2.82 ± 0.6 Ma for the Guadalupe lava, which formed the dam for the Valsequillo Pleistocene lake. Figure 2 shows a composite stratigraphy and a compilation of dating results for the basin. Figure 3 shows a schematic profile across the basin showing simplified geological units.

The Early Pleistocene Xalnene Ash was formed by a small, initially subaqueous, hydromagmatic basaltic eruption (Table 1) from Cerro Toluquilla (Malde, 1968; Gonzalez *et al.*, 2006a), one of several monogenetic volcanoes in the basin (Fig. 3). The initial volcanic eruption was explosive and wholly subaqueous, but subsequently the eruption built a subaerial volcanic cone, overlain by a thin unit of subaerial basaltic lava that crops out on the Toluquilla summit cone. The ash is at least 5.4 m thick close to Cerro Toluquilla, but thins rapidly to 10 cm within 4 km north-west of the vent, although the thickness is controlled by the irregular basin floor topography over which it was deposited, both as subaerial ashfalls and as subaqueous density flows. Outcrops of the highly distinctive Xalnene Ash are seen across the basin and consist predominantly of graded units of coarse lapilli ash (with baked orange sandy-silt angular fragments), interbedded with fine ash, with evidence of cross-bedded, base surge deposits close to the volcano. As described above, the Xalnene Ash horizon divides the apparent lacustrine sediments within the Valsequillo Basin into lower and upper units. Gonzalez *et al.* (2006a) reported the occurrence of what seemed to be both human and animal footprints preserved in the upper layers of the Xalnene Ash, which they estimated to be older than 40 000 a BP using optically stimulated luminescence, electron spin resonance, radiocarbon (^{14}C) dating and stratigraphic position. Subsequent Ar–Ar dating of the ash by Renne *et al.* (2005) and Mark *et al.* (2010) has shown that it is significantly older (1.3 or 1.28 Ma) and the marks found in the ash are now interpreted to be the

Table 1. Geochemical composition (%) of volcanic ashes found in the following sites: site V-25 (Atepezingo river) ash layers B9, B11, B20 and B22; Site FQ: Quarry Wall, Xalnene Ash.

Sample name	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Observations
V-25: (B9)	65.55	0.24	14.38	3.15	0.10	0.25	1.31	2.19	6.31	0.04	Blue-grey clayey dacitic ash
V-25: (B11)	69.20	0.15	12.93	2.65	0.10	0.05	0.88	2.58	6.66	0.01	White silty rhyolitic ash
V-25: (B20)	68.31	0.23	13.80	1.66	0.06	1.95	2.34	2.62	3.34	0.09	Buff clayey dacitic ash
V-25: (B22)	63.85	0.49	14.39	4.88	0.05	3.68	2.38	0.94	1.80	0.04	Olive silty-clay andesitic ash
FQ: (Xalnene Ash)	52.29	1.94	13.86	9.58	0.21	5.39	10.68	3.80	1.04	0.29	Black basaltic lapilli ash

result of recent quarrying activity (Morse *et al.*, 2010). The new Ar–Ar dating of the volcanic ash (Mark *et al.*, 2010) confirms an Early Pleistocene age for the associated mainly non-volcanic, possibly lacustrine sediments in the basin and here we use the Xalnene Ash as an easily identifiable and isochronous tephra marker horizon within many of the Valsequillo basin deposits.

In the Late Pleistocene, the Rio Atoyac and its tributaries incised the basin deposits, and the subsequent valley system was filled by alluvium. The alluvial deposits, known as the Valsequillo Gravels, which are up to 30 m thick in the Barranca Caulapan (Fig. 4), have radiocarbon dates from 9 to 40 ka, suggesting a Late Pleistocene age (Gonzalez *et al.*, 2006a; Stevens *et al.*, 2012). The Valsequillo Gravels contain abundant megafaunal remains, human artefacts (Armenta Camacho, 1959, 1978; Irwin-Williams, 1967, 1978) and molluscs (Gonzalez *et al.*, 2006b; Stevens *et al.*, 2012).

The basin has been an important, but controversial, area regarding the early peopling of the Americas since the discovery in the 1960s of Quaternary vertebrate megafaunal bones in association with stone tools in fine-grained sediments at the Hueyatlaco archaeological site in the Tetela Peninsula (Fig. 4) (e.g. Armenta Camacho, 1959, 1978; Irwin-Williams, 1967, 1978; Pichardo, 1997; Ochoa-Castillo *et al.*, 2003; Gonzalez *et al.*, 2006a,b; Huddart *et al.*, 2008). Based on U-series and fission-track dating methods (Szabo *et al.*, 1969; Steen-McIntyre *et al.*, 1981) a date of last interglacial or older was assigned to these deposits (Fig. 2), which VanLandingham (2004) apparently confirmed based on the presence of Sangamonian age (75–125 ka) diatoms. These ages have been highly disputed and regarded in the past as 'too old' in terms of proving early human presence.

Our re-mapping of the basin deposits confirmed the original geological descriptions by Malde (1968) of large expanses of sedimentary and volcanic deposits, with evidence for extensive reworking, but there remains significant uncertainty regarding the Early Pleistocene basin environment, in particular the nature, extent and timing of lake deposits identified by Malde, who suggested that the basin was occupied by a lake more than 100 m deep. Volcanic activity has been intense and a dominant factor in the development of the basin and there are very few stratigraphic sections where non-volcanic sediments are found. Here we report results from sediment sequences both below and above the Xalnene Ash, which represent the lower (Amomoloc) and upper (Atoyatenco) lake deposits described by Malde (Fig. 2). The study sites include (1) the Atepezingo site (V-25) and (2) the Waterfall site (V-3) that lie below the ash and two others that lie above it, (3) the Tepejilera site (V-28) and (4) the Quarry site (FQ) (Fig. 4). These different relationships to the Xalnene Ash allow these sediment sequences to be put into a stratigraphical and chronological context. We present the results from sites first below and then above the Xalnene Ash and then discuss a general interpretation for the basin palaeoenvironment during the Early–Mid Pleistocene, making comparisons with earlier work. This reconstruction is important as the basin is one of very few in Central Mexico with reliably dated Early–Mid Pleistocene deposits.

Methods

The stratigraphy was described and recorded in the field and sediments sampled for further analysis from the four field sites described above (Fig. 4). These sites were part of a wider study of palaeoenvironments in the basin, which focused on the application of stable isotope analysis, particularly to Late Pleistocene deposits (the Valsequillo gravels) (see above). Stable isotope analysis forms the basis of the records presented here, but is complemented by the use of other methods, which were applied to some or all the study sites. A number of these focused on identifying the possible source of the organic material in the sediments ($\delta^{13}C$, C/N ratios, and lipids), while it was hoped that diatom analysis would provide information about the depth and chemistry of water bodies.

Loss-on-ignition (LOI) analysis was carried out in stages, with weight loss at 550 °C used to calculate the percentage organic matter and the weight loss at 950 °C to calculate CO_3 content (total inorganic carbon, TIC). $\delta^{13}C$ and C/N analyses of organic material were performed by combustion in a Costech Elemental Analyser (EA) online to a VG TripleTrap and Optima dual-inlet mass spectrometer, with

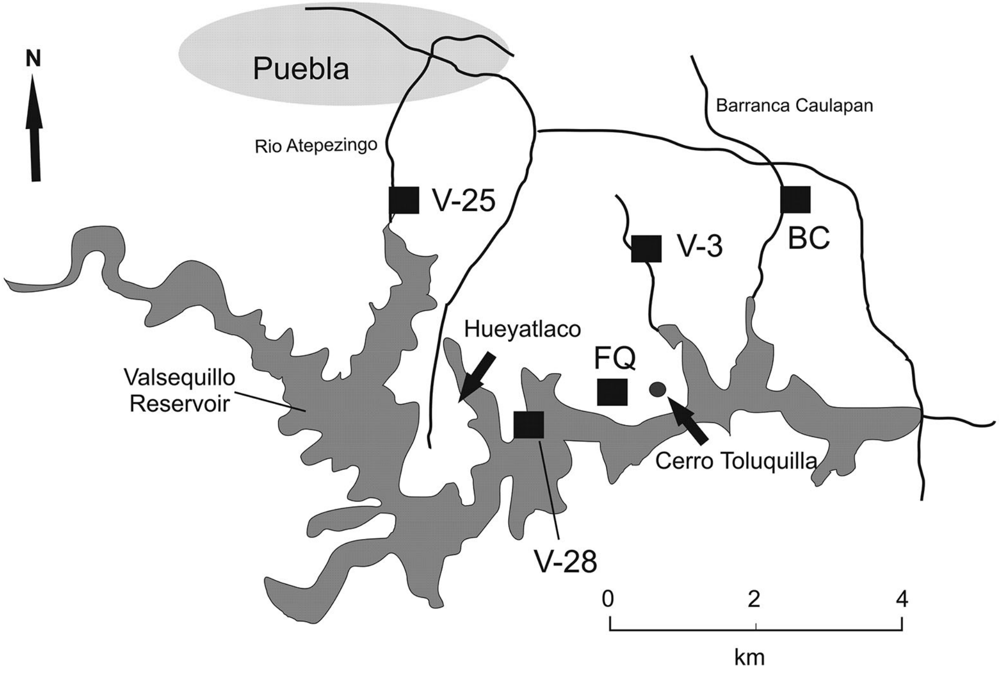

Figure 4. Location of field sites studied for palaeoenvironmental reconstructions in the Valsequillo Basin: Atepezingo River (V-25), Waterfall section (V-3), Tepejilera (V-28) and Quarry Wall site (FQ). The locations of the important Hueyatlaco archaeological site on the Tetela Peninsula and of Barranca Caulapan (BC) are also shown.

$\delta^{13}C$ values calculated to the VPDB scale using a within-run laboratory standard calibrated against NBS-18, NBS-19 and NBS-22. Replicate analysis of well-mixed samples indicated a precision of $\pm <0.1$‰ (1σ). C/N ratios are measured as part of this process and these are calibrated against an acetanilide standard. Replicate analysis of well-mixed samples indicated a precision of $\pm <0.1$. Sedimentary organic matter represents the proportion of organic matter that has not been remineralized, while C/N can be useful to distinguish the provenance of the organic matter as aquatic and land sources tend to have distinct C/N ratios. Organic matter from phytoplankton has low C/N (commonly between 4 and 10) while vascular land plants, which are cellulose-rich and protein poor, have much higher C/N, ≥ 20.

For carbonate $\delta^{13}C$ and $\delta^{18}O$ analysis the sample material was ground in agate and the equivalent of 10 mg of carbonate was reacted with anhydrous phosphoric acid *in vacuo* overnight at a constant temperature of 25 °C. The CO_2 liberated was separated from water vapour under vacuum and collected for analysis. Measurements were made on a VG Optima mass spectrometer. Overall analytical reproducibility for these samples is normally better than 0.2‰ for $\delta^{13}C$ and $\delta^{18}O$ (2σ). Isotope values ($\delta^{13}C$, $\delta^{18}O$) are reported as per mil (‰) deviations of the isotopic ratios ($^{13}C/^{12}C$, $^{18}O/^{16}O$) calculated to the VPDB scale using a within-run laboratory standard calibrated against NBS standards.

Total lipids were extracted from selected 50 g sediment samples. The distribution of carbon number (nC) can be used to indicate the source of the organic molecules. The terrestrial/aquatic ratio (TAR) is defined as the sum of nC_{27}, nC_{29} and nC_{31} divided by the sum of nC_{15}, nC_{17} and nC_{19}, and this is used to infer whether the organic matter from lake sediments is of terrestrial or aquatic origin (Filley *et al.*, 2001; Meyers, 2003). The TAR proxy is based upon two end members, namely aquatic flora (TAR = 0.4), such as algae, which are dominated by odd numbered n-alkanes centred at $\sim nC_{17}$, or solvent-extractable land plant components (TAR = 6), such as epicuticular leaf waxes, which are centred at $\sim nC_{31}$ (Meyers, 2003). However, the contribution of land plants may be amplified in some sediments due to the preferential microbial decomposition of lower molecular-weight n-alkanes (nC_{15}, nC_{17} and nC_{19}) and because terrestrial plants produce proportionately greater concentrations of n-alkanes than algae (Meyers, 2003). Another ratio, P_{aq} ($= n\text{-}C_{23} + n\text{-}C_{25}/(n\text{-}C_{23} + n\text{-}C_{25} + nC_{29} + n\text{-}C_{31})$), can also be used to differentiate the contribution from emergent and submerged plants to lacustrine organic matter. Ficken *et al.* (2000) reported ranges for submerged/floating aquatic plants (0.48–0.94), emergent plants (0.07–0.61) and terrestrial plants (0.01–0.23).

Pollen was extracted from only one sample obtained from a block of Xalnene Ash, which was dissolved in acid, with visible lath-like organic traces from the contact with the lower Amomoloc sediments from the Waterfall section (V-3; Fig. 4).

Diatom samples were prepared using standard methods to remove carbonate and organic matter (Battarbee, 1986) from each major stratigraphic unit at all sites except Tepejilera (V-28). Due to the scarcity of diatoms, merely the presence/absence of dominant taxa were recorded in most cases. Partial counts were obtained from the Atepezingo site (V25).

Selected tephra (volcanic ash) samples from the Atepezingo river site (V-25) and the Quarry site (FQ) were analysed for major element geochemistry of the volcanic glass component (Table 1). The samples were analysed at the NERC Electron Microprobe Unit, University of Edinburgh, UK, using a Cameca SX100 Electron Probe Microanalyser. Samples were impregnated in Araldite on microscope slides; sample surfaces were polished with 6 and 1 μm diamond paste and then cleaned in an ultrasonic bath for 40 min with deionized water. The slide samples were carbon-coated and analysed using the wavelength dispersive method, with an acceleration voltage of 15 kV, a beam size of 5–8 μm and a beam current of 2 nA. Homogeneous Lipari glass and an andradite (garnet) were analysed at regular intervals every 30–40 analyses, as a quality check and to establish the probe stability. Oxide totals above 95% were normally achieved.

Stratigraphy, results and discussion

Rio Atepezingo site (V-25)

The Rio Atepezingo valley section exposes an 8 m section of 23 beds (B1–B23) of soft calcareous silty clays and siltstones, and silty limestones, including four volcanic ash layers (Fig. 5). The Xalnene Ash lies immediately above the section. The beds range from a few centimetres thick to a maximum of 1.6 m, and most have sharp or loaded bases suggesting they were deposited as individual units. Several of the beds in the lower part of the section have traces of organic material, showing tubular structures and irregular laminae giving the impression of algal structures. Two distinct blue/grey tephra layers occur in the upper part of the section (samples B9 and B11). These tephras (15 and 30 cm thick, respectively) have sharp or loaded bases, contain fine (<0.5 mm) white laminae and the overlying sediments contain load structures and rip-up clasts from the tephra. These features are consistent with deposition in an aqueous, low-energy environment. Geochemical analysis of the two tephra layers indicates: (i) tephra B9 has $SiO_2 = 65.5\%$, indicating dacitic composition, and (ii) tephra B11 has $SiO_2 = 69.2\%$, indicating rhyolitic composition (Table 1). After geochemical and diatom analysis of the section, two additional freshwater limestone layers with significant tephra contributions were identified towards the base of the section (but not evident in the field). These are layer B20 ($SiO_2 = 68.3\%$, dacitic, 200 cm thick) and layer B22 ($SiO_2 = 63.8\%$, andesitic, 60 cm thick). Thin sections of the limestones show that they contain abundant, volcanogenic, silt-sized grains. Bulk samples were collected from each of the 23 beds (B1–B23) from the upper limestone exposed in the top of the outcrop (B1) to the protruding stromatolitic limestone exposed in the stream (B23) (Fig. 5a). No calcareous fossils were observed.

Based on the correlation of the TIC and the isotope data the section has been divided into four zones (Fig. 6, right side scale), which are referred to when describing the isotope and diatom data below. Zone 1 is essentially defined by the large $\delta^{13}C_{organic}$ excursion to some of the lowest values in the section (around −25‰) and corresponds to a decrease in TIC within freshwater limestones with a significant tephra component (see above). Zone 2 is more stable, although $\delta^{13}C_{organic}$ swings to a lower value at the upper boundary. Zone 3 includes two tephra layers (B9 and B11) separated by one sandy carbonate layer. Zone 4 shows a decrease in $\delta^{13}C_{organic}$ and $\delta^{18}O_{carbonate.}$ Below we present the geochemical data from the Atepezingo section, which is then compared with the (incomplete) diatom record from this site.

LOI analysis at 550 °C shows an average organic content of 6%, while the C/N ratio of all the samples is about 6 (Fig. 6). Even in the significant tephra layers (B9 and B11) LOI reaches 5.4%. In the Atepezingo section the consistently low C/N (6 ± 2) suggests algae-derived organic matter, which is

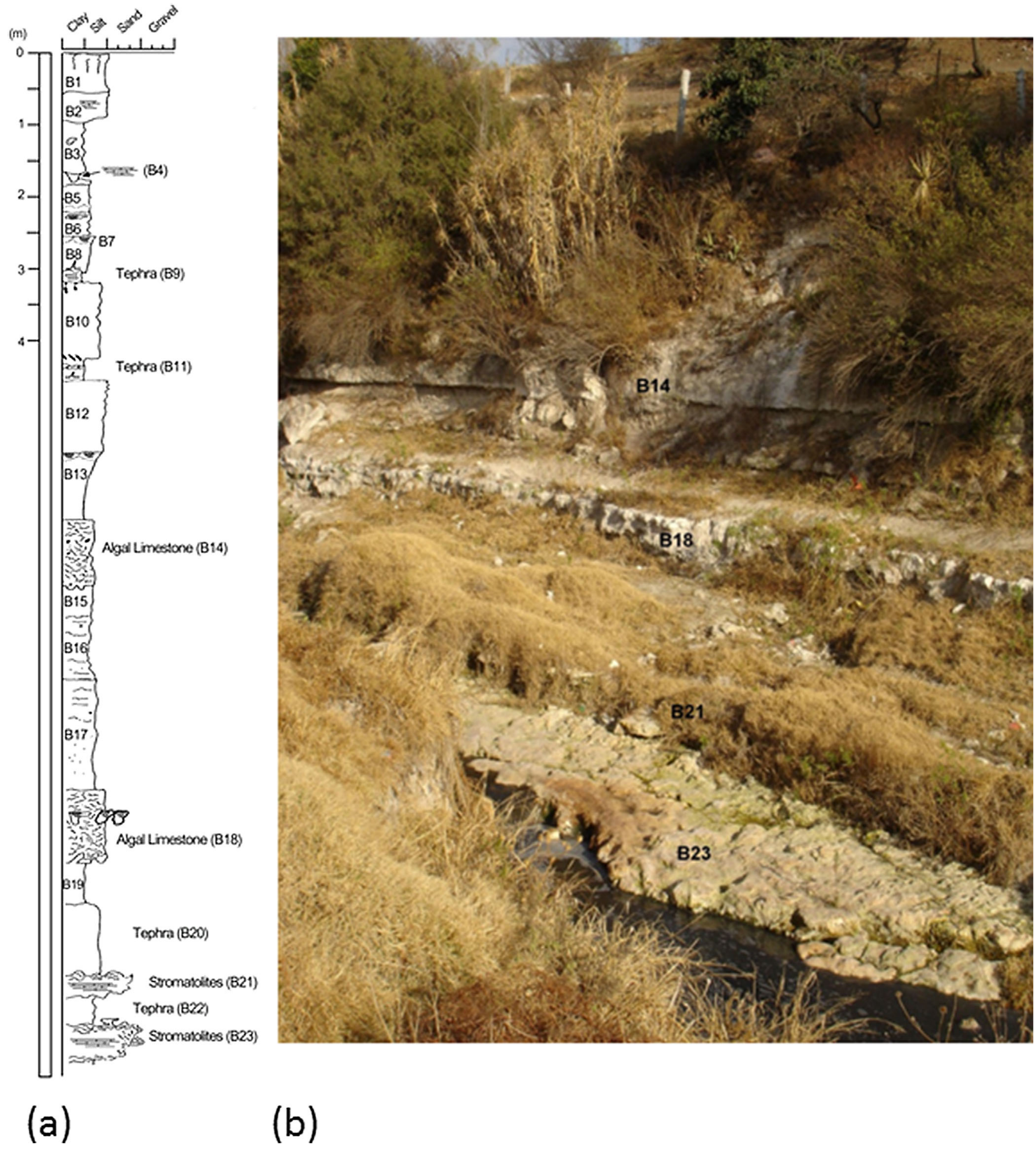

Figure 5. (a) Stratigraphy of the Rio Atepezingo site (V-25) showing the position of the main freshwater limestones, stromatolites and tephras. (b) Photograph of the Atepezingo site, showing the position of some of the hard freshwater limestone layers.

consistent with the algal structures seen towards the base of the section within the stromatolitic limestones (Fig. 5a).

Based on TIC the Rio Atepezingo sediments have variable carbonate content, ranging from 0% in the tephras to 45% in the limestones. Within the limestones it seems most likely that carbonate was precipitated *in situ*, although no biogenic components were observed.

The carbon isotope composition of the organic matter ($\delta^{13}C_{organic}$) has an average value of $-22.3 \pm 2‰$ through the section. Based on Meyers and Teranes' (2001) limit values of $\delta^{13}C_{organic}$ for freshwater algae (-25 to $-30‰$), this value is not typical of freshwater lacustrine algae (as suggested by C/N), but there are multiple controls on the carbon isotope composition of organic matter. $\delta^{13}C$ from lacustrine organic matter acts as a tracer for past changes in the aquatic carbon cycle if C/N shows that terrestrial inwash of organic material is limited, as here. On this basis, we use $\delta^{13}C_{organic}$ to provide information on within-lake processes assuming limited post-depositional changes. Lacustrine plants utilize dissolved CO_2 and HCO_3^-; variations in the isotope composition of this dissolved CO_2 and HCO_3^- are due to many factors, but of particular note are changes in the $\delta^{13}C$ of the C supplying the

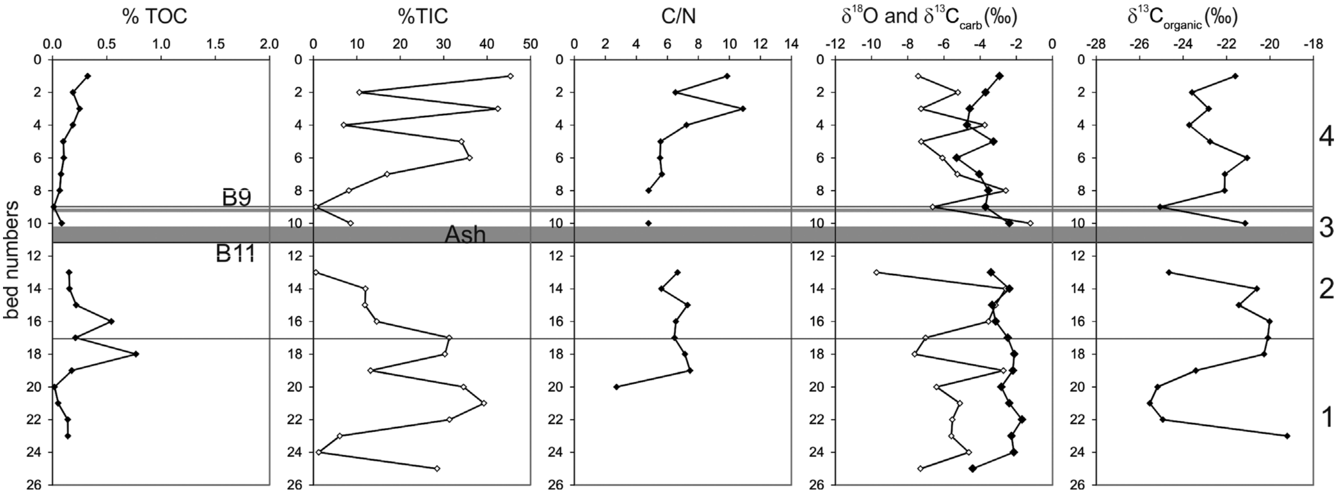

Figure 6. Geochemistry of the Rio Atepezingo site (V-25): %TOC (LOI at 550 °C), % TIC, C/N (grey circles), δ^{18}O and δ^{13}C (‰, open and closed symbols, respectively), and $\delta^{13}C_{organic}$ (‰). Two very distinctive tephras are marked at B9 and B11; two other layers with significant tephra contributions at B20 and B22 are not marked as they were not obvious in the field.

organic matter and changes in $\delta^{13}C_{organic}$ related to productivity and nutrient supply. Because we have also measured the $\delta^{13}C_{carbonate}$ from the inorganic carbon, and the value changes from bed to bed, we know that there were changes in the total dissolved inorganic carbon (TDIC) from which the limestones and calcareous (TIC) sediments were precipitated (see discussion in McKenzie, 1985; Talbot, 1990; Leng and Marshall, 2004). The TDIC pool would also have been utilized by plants. The organic material from each of the beds sampled at Rio Atepezingo has an average $\delta^{13}C_{organic}$ 19‰ lower than the $\delta^{13}C_{carbonate}$, and similar variations have been seen elsewhere between phytoplankton and TDIC (average δ^{13}C 20‰ lower) (Meyers and Teranes, 2001). This suggests that changes in TDIC largely control the observed variation in the $\delta^{13}C_{organic}$ of the organic material and that there was little influx of terrestrial organic matter, as indicated by C/N data.

Bicarbonate ions are derived from the interaction of groundwater with rocks and soils in the catchment, and these ions are the basis of calcareous deposits such as those found in the Rio Atepezingo section. Changes in the supply of carbon into the lakes may be important, especially in volcanically active environments such as Valsequillo with ready access to geologically old marine carbon from the underlying calcareous Cretaceous bedrock. For example, incorporation of carbon into lake water via spring water that has interacted with the Cretaceous conglomerates (mean pebble $\delta^{13}C_{carbonate} = -1.4$‰, $n = 6$) will result in a ^{13}C-enriched TDIC reservoir. Where soils develop in the catchment there will be also be a supply of ^{13}C-poor CO_2 to the groundwater; in soils developed from predominantly C_3 plants, the respired CO_2 will precipitate δ^{13}C with values typically −11 to −8‰ (Andrews, 2006), although these values are higher where C_4 vegetation is more common. This process of differing supplies of ^{13}C into a lake's carbon budget also occurred in northern Sweden whereby soil development led to decreasing δ^{13}C in the carbonates (Hammarlund *et al.*, 1997). In the Atepezingo section there is a general lowering of $\delta^{13}C_{carbonate}$ (especially between the base and Zone 4) and $\delta^{13}C_{organic}$ (notably between Zones 2 and 4) up through the section (Fig. 6), perhaps suggesting progressive soil development, apart from Zone 1 (beds B22-19). In Zone 1 there is $\delta^{13}C_{organic}$ variation that is independent of $\delta^{13}C_{carbonate}$. The low $\delta^{13}C_{organic}$ values of the sequence suggest inclusion of different types of plant material (but likely to be algal material as suggested by C/N) although undifferentiated (by the means we used here) from the organic material higher in the section. Other differences are evident: δ^{13}C values are higher overall in beds B22–19, %N (not shown) was below detection in two of the lower beds, while one measurement (bed B20 tephra) has the lowest C/N of 2.7 (although bed B19 has C/N similar to the rest of the section).

Palaeoclimatic information can be extracted from the oxygen isotope composition of freshwater carbonates. The composition of the carbonate can be used to infer changes in either temperature or the oxygen isotopic composition of lake water, although the latter can be affected by a change in a lake's hydrology or in the climate (precipitation − evaporation) (Leng and Marshall, 2004). Assuming an open lake with inflows and outflows and limited evaporation, and that the carbonate formed in isotopic equilibrium, then equations can be used to estimate palaeotemperatures, if there is no concurrent change in the oxygen isotope composition of the lake water. The interpretation of oxygen isotope compositions in practice, however, is complicated because both temperatures and water oxygen isotope composition can be affected by changes in climate. In the Rio Atepezingo section the large variation we see in $\delta^{18}O_{carbonate}$ (Fig. 6) suggests that evaporation was the dominant effect on the water oxygen isotope composition because the amount of variation (−7.6 to −1.2‰ Zone 3) is too large to be a function of temperature (a temperature change of 26 °C would be needed to achieve this magnitude of change) (Leng and Marshall, 2004). Assuming groundwater (similar in composition to the present day, −7.7 to −8‰) was the major water filling the lake when the sediments at Rio Atepezingo were formed, then we would expect carbonates precipitating from this water to have $\delta^{18}O_{carbonate}$ in the range −8 to −10‰ (which would cover an average annual temperature range of +15 to +25 °C). All the beds at Rio Atepezingo have $\delta^{18}O_{carbonate}$ higher than this (mainly in the range −8 to −4‰), with values reaching −1.2‰. If we therefore conclude that evaporation was the major influence on the isotope composition of the Early Pleistocene palaeo-Lake Valsequillo (through evaporative concentration), then the large swings in composition indicate changes in lake level/area, as well as the degree of openness of the lake.

In sediments from hydrologically closed lakes, the simplest interpretation is that the highest levels/largest lakes occur

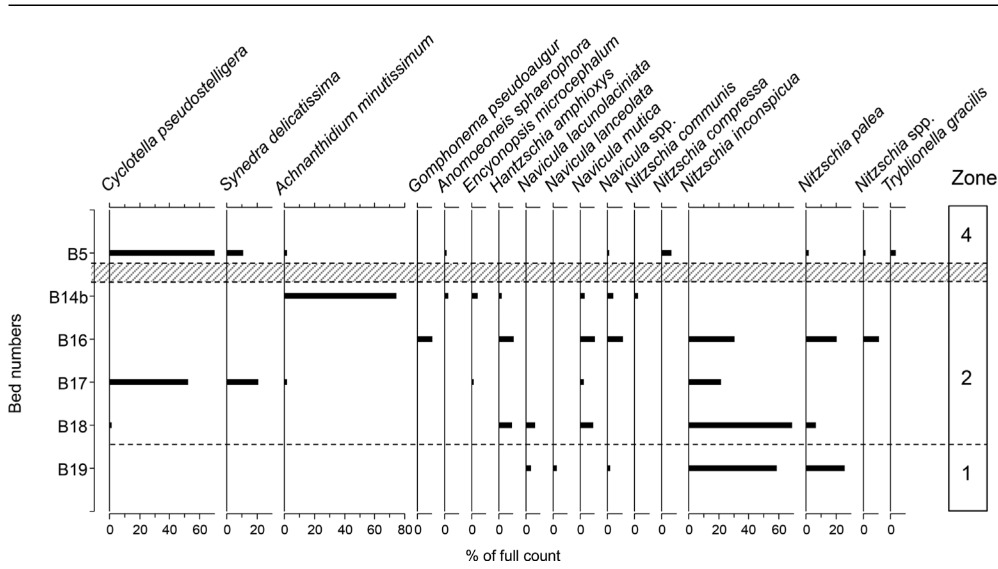

Figure 7. Percentage diatom diagram for the Rio Atepezingo site (V-25) for beds with sufficient valves to permit a count ($n > 300$, except B16). Grey shading indicates part of section with no diatom preservation.

during wet periods and are effectively open systems, and produce low $\delta^{18}O_{carbonate}$ (more negative). The low levels/smallest lakes form during dry periods when the lakes become closed and the $\delta^{18}O_{carbonate}$ is high. However, given that volcanic activity may have changed the morphology of the Valsequillo Basin at various times, there may also be complications due to changing hydrology and lake surface area and depth. The values of $\delta^{18}O_{carbonate}$ are, however, most stable in the lower beds (Zone 1), interestingly coincident with the large spike in $\delta^{13}C_{organic}$ to most negative values, perhaps representing a period of relative stability within a larger lake. Co-variation between these two parameters is common in long-lived, stable lakes (e.g. Talbot, 1990), but overall here there is no statistical relationship between $\delta^{18}O_{carbonate}$ and $\delta^{13}C_{carbonate}$.

Diatoms are widely used as indicators of water balance, and chemical change in lakes and in closed-basin lakes would be expected to show similar changes to $\delta^{18}O_{carbonate}$. Unfortunately, diatoms were only preserved in some samples from this sequence. The lower part of the Atepezingo section shows variable diatom preservation (no diatoms were found in B20, one of the tephra layers) and full counts (>300 valves) were only possible for a few levels (Fig. 7). Species of *Nitzschia* are most common towards the base of the section, with a transition to flora more typical of open freshwater (*Cyclotella pseudostelligera*, *Synedra* spp., presence of Mallamonas scales) at the base of Zone 2. The apparent deepening of the lake at this site is coincident with higher $\delta^{13}C_{organic}$ values (Zone 1 to Zone 2), but not with the higher $\delta^{18}O_{carbonate}$ near the base of Zone 2. Fewer valves are preserved in the upper part of Zone 2, but those present indicate generally shallower conditions with increased aquatic vegetation (e.g. *Achnanthidium* spp., *Gomphonema* spp., *Hantzschia* spp., *Cocconeis*). These samples are notable for the presence of more organic material and less mineral matter than most in this section. Diatoms are very sparse, or absent, from the tephra layer, B11, and just above it (Zone 3) and from the upper tephra layer, B9. Above the tephras (Zone 4) the diatoms indicate a transition from very shallow water (benthic and aerophilous taxa) towards an open water flora in B5 quite similar to that in B17 (Fig. 7). *Cyclotella psuedostelligera* and long thin *Synedra delicatissima* were most common. This shift in flora is consistent with the trend to lower $\delta^{18}O_{carbonate}$ recorded through Zone 4. B5 was, however, also marked by an unusual mix of diatom types and some reworking cannot be discounted. The diatoms from the uppermost samples (excluding B1) indicate a general shallowing, with distinctly more alkaline conditions indicated in B2 (*Anomoeoneis* spp., *N. cuspidata*).

The variable Rio Atepezingo data suggest a lake that was in a hydrological state of flux with periods of evaporation and periods of freshwater; the amount of variability and the lack of steady state conditions could have been due to volcanic activity within the basin, which could have changed the lake's level and hydrology. The presence of tephras indicates distal ash deposition in water from either La Malinche or Popocatépetl volcanoes but these tephras are the first known of Early Pleistocene age from this basin and it cannot be certain which stratovolcano was responsible for the tephra component. Overall, the change in $\delta^{18}O$ between the beds from low to high values and the diatom assemblages suggest that the Rio Atepezingo sediments were deposited in a rapidly changing lake that was probably at times heavily influenced by spring water and at other times became much shallower due to evaporation and lower groundwater recharge rates. The carbon isotopes indicate that soils developed through this time span and had an increasing influence on the carbon isotope composition, although this must at times have been offset by changes due to evaporation.

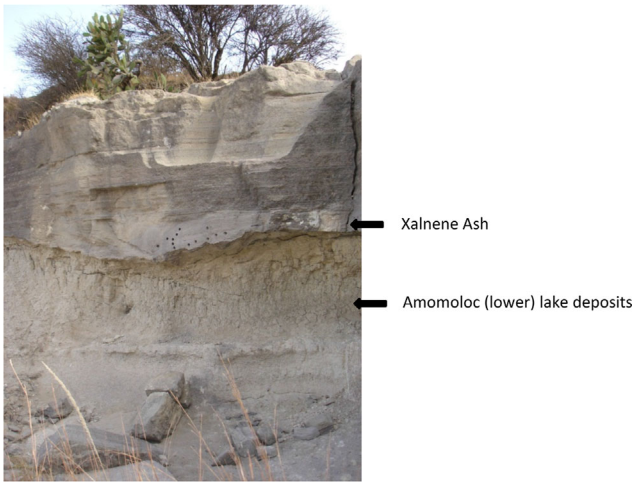

Figure 8. Photograph of the Waterfall site (V3) showing the Xalnene Ash at the top and the Amomoloc sediments below. The Xalnene Ash is the top part of the section above the marked overhanging ledge.

Our stratigraphy from the Rio Atepezingo is consistent with that reported by Malde (1968), including the presence of tephra layers below the Xalnene Ash and the presence of distinct 'hard ledges', here identified as algal limestones and stromatolites (Fig. 5). Isotopic and C/N data indicate a system dominated by algal organic matter, with periods of enhanced evaporation. The limited diatom data indicate a fairly shallow, generally freshwater lake, but again with some periods of greater evaporation.

The Waterfall site (V-3)

The base of the Xalnene Ash is well exposed at this site forming a prominent ledge (Fig. 8). A bulk sample was taken for organic analysis from the base of the ash at the contact with the Amomoloc (lower) lake sediments, as small flakes of lignin (up to a few millimetres in length) were seen on bedding surfaces indicating organic content. In the ash, organic content is low (0.1‰) and comprises mostly amorphous dark patches in thin section and rare pollen grains. The straight chain alkanes (n-alkane) from the organic material obtained are presented in Fig. 9(a). The nC is dominated by high numbers (nC_{25}, nC_{27}, nC_{29} and nC_{31}) typical of land plants, but with a secondary peak at nC_{17}, typical of aquatic organic material. This mixture of sources is confirmed by the presence of a few shallow-water diatoms (e.g. *Hantzschia* sp.) from just below the ash and very occasional valves in the sediments extending more than 1.5 m below the ash. The TAR value indicates that terrestrial organic material forms a component of the organic content even though $\delta^{13}C_{organic}$ and C/N suggest that it is dominated by aquatic organic material. nC values have also been used to distinguish between aquatic plants and emergent/subaerial and terrestrial plants. The Xalnene Ash organic material has a P_{aq} value of 0.3–0.4 suggesting that the n-alkanes were derived from macrophyte sources.

Overall these data suggest that the volcanic ash at the Waterfall site was deposited in pools of shallow water or that the water table was sufficiently high to enable pools to form in depressions on the surface. There is little evidence to support the identification of the sediments below the Xalnene Ash at this site as true deep lake sediments, because they are mainly fine sands and gravels that pass down into silts, although they have been described as part of the lower (Amomoloc) lake beds according to Malde's (1968) map. There is only ash on top of the Xalnene Ash at this location (Fig. 8).

Pollen analysis of a bulk sample of Xalnene Ash, taken at the contact with the underlying sediments, showed low pollen concentration and poor preservation. However, the fact that pollen was preserved at all within the ash indicates a low depositional temperature of the ash at this site. The pollen spectra (Table 2) are dominated by arboreal pollen, in particular pine and to a lesser extent oak and alder. The presence of these types of pollen suggests the regional presence of pine–oak forests, which were the characteristic vegetation community of large areas of upland Mexico throughout much of the late Quaternary (e.g. Clisby and Sears, 1955; Watts and Bradbury, 1982; Lozano-García and Vázquez-Selem, 2005) and remain in the less disturbed parts

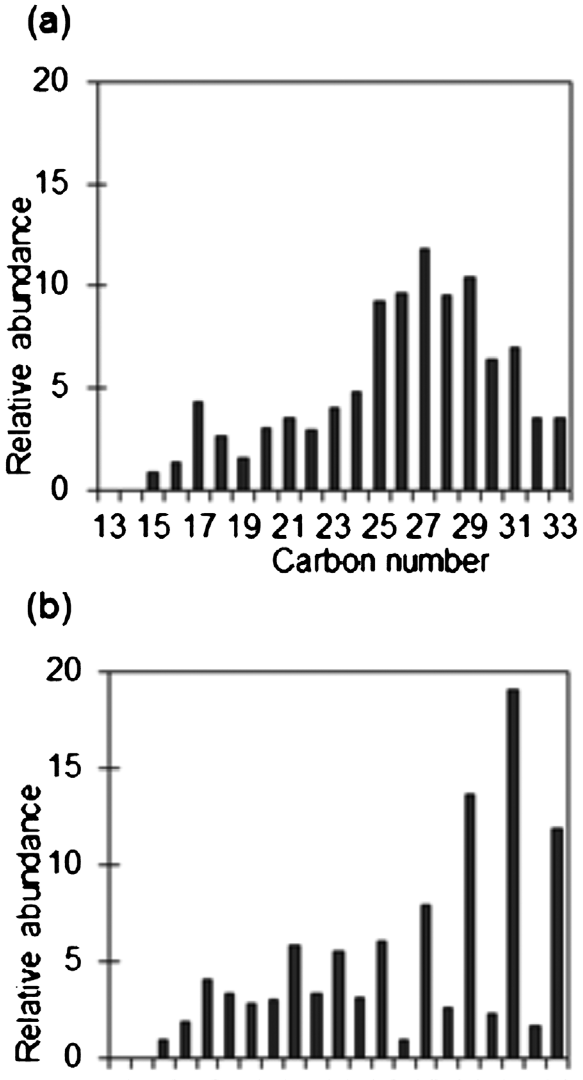

Figure 9. Organic geochemistry spectra of organic material (n-alkanes) from: (a) organic material obtained from the base of the Xalnene Ash at the Waterfall Site (V-3) and (b) sediment sample taken 85 cm above the Xalnene Ash at the Quarry Wall site (FQ).

Table 2. Pollen types identified from a dissolved sample of Xalnene Ash, taken at the contact with the Amomoloc lower sediments at the Waterfall section (V-3).

Pollen type	Raw count
Arboreal pollen	
Pinus	57
Quercus	13
Alnus	8
Picea	1
Tilia	2
Tsuga?	1
Betula?	1
Non-arboreal pollen	
Poaceae	8
Cyperaceae	4
Asteraceae/Ambrosia	2
Chenopodiaceae/Amaranthaceae	3
Aquatics/spores	
Isoetes	1
Trilete fern	3
Pre-Quaternary palynomorph	1
Others	
Unid-unknown type 1	4
Unid-unknown type 2	1
Unid-corroded/broken	35

of the Valsequillo Basin today. Pollen from pine, in particular, is often over-represented in fossil sequences because it is produced in abundance, wind dispersed from a canopy, robust and better preserved than other types, and is consequently more readily recognized in poorly preserved samples. Also in this context, it is likely that pollen contained within an ash fallout and base surges will be biased towards pollen from the regional pollen rain. There is a non-arboreal component (e.g. grasses and sedges) found within the ash, which provides information on the local vegetation suggesting an environment similar to present. Pollen sequences dominated by pine have been taken to represent a dry climate in Mexico while those with oak and alder (or more deciduous trees in general) indicate wetter conditions (Clisby and Sears, 1955). Subsequent work, however, has challenged this basic climatic interpretation (Lozano-García and Xelhuantzi-López, 1997). In the modern environment, alder certainly indicates wetter conditions and oak can generally be found at lower elevations than pine. While the limitations in the pollen data here preclude any clear palaeoclimatic interpretation, work on the relationship between modern vegetation and pollen spectra may enable a combined temperature/precipitation signal to be obtained which could be applied to analogous Pleistocene fossil sequences (for an example of this approach see Correa-Metrio *et al.*, 2012).

Tepejilera site (V-28)

The Tepejilera section, located by the present Valsequillo lake shoreline (Fig. 4), comprises > 2.30 m of laminated Xalnene Ash overlain by alternations of soft calcareous silty clays and silty freshwater limestones. The beds range from a few centimetres thick to a maximum of 33 cm, with sharp bases and upper contacts (Fig. 10a). These features are common in aqueous, low-energy, environments and the sediments could represent part of Malde's (1968) Atoyatenco upper lake beds. Thin sections of the limestones show that they contain abundant, volcanogenic, silt-sized grains. As at the River Atepezingo sequence, no calcareous fossils were found.

Six samples were taken for carbonate isotope analysis from the individual limestone beds that are stratigraphically above the Xalnene Ash (Fig. 10b). As only very small samples were taken they could not be analysed for organic composition or diatoms. In contrast to the Rio Atepezingo limestone sequence, the isotope values from the carbonates are relatively stable (Fig. 10b), with mean $\delta^{13}C_{carbonate}$ $-3.7 \pm 0.2‰$. The $\delta^{18}O_{carbonate}$, however, shows a distinct change about half way up the sequence, between beds T4 and T3, with underlying values of $-8.2 \pm 0.1‰$ and overlying values of $-6.2 \pm 0.7‰$. These values are consistent with the lowest values at Rio Atepezingo (zone 1) where it has been suggested that they represent a period of stability. The very low $\delta^{18}O_{carbonate}$ and thin beds at Tepejilera suggest that the carbonates were probably precipitated from a spring-water-dominated, shallow lake with a short water residence time and constant spring water inflow and seepage that led to minimal change due to evaporation. Such shallow lakes might have established in topographic lows after the deposition of the Xalnene Ash. The change in $\delta^{18}O_{carbonate}$ midway up the sequence suggests a change to wetter conditions, but there are no other data to confirm this reconstruction.

The Quarry site (FQ)

The Xalnene Ash at this site consists predominantly of multiple, graded units of basaltic coarse olivine lapilli (Table 1), interbedded with fine ash, although silt-rich, inversely graded ash units occur, mainly at the base of the sequence. Baked, orange, sandy–silty, angular fragments are common and there is local evidence of cross-bedding, ripples, dunes and scour structures, which indicate base surges close to the crater of the Toluquilla Volcano. Welded ash and palagonite horizons occur locally towards the base of the sequence, and suggest that in part the ash was deposited hot and then cooled rapidly, indicating that it was deposited at least partially in water. Accretionary lapilli and ash tails behind the lapilli are common features in the ash.

Above the ash are beds of partly reworked sediments (Fig. 11), comprising mostly silts and sands which could correspond to Malde's upper (Atoyatenco) lake beds. There are some very thin ashes interbedded within these sediments, suggesting that episodes of volcanic activity alternated with periodic reworking events. The quarry

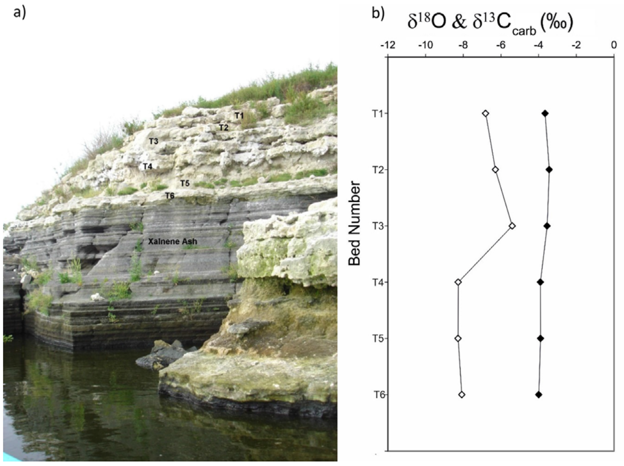

Figure 10. (a) Tepejilera site (V-28) showing the position of the sampled freshwater limestones and siltstones (T1–T6) on top of the Xalnene Ash at the Valsequillo reservoir shore. (b) Oxygen and carbon isotope composition of those limestones. $\delta^{18}O$ and $\delta^{13}C$ are given as open and closed symbols, respectively.

Figure 11. Quarry Wall site (FQ) showing the Xalnene Ash at the base with the reworked lake and ash sediments on top of the ash. The position of the sample for the n-alkane determinations was 85 cm from the top of the Xalnene Ash contact (black square hole with arrow).

wall sediments contain only sparse diatoms (e.g. *Hantzschia amphioxys*), indicative of subaerial or very shallow water conditions. Only one sample, about 60 cm above the ash, might reflect a period of more permanent standing water. The n-alkane results from a sample from the sediments taken 85 cm above the top of the ash at the Quarry wall site are shown in Fig. 9(b). The organic material is dominated by odd numbered components in the range nC_{21}–nC_{33} and has a maximum at nC_{31}. This distribution is typical of terrestrial plants as the main source of organic material and is consistent with the diatom data. There is little or no evidence at this site for the presence of true lake sediments (i.e. the Atoyatenco lake beds), but these would pinch out in marginal positions adjacent to Cerro Toluquilla.

Conclusions

We present stable isotope, tephra, diatom and pollen data for Central Mexico from stratigraphic sections of mainly non-volcanic sediments, which have been dated to the Early–Mid Pleistocene by their position relative to the Xalnene Ash. The sediments at the Atepezingo site (below the Xalnene Ash) and Tepejilera site (above the Xalnene Ash) have stable isotope compositions that suggest that small and medium-sized lakes occurred in the basin and that a terrestrial signal became increasingly abundant through the period. There is evidence to support the presence of lacustrine conditions before the eruption of the Toluquilla Volcano during the Early Pleistocene. We do not, however, find evidence in support of Malde's (1968) suggestion of 'deep lake sediments' which we now interpret as reworked volcanic deposits, with the presence of localized shallow lakes infilled with calcareous sediments. Diatom preservation is generally poor in these sediments and the assemblages do not indicate deep water at the sites described here. The only genuinely deep water flora for Valsequillo was found in a sample taken from Malde's deep core 2, taken from Hueyatlaco on the Tetela peninsula, for which we do not have chronological control (Fig. 4). This core was also studied by VanLandingham (2006), but it is difficult to relate his findings to ours. It seems, however, that the sample with deep water diatoms seen in our study came from above the layers he identified as the Amomoloc deposits.

Trace amounts of organic material found at the base of the Xalnene Ash itself suggest that the organic material came from both terrestrial and wetland-type plants. Sparse pollen, which was extracted directly from the base of the ash layer, indicates the presence of terrestrial plants, including pine and woody shrubs. After the deposition of the Xalnene Ash there was a change in the hydrological regime in the Valsequillo Basin, with no evidence of an extensive lake at the locations studied, although there were pools present, with much volcanic ash deposition and reworking. The diatom evidence for any significant lake post-dating the Xalnene eruption is scanty at best from these locations. Small, shallow water lakes were more typical of the Valsequillo Basin at around 1.3 Ma and terrestrial organic matter was more important in the sediments deposited. Malde (1968) suggests that the Atoyatenco deposits represent freshwater conditions with intermittent desiccation and our data are consistent with this. It may be that the Valsequillo Basin followed the same general pattern as that reported for the central and western lakes of the TMVB by Israde-Alcántara *et al.* (2010). Here, Quaternary vertebrate fossils and diatoms from lake sequences indicate a transition from deeper to shallow lakes and then more fluvial deposits over the period from the mid-Pliocene to the Early Pleistocene in response to both Plio-Pleistocene tectonism and gradual drying of the climate in Central Mexico.

Overall, our data show that although the basin has been in general a volcanically dynamic environment, groundwater levels must have been high enough at times to allow spring-fed, small pools to form in the relatively low-lying parts and sometimes to form shallow lakes. There is no evidence for Malde's (1968) deep and extensive lake system at the sites presented here. However, this may be explained by these sites being in a marginal lacustrine environment, as suggested by Gonzalez *et al.* (2006a). Unfortunately, like Malde, our sampling has been restricted by the presence of the modern Valsequillo reservoir, which might overlie deeper basin deposits. Deep coring at sites such as Hueyatlaco, or within the reservoir itself, might help to resolve outstanding questions about palaeolake Valsequillo.

The Valsequillo Basin was more humid than today immediately before and after the Xalnene Ash eruption, during the Early to Mid-Pleistocene, supporting a large community of Quaternary fauna that included mammoth, glyptodont, horse, wolf and camel. The evidence for Pleistocene environmental conditions between the period after 1.3 Ma and the deposition of the Late Pleistocene Valsequillo Gravels (including the Hueyatlaco Ash) remains elusive and much of the basin must have had an erosional geomorphology with extensive fluvial down-cutting and slope sediment reworking. The relationship with the sediment sequences described in this paper and the archaeological record and sediments (and their ages) recorded on the Tetela peninsula remains uncertain.

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Abbreviations. LOI, loss-on-ignition; TAR, terrestrial/aquatic ratio; TDIC, total dissolved inorganic carbon; TIC, total inorganic carbon; TMVB, Trans-Mexican Volcanic Belt.

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