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# Climatic changes from 12,000 to 4,000 years ago in the Austrian Central Alps tracked by sedimentological and biological proxies of a lake sediment core

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## Abstract

Major and trace elements, minerals, and grain-size were analysed from the early to mid-Holocene (12 to 4 ky BP) period of a sediment core from the Alpine lake Oberer Landschitzsee (ObLAN, 2076 m a.s.l.), which is located on predominantly crystalline bedrock on the southern slopes of the Austrian Central Alps. Geochemistry and mineralogy were compared with diatom-inferred (Di-) 'date of autumn mixing' ($A_{mix}$), DOC, pH, and selected indicator pollen species from the same sediment core. Principal components analysis (PCA) indicated a positive correlation between processes triggered by temperature and precipitation (e.g., lake mixing, DOC). PCA grouped indicators of physical weathering and enhanced catchment run-off (sand, quartz, feldspar), elements of weathering (e.g., Ti, Rb, Mn) under dryer conditions (clay to silt fractions), and elements that probably were related to changes in redox conditions (Cu, Fe, S, Zn). The duration and height of the snow-pack played an important role in this high-alpine environment, affecting weathering, erosion, pH, and lake stratification. Low *Alnus viridis* pollen abundance, together with markers for increased elements of erosion, indicated extensive snow-pack. Changes in S coupled with As, and elements indicating increased weathering, reflected climate oscillations. LOI was affected by productivity and erosion. High (late) Di–$A_{mix}$ coupled with increased Di-DOC indicated prolonged summers with increased productivity. Cold and wet (snow-rich) phases and subsequent melting caused low pH and a decoupling of the significant linear correlation between sedimentary Ca and Di-pH. Weathering and leaching during climate deteriorations opposed the long-term trend in a loss of cations and forced in-lake alkalinity generation during the following lake warming. Overall, the multi-proxy study indicated complex climate-driven processes within different time-scales (long-term trends, climate oscillations, seasonality). The climate oscillations within 12–5 ky BP corresponded well with the cool and wet phases known from central Europe suggesting a dominant common Atlantic climate impact. When Mediterranean climate established between 5 and 4 ky BP, its influence on the southern slopes of the Alps increased.

## Introduction

Solar forcing (Stuiver and Braziunas 1993; Haigh 1996; Stuiver et al. 1997; van Geel and Renssen 1998; Björck et al. 2001) was assumed by Bond et al. (2001) to trigger the North Atlantic ice-rafted debris (IRD) cycles of about 1500 years (Bond et al. 1997), thus controlling contemporaneous

European climate oscillations. Investigations on lake levels in the Jura, French pre-Alps, and the Swiss Plateau by Magny (2004) showed that high lake levels coincided with the cooling of the North Atlantic. Magny et al. (2003) suggested that variations in the strength of the Atlantic westerly jet-stream system, in relation to thermal gradients, are the main reasons for the differences in precipitation at different latitudes in Europe.

For the Austrian Alps, modern precipitation shows a 'dipole' distribution (Böhm et al. 2003). North of the main Alpine ridge Atlantic cyclones cause early summer precipitation maxima. South of the ridge Mediterranean cyclones (mainly the Genua depression) cause autumn and winter precipitation maxima that can extend towards the Alps (Wanner et al. 2003). Snow-pack and snow-cover duration, which play an important role in alpine environments (Beniston et al. 2003), are linked to changes in large-scale climate forcing (Beniston 1997; Hantel et al. 2000). Recently, Pla and Catalan (2005) showed for the Pyrenees that seasonal climate patterns changed during the Holocene.

Thermistor data, measuring water temperatures in lakes of the Austrian Alps (Schmidt et al. 2004a, b), indicated a non-linear relationship between lake water temperatures and altitude. Some of the lakes followed the altitude air temperature model developed by Livingstone and Lotter (1998), while others were colder than expected by this model (Thompson, unpublished data).

The sediments of Alpine lakes, and especially those near the tree line, store information on climate and climate-related processes such as erosion and weathering rates and catchment vegetation and soil formation (e.g., Kauppila and Salonen 1997; Koinig et al. 2003; Karst-Riddoch et al. 2005; Solovieva et al. 2005; Velle et al. 2005). Diatoms are good indicators for tracking climate-driven environmental changes in lakes near the tree line (e.g., Lotter et al. 1999; Smol and Cumming 2000; Smol et al. 2005). Schmidt et al. (2004a) established a diatom transfer function for the 'date of autumn mixing' ($A_{mix}$) using thermistor records and diatoms from surface sediments of 40 lakes between ca. 1500 and 2300 m in the Austrian Alps (Niedere Tauern). In this data-set $A_{mix}$ appeared to vary independently from pH (or alkalinity). $A_{mix}$ was next in explanatory power to pH; pH explained most of the variation in the diatom assemblages of the lake training set. The $A_{mix}$ model resulted in a better prediction than models on mean monthly summer water temperatures, which had a weak impact on diatoms. The most relevant external forces to induce lake mixing are surface water temperature, wind turbulence, water inflows, as well as lake morphometry (e.g., Imboden and Wüest 1995; Ventura et al. 2000). Hence, $A_{mix}$ is mainly a climate-driven variable.

The diatom-inferred $A_{mix}$ and pH models from the Niedere Tauern training set were applied to a Holocene high-alpine lake sediment core from Oberer Landschitzsee in the Austrian Alps (Schmidt et al. 2004a). $A_{mix}$ showed marked changes during Holocene. The long-term trend of diatom-inferred pH showed a decline from early to mid-Holocene. In this paper we combine the diatom-inferred variables $A_{mix}$, pH, and DOC with geochemical and mineralogical analyses from the same sediment core. The aim of the present study was to improve our understanding of the climate development in the area of the southern slopes of the Austrian Central Alps. We selected the early to mid-Holocene period (12–4 ky BP) when anthropogenic impact in the study area was lacking or scarce (Schmidt et al. 2002).

## Study site

The oligotrophic Alpine lake Oberer Landschitzsee (ObLAN, 47°13′15″ N/13°36′06″ E, 2076 m a.s.l., max depth 13.6 m, lake area 8.8 ha) is located on crystalline bedrock with mica-shists and metamorphic carbonates at the southern slope of the Niedere Tauern, Lungau (illustrated in Schmidt et al. 2004a). The lake is located slightly above the present tree line, which is formed by *Pinus cembra*. Scattered dwarf pine (*Pinus mugo*) extends above the timberline, which is formed by *P. cembra*, *Larix*, and *Picea* at about 1900 m a.s.l. At locations with prolonged snow-cover, green alder (*Alnus viridis*) replaces *P. mugo*. Fir (*Abies*) is rare and beech (*Fagus*) is not present in the mountain forests of Lungau. The lake is surrounded by alpine meadows. The present pH is 7.1, alkalinity is 130 $\mu$eq $l^{-1}$, and DOC is 0.69 mg $l^{-1}$. For details on lake-water chemistry, see Schmidt et al. (2004b).

## Materials and methods

A total of 155 sediment samples were analysed for bulk geochemistry in contiguous 1 cm intervals. The samples were dried at 105 °C (used for LOI analysis) and ground with an agate ball mill. Selected major and trace elements (Al, As, Br, Ca, Cl, Cr, Cu, Fe, K, Mn, Ni, Pb, Rb, S, Si, Sr, Ti, Y, Zn, Zr) were analysed from 0.5 to 1.5 g dried material with an energy-dispersive miniprobe multi-element analyser (advanced version of EMMA, for detailed description see Cheburkin and Shotyk 1996; Cheburkin et al. 1997).

Mineralogy was analysed on air-dried and powdered bulk samples using X-ray diffraction (XRPD, AXS-Bruker D8), calibrated with the Rietveld-based quantitative XRD-software Siroquant®.

Grain-size fractions (clay $< 2$ $\mu$m, silt 2–63 $\mu$m, and sand $> 63$ $\mu$m) and median grain-size were determined on untreated bulk sediments suspended in Calgon® using a Laser-Particle-Analyser (Malvern Mastersizer2000®). Each result represents the mean of three single measurements obtained after 3 min ultrasonic disintegration and simultaneous stirring and pumping through the measurement cell.

Schmidt et al. (2004a) presented AMS $^{14}$C dating, loss-on-ignition (LOI, see Heiri et al. 2001; Boyle 2004), selected pollen, and the diatom-inferred (Di-) models for the 'date of autumn mixing' ($A_{mix}$), pH, and DOC. All given dates are calibrated calendar years before present (BP).

The variation of centred and standardised environmental variables was summarised by principal component analysis (PCA) using CANOCO version 4.5 (ter Braak and Šmilauer 2002).

Stratigraphic zones were established with the optimal sum of the squares partitioning method (Birks and Gordon 1985) as implemented in the program ZONE (Lotter and Juggins 1991). Since data were measured at different scales, the samples were ranged prior to analyses (Legendre and Legendre 1998). The significance of the zones (DZ = diatoms, GZ = geochemistry, MZ = mineralogy, PZ = pollen) was tested with the broken stick model (Bennett 1996). Time series were smoothed by locally weighted regression (Cleveland and Devlin 1988) using the LOESS smoother implemented in the programme SigmaPlot 2000 (span for all diagrams = 0.1).

## Results

### *Principal components analysis (PCA)*

The PCA-biplot (Figure 1a) summarised the elements, minerals, grain-size fractions, LOI, the diatom-inferred variables Di-$A_{mix}$, Di-pH, and Di-DOC, and selected indicator pollen (*P. mugo*) for sub-alpine pine shrub vegetation, *A. viridis* for snow-cover, *Picea* for timberline movement, *Abies* + *Fagus* for humidity and lacking or less frost (Gams 1931/1932). Pollen percentages of *Abies* and *Fagus* were summarised because of their similar ecology and pollen transport from a lower altitude.

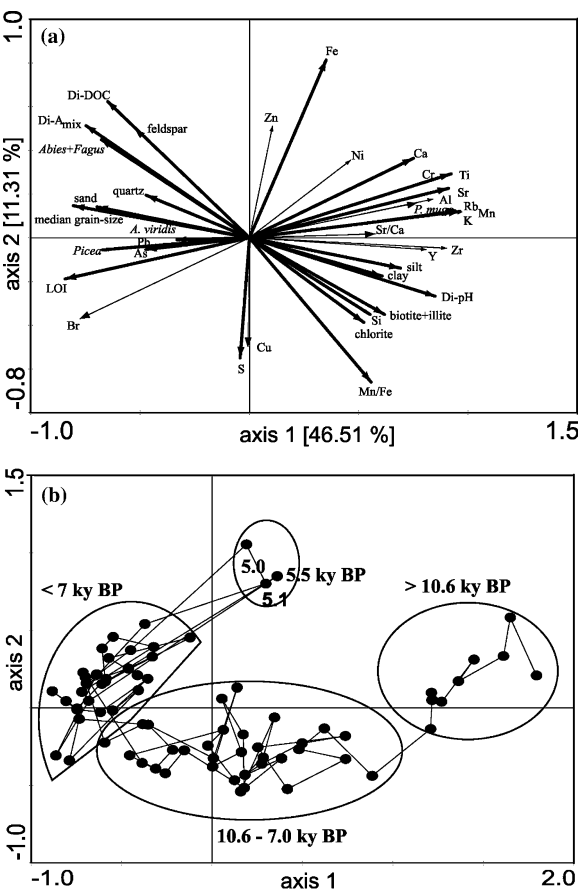


*Figure 1.* (a) Principal components analysis (PCA) of major and trace elements, minerals, grain-size fractions, diatom-inferred variables (Di-$A_{mix}$, Di-pH, Di-DOC), and indicator pollen in the sediment core ObLAN. Variables plotted against time (see Figures 2–5) are indicated by bold arrows. (b) Sample trajectories along PCA axes 1 and 2. Four sample clusters (circled) with dating are shown.

The first two axes explained 57.8% of total variance. Mn, K, Rb, Ti, and Sr had the highest positive PCA axis 1 scores and were grouped with clay and silt. Biotite + illite, chlorite, as well as the Mn/Fe and Sr/Ca ratios, the diatom-inferred pH, and *P. mugo* pollen also had positive PCA axis 1 scores. LOI, Br, Di-$A_{mix}$, *Abies* + *Fagus* pollen, *Picea* pollen, Di-DOC, and median grain-size had the highest negative PCA axis 1 scores. They were ordinated together with As, Pb, the sand-fraction, quartz, feldspar, and *A. viridis* pollen along axis 1. Fe showed the highest positive and S had the highest negative loading at the PCA axis 2. As, Cu, and S showed the highest positive scores at the PCA axis 3 (9.03 % of the total variance).

PCA sample trajectories along the axes 1 and 2 indicated four clusters (Figure 1b), > 10.6, 10.6–7.0, < 7 ky BP, and three samples between 5.5 and 5 ky BP.

*Stratigraphy*

Di-$A_{mix}$ was high in early DZ2, and showed the lowest values in DZ3, which increased again in DZ4, and remained at a high level in DZ5. Di-DOC revealed a similar pattern (Figure 2).

Rb and Ti, which reflected the changes of most elements (high PCA axis 1 scores with Al, Ca, Cr, K, Mn, Sr, Y, Zr) showed high values during the early Holocene (GZ1), followed by a decline, and increasing values during late GZ2 and early GZ4 (Figure 2). Marked short-term fluctuation occurred in GZ1 and GZ4.

Mn and Fe showed similar patterns in GZ1 and GZ4, and successive divergence in GZ2 and GZ3. The Mn/Fe-ratio showed corresponding patterns with Si (Figure 2).

The sand-fraction increased from the late to mid-Holocene. Marked peaks occurred at 7.9, 6.2, and 4.8 ky BP, mainly when *A. viridis* was low (Figure 2).

*Picea* and *Abies* + *Fagus* increased from early (PZ1) to mid-Holocene (PZ3) while *P. mugo* showed an inverse trend. *Picea* showed a decline at the expense of *P. mugo* during PZ2 and declined during PZ3 and PZ4, when *Abies* + *Fagus* increased (Figure 3).

Sulphur showed peaks in all four zones, which are consistent with those of As. During GZ2 and early GZ3, increased LOI corresponded with peaks of S. During late GZ3 and during GZ4 both of them diverged, resulting in different PCA ordinations. LOI and mean grain-size showed similar patterns (Figure 3).

Di-pH was highest in DZ2 and then declined towards the present pH (pH 7.1). With the exception of late GZ2, which showed a distinct peak in Sr but not in Ca, Sr and Ca showed similar patterns. During most of GZ2 and GZ3, Ca remained at a nearly constant level (Figure 3). A linear regression between Di-pH and calcium showed more scattering at higher Ca. Four samples of higher Ca were outliers (Figure 4).

Feldspar and quartz increased from older to mid-Holocene, and consequently biotite + illite and chlorite decreased. Feldspar peaked in MZ5 and quartz in MZ6. Chlorite increased again in MZ3 and MZ5. Biotite + illite and quartz showed individual peaks in MZ2 and MZ3 (Figure 5).

## Discussion

*PCA analyses*

The grouping of Di-$A_{mix}$, *Abies* + *Fagus*, and elements of physical weathering (sand, quartz, feldspar) in the PCA indicate a positive relationship of temperature and precipitation. It corresponds with observations that the lowering of temperature at high elevations in the Alps is commonly coupled with increased rain or snowfall (Auer and Böhm 1994). Di-DOC, which also belongs to the same PCA cluster, can be affected either by in-lake productivity or by outwash of humic substances during erosion in relation to the vegetation cover of the catchment. DOC in Alpine lakes is closely related to altitude and hence to temperature and vegetation (Sommaruga et al. 1999). The negative ordinated *Picea* and *P. mugo* pollen along the PCA axis 1 indicate timberline dynamics.

The elements Al, Ca, K, Mn, Rb, Sr, Zr, and Y along axis 1 are negatively correlated with the cluster above. In contrast to the indicators of physical weathering and enhanced catchment runoff, they characterise weathering of the silicate bedrock under dryer conditions (White et al. 1999). This gradient of surface water flows is supported by their association with the silicate clay (Koinig et al. 2003) and silt fractions. Similar PCA scores of the Mn/Fe-ratio with the aforementioned elements,

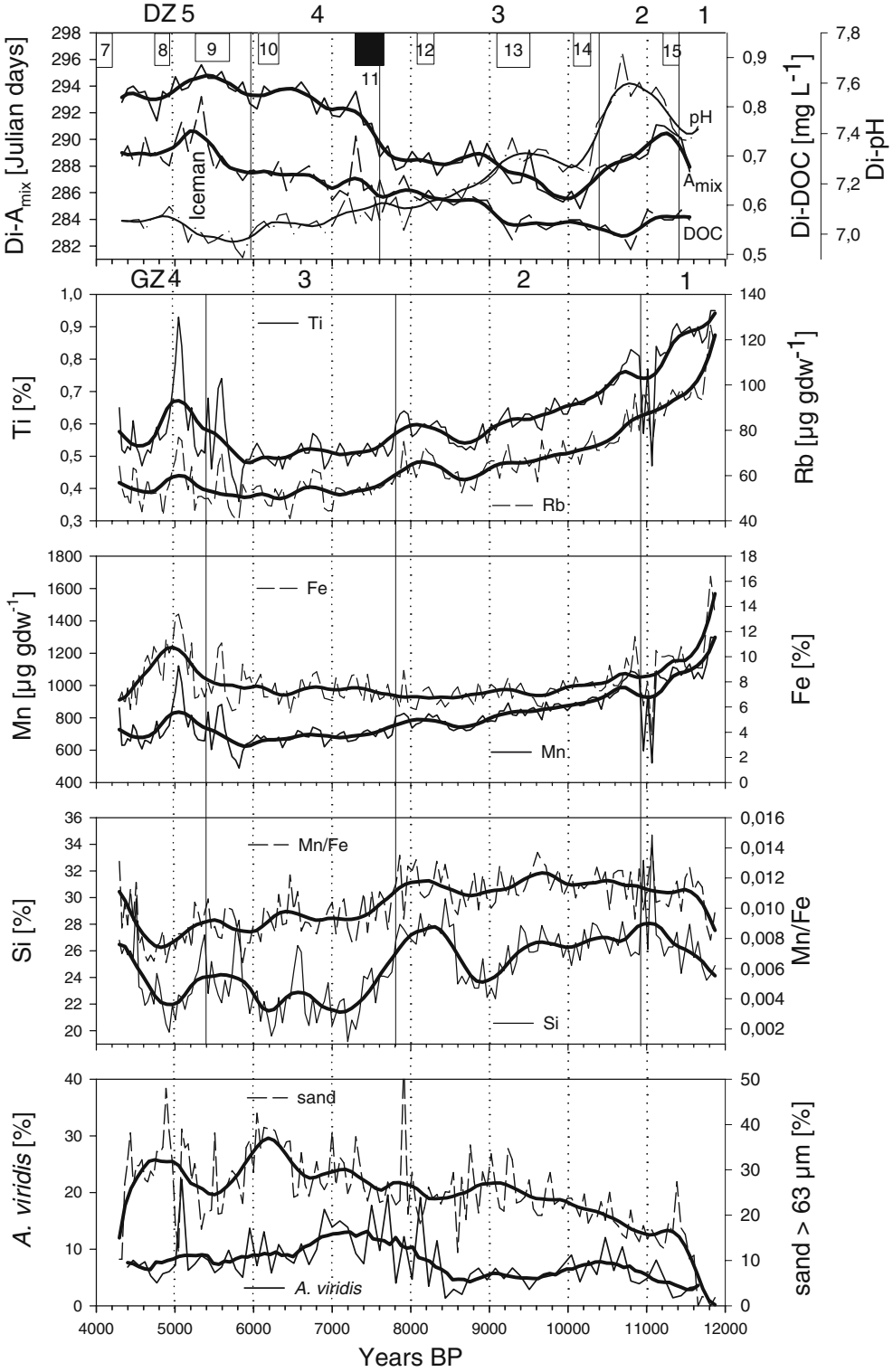


*Figure 2.* From the top to bottom: Diatom inferred 'date of autumn mixing' ($A_{mix}$) and dissolved organic carbon (DOC). High lake levels in central Europe ('phases 7 to 15' from Magny 2004, the maximum is marked by a black box), the occurrence of the Iceman, and the significant diatom zones (DZ1–DZ5) are shown; concentrations of rubidium (Rb) and titanium (Ti) and geochemical zones (GZ1–GZ4); concentrations of manganese (Mn) and iron (Fe); silica (Si) and the iron/manganese (Fe/Mn) ratio; sand fraction and pollen percentages of *Alnus viridis*.

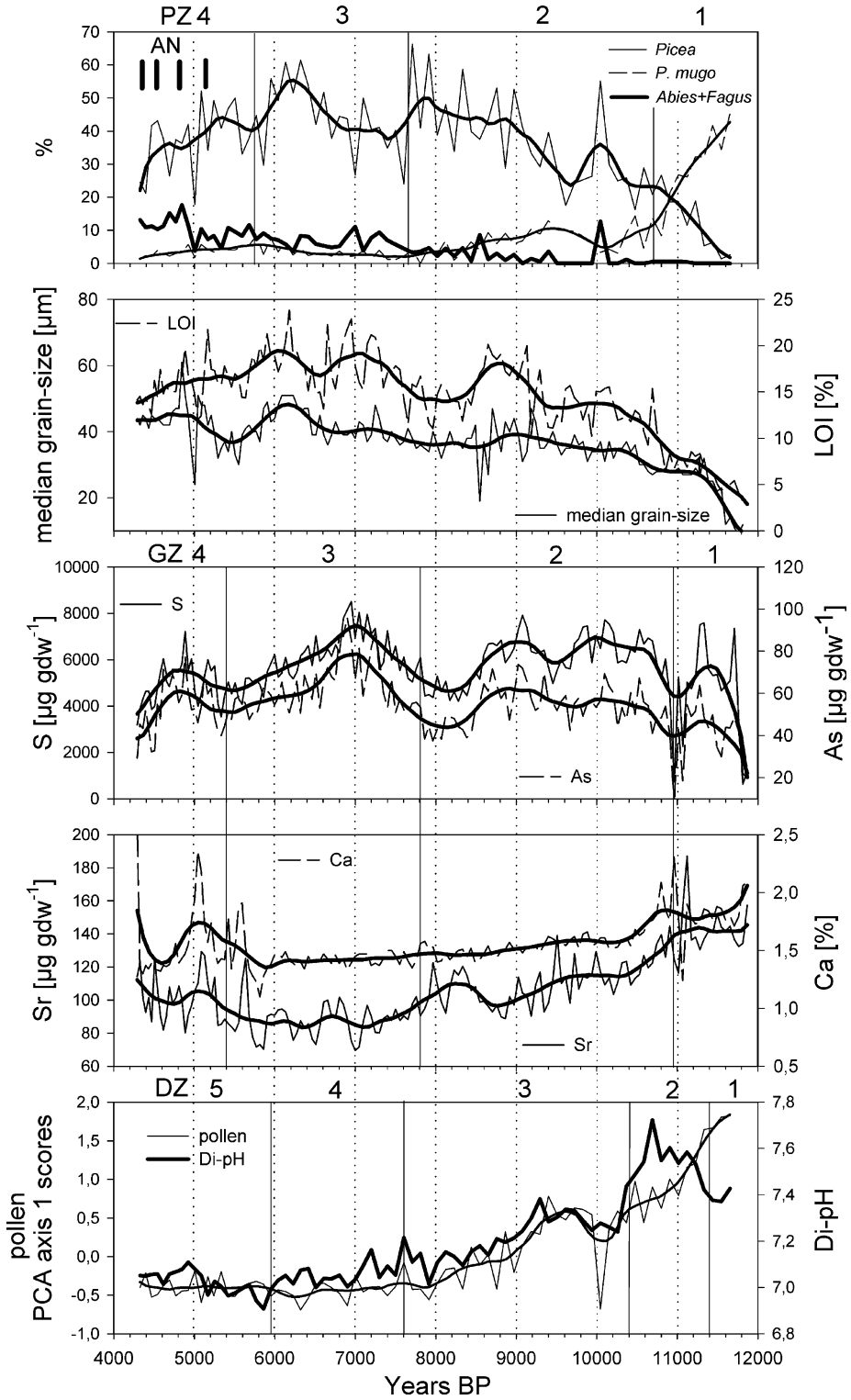


*Figure 3*. From the top to bottom: Pollen percentages of *Picea*, *Pinus mugo*, and *Abies* + *Fagus*. Pollen zones (PZ1–PZ4) and occurrences of anthropophytes (AN) are shown; loss on ignition (LOI) and median grain-size; concentrations of sulphur (S) and arsenic (As) with geochemical zones (GZ1–GZ4); concentrations of strontium (Sr) and calcium (Ca); PCA axis 1 scores of pollen and diatom-inferred pH.

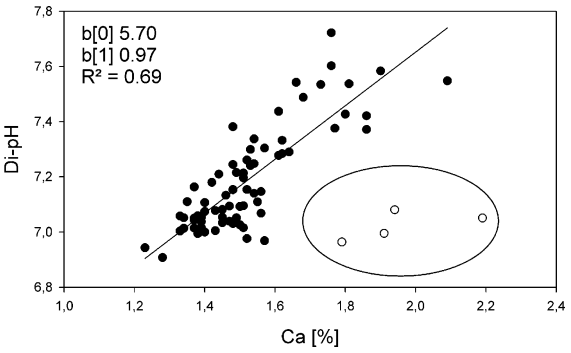


*Figure 4*. Linear regression between diatom-inferred pH and calcium in the sediment core ObLAN. Outliers (circled) are excluded (samples at 5.0, 5.1, 5.4, and 5.5 ky BP). Coefficients of the linear regression (Di-pH = 5.7 + 0.97 * Ca) and the amount of variation explained by Ca ($R^2$) are shown.

and with Si, biotite + illite, and chlorite, indicate that Mn/Fe was mainly affected by weathering.

Modern alkalinity and pH of the Niedere Tauern lakes were strongly associated with bedrock geology (Kamenik et al. 2001). The Di-pH was also affected by weathering, as indicated by the grouping with biotite + illite and elements that are constituents of calcium-bearing heavy mineral phases from the bedrock, such as yttrium (garnet, apatite etc.).

For Cu, Fe, S, and Zn, which are ordinated along axis 2, redox processes seemed to be important. Positive PCA axis 2 scores (Fe, Zn) indicate oxidising conditions (e.g., Fe-oxides), negative ones (S, Cu) point to reducing conditions (e.g., Fe-sulphides). Sulphur and copper, which were highly significantly ($p < 0.001$) correlated, were probably affected by organic matter accumulation (LOI, Br) and hypo-limnetic redox conditions. The positive correlation of LOI with As suggests hypolimnetic oxygen depletion (Schaller et al. 1997). The Di-DOC concentrations $< 0.9$ mg $l^{-1}$ were too low for diagenesis of sulphur-rich humic matter resulting in S enrichment (Ferdelman et al. 1991). The positive correlation between LOI and Br indicates that Br was adsorbed to organic matter (Lange 1970) and that catchment sources might have prevailed over in-lake productivity (Aritztegui et al. 1996; Boyle 2001). The positive correlation with median grain-size supports this assumption.

PCA sample trajectories along the axes 1 and 2 indicated four clusters. They were mainly related to (1) increased pH and to elements indicating weathering under dryer conditions and low vegetation cover (>10.6 ky BP), (2) pH decrease and/or low (early) $A_{mix}$ (10.6–7 ky BP), (3) increased $A_{mix}$ and markers indicating changes in humidity (<7 ky BP), and (4) increased Fe (samples 5.0 and 5.5 ky BP) probably due to oxidising conditions (iron hydroxides).

### *Stratigraphy*

With the exception of the zone boundary DZ1–DZ2, the diatom-based zone division was close to those of geochemistry (four zones) and pollen (four zones). Mineralogy showed a higher variation (six zones). We used the diatom zonation (DA) for the following stratigraphic discussion, but amalgamated DZ1 and DZ2 (see sample cluster >10.6 ky BP in the PCA, Figure 1b).

### *>10.4 cal. BP (DZ1 + DZ2)*

The increase of spruce at the expense of *P. mugo* pollen (Figure 3) indicates the progression in timberline due to climate warming. The low proportions of quartz and feldspar (Figure 5) and the lowest median grain-size prior to 11 ky BP (Figure 3) indicate low erosion due to soil stabilisation by vegetation (*P. mugo* dominance) and predominant dry climate conditions. Di-$A_{mix}$ during DZ1 and early DZ2 was based on poor modern analogues. If average Di-$A_{mix}$ are reliable for early DZ2, they correspond to a hypothetical lake-altitude up-shift of 100 m (Kamenik and Schmidt, unpublished) or temperature drop of ca. 0.5 °C (Agustí-Panareda and Thompson 2002) when compared with the present conditions. DZ2 was, however, climatically heterogeneous. The temporary increase in quartz around 11 ky BP indicates wet conditions, although grain-size remained low, probably due to the preceding dry climate and soil stabilisation. The marked fluctuations in nearly all of the elements around 11 ky BP (extrapolated) indicate unstable environmental conditions. The decoupling of Sr and Ca from elements that according to PCA (Figure 1a) were correlated indicate different sources; e.g., a possible origin from aerial dusts. The cool and wet phase most probably corresponds with the Preboreal Oscillation (Björck et al. 1997; Ammann

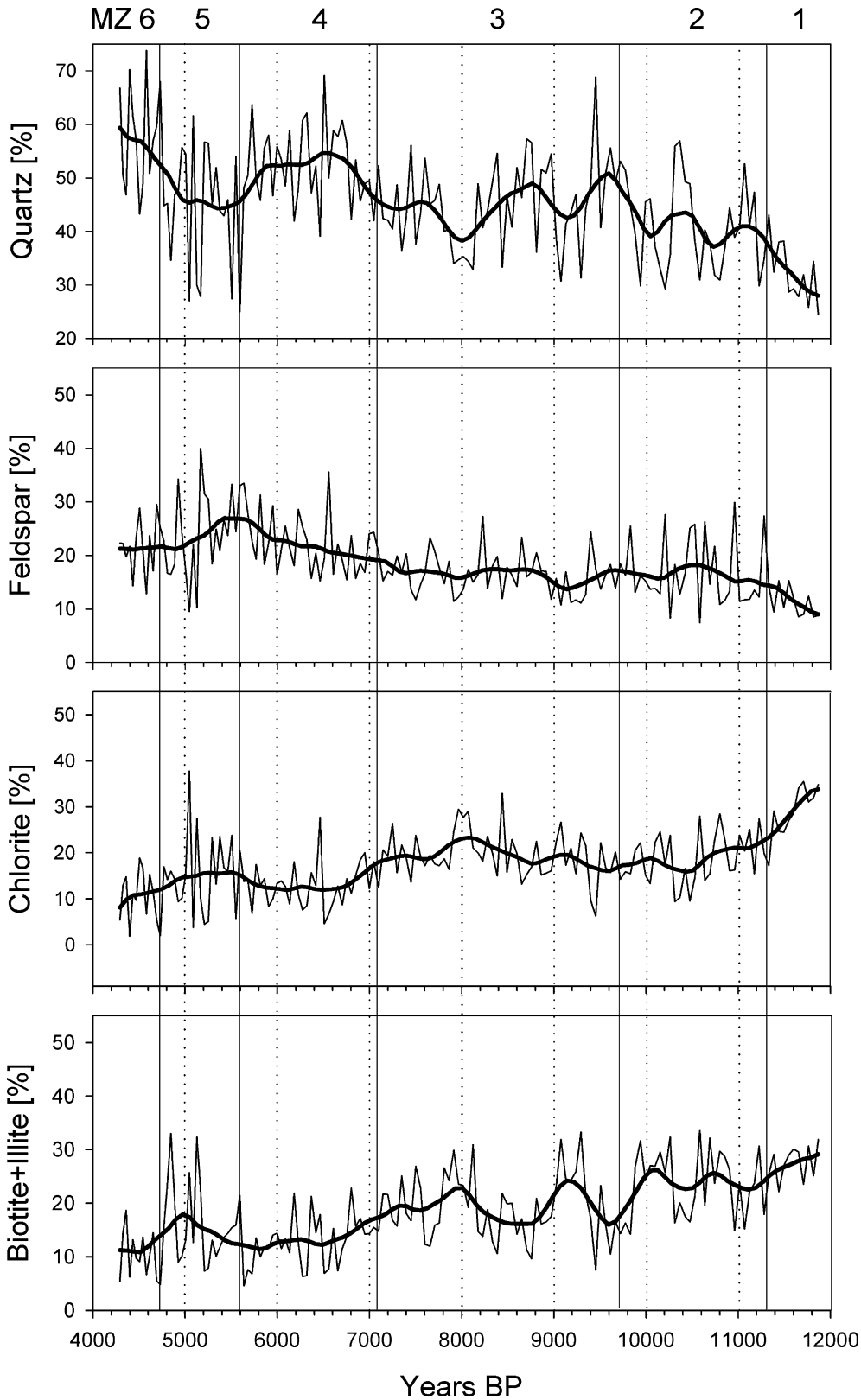


*Figure 5*. Mineral composition with mineralogical zones (MZ1–MZ6) in the sediment core ObLAN.

et al. 2000) or the 'wet phase 15' from Magny (2004). The later part of DZ2 was cooler, probably with wetter autumns (decrease in $A_{mix}$, increase in grain-size), than the period prior to the Preboreal climate oscillation.

### *10.4–7.6 cal. BP (DZ3)*

The cooling trend, which started during late DZ2, culminated at 10.2 ky BP. Snow-rich conditions probably caused the formation of perennial snowfields. Schmidt et al. (2002) argued that extensive snow-pack and/or prolonged snow-cover lowered or suppressed the flowering of the green alder (*Alnus viridis*) resulting in a low pollen abundance, which probably explains its decrease during early DZ2. This cold and wet phase coincides with 'phase 14' from Magny (2004). The following warming is indicated by the increase in *Picea*, LOI, and S (Figure 3). However, Di-$A_{mix}$ responded with a short time lag (Figure 2). This discrepancy might be explained by warm and dry summers followed by early freezing, both of which enhance hypolimnetic oxygen depletion (see Figure 1b), which might be expressed by high S concentrations (Ohlendorf et al. 2000). The warming was followed by climate deterioration as indicated by the *P. mugo* increase towards 9.5 ky BP at the expense of *Picea*, corresponding with lowering of *A. viridis* pollen, low LOI and S. This cold and wet (snow-rich) phase coincides with 'phase 13' from Magny (2004).

The following concurrent increase of Di-$A_{mix}$ and *Picea* pollen indicates climate warming from 9.2 to 8.7 ky BP. Percentages of quartz and sand were high (Figures 2 and 5), indicating melt-water impact (run-off, erosion) from snowfields, which have accumulated during the preceding cold and snow-rich period. Pla and Catalan (2005) found a similar warm period in the Pyrenees following the 9.2 ky cooling. The observed warming also corresponds with an oxygen isotope increase in the GISP2 record (Stuiver et al. 1997).

From 8.7 to 7.6 ky BP the increase in Rb, Ti, Si, Mn, and Si (Figure 2), and the concurrent distinct decline in LOI, S, and As (Figure 3), indicate enhanced weathering and climate deterioration. During this period Di-$A_{mix}$ and changes in the mineral proportions indicate two colder phases with increased erosion (peaks in quartz) interrupted by a warmer and drier phase (sudden increase of chlorite and biotite at the expense of quartz between 8.2 and 7.9 ky BP, Figure 5). The older phase of climate deterioration might include the so-called 8.2 ky cooling event (Alley et al. 1997) as recorded by Greenland ice cores (Dansgaard et al. 1993; Grootes et al. 1993). In the Alps, the 8.2 ky cooling was inferred from biogenic oxygen isotope fluctuations in pre-Alpine lakes (von Grafenstein et al. 1998) as well as indicated by abrupt changes in the relative pollen abundance of climate-sensitive trees and shrubs in annually laminated Swiss lake sediments (Tinner and Lotter 2001). The oxygen isotopes suggested a climate cooling of ~2.8 °C in Greenland and 1.7 °C in mean annual air temperatures in Central Europe (von Grafenstein et al. 1998). In ObLAN, the short-term fluctuations of $A_{mix}$ around this event range within the error of prediction. The $A_{mix}$ minimum at 8.3 ky BP of ObLAN refers to a temperature anomaly of $-1.4$°C when compared with modern temperatures (see Section '> 10.4 cal. BP'). The younger phase of climate deterioration at ca. 7.6 ky BP of ObLAN, according to the redating of the Frosnitz oscillation (Patzelt and Bortenschlager 1973) by Nicolussi and Patzelt (2000), might correlate with a marked glacier advance in the Hohe Tauern. The patterns observed in ObLAN are also comparable with the results from Magny (2004) and Haas et al. (1998), who found two close-by cold and wet periods during the interval 8.3–7.2 (phases 12 and 11 from Magny 2004). During this interval changes between wet and dry phases are also known from the Adriatic and central Mediterranean. Dating uncertainties of the relatively short events hamper, however, correlation. Within the PALICLAS project (Guillizzoni and Oldfield 1996), pollen records from central Italian crater lakes were synchronised with the development of the Adriatic Sea. According to pollen records (especially the expansion of *Abies*), Allen et al. (2002) interpreted the regional climate around 8.2 ky BP as probably cooler and/or wetter. This was in agreement with the pollen records and changes in the litho-facies from Lago di Mezzano, central Italy (Ramrath et al. 2000). From approximately 9 to 7 ky BP, Wunsam et al. (1999) inferred freshwater incursions and lake-level rise for the Adriatic lagoon lake Malo Jezero, which they related to sapropel formation (S1) in the Adriatic (Fontugne et al. 1989) and central Mediterranean (Kallel et al. 1996,

1997). The wet periods at Malo Jezero were interrupted by a drier phase around 8.2 ky BP, which lasted approximately 150 years. The sapropel S1 in the Adriatic was also interrupted by a drier period (Aritztegui et al. 2000). Similarly, Pla and Catalan (2005) found the 8.2 cooling event in Lake Redó (Pyrenees) embedded in a warm period.

### *7.6–6 ky BP (DZ4)*

By 7 ky BP, the marked Di-$A_{mix}$ increase might indicate that perennial snowfields at ObLAN disappeared (Schmidt et al. 2004a). The gravel layer of about 7 ky BP, which in Unterer Landschitzsee (lake of the same drainage area) has precluded deeper coring, points to this period of enhanced melt-water discharge (Schmidt et al. 2002). Although the modern analogues for the $A_{mix}$ inference are poor, increased *A. viridis* support the hypothesis of less summer snow-pack during early DZ4. It also corresponds with a mid-Holocene temperature maximum as indicated by a high timberline and low glacier extension in the Alps (e.g., Tinner et al. 1996; Wick and Tinner 1997; Nicolussi and Patzelt 2000; Hormes et al. 2001). Increased mean July water and air temperatures inferences (diatoms, chironomids) in northern Europe (e.g., Korhola et al. 2000; Velle et al. 2005) and an oxygen isotope ratio increase in the Greenland ice-core (GISP2) record (Stuiver et al. 1997) indicate climate warming on a larger (northern hemispheric) scale. High Di-$A_{mix}$ (Figure 2) is also in accordance with increased autumn insolation (Berger 1978).

At 7 ky BP increases in LOI and S (Figures 2 and 3) indicate increased productivity due to climate warming. Long-term trends of Mn and Fe clearly differed (Figure 3); Mn, which was positively correlated with Rb and Ti, decreased probably because of the continued vegetation and soil development (Engstrom and Wright 1984). In contrast, Fe increased due to the formation of iron oxides in soils under warm and dry climate conditions and/or enhanced precipitation of iron sulphide caused by a chemical reduction in the sediment (Davison 1993; Schaller et al. 1997).

During DZ4, climate was heterogeneous. Our proxies indicate two major periods. The younger period had probably more snow than the older one as indicated by the decline of *A. viridis* pollen (Figure 2). Concurrent with *A. viridis* the pollen abundances of *Abies* and *Fagus* declined, probably due to spring frost. As a result *Picea* pollen abundance increased (Figure 3). With the exception of the transition of DZ4 to DZ5 (6 ky BP), with probably cool and wet summers/autumns, Di-$A_{mix}$ remained high (Figure 2). Hence, the increase in quartz and grain-size during younger GZ3 were explained by melt-waters from high and/or extended winter snow-packs. Run-off as the main source of quartz can also explain the negative correlation of quartz and Si in the PCA (Figure 1a) and could indicate a gradient in precipitation during the younger GZ3. Increased leaf-litter input from erosion might explain the high LOI during late GZ3. The decrease of sulphur after 6.7 ky BP (Figure 4) suggests a weakening of the lake's summer stratification when melt-water impact extended towards the summer.

The cold and wet (snow-rich) conditions at the end of DZ4 (6 ky BP) corresponded with that of UL-6 from Unterer Landschitzsee. This climate deterioration likely correlates with 'phase 10' from Magny (2004).

The long-term decline of Di-pH stopped during DZ4 when climax-vegetation, which was initiated during DZ3, had established (Figure 3). Engstrom et al. (2000) observed a similar relationship in recently deglaciated lakes in Alaska. After 7 ky BP, Di-pH fluctuated within a narrow range (0.6 pH units; error of prediction = 0.13 pH units) around the present pH (7.1).

### *6–4.2 ky BP (DZ5)*

Two phases of enhanced weathering occurred during 5.8–5.4 and at 5.1 ky BP as indicated by major shifts in Rb, Ti, grain-size, and feldspar. Peaks in Fe may result from catchment erosion and the formation of iron hydroxides due to oxidising conditions in the watershed (see Figure 1a). Warming interrupted both phases (highest Di-$A_{mix}$ at 5.3 ky BP). The dominance of feldspar at the expense of quartz at the beginning of the climate deteriorations is noteworthy (Figure 5). Summer snow ablation was probably reduced by climate deterioration that lowered erosion by melt-waters (low quartz). Rapid fluctuations between cold and warm periods and seasonal shifts between wet and dry conditions could explain the following findings. The high $A_{mix}$ plateau indicates that no

perennial snowfield could form for a longer time, which kept $A_{mix}$ low during DZ3. Short-term fluctuations in $A_{mix}$ ranged within the error of prediction. A marked increase in sand, which followed the peaks in weathering (Figure 2), indicates pulses of enhanced catchment run-off. Because they were concurrent with the onset of warming, they originated mainly from melt-waters. Although sedimentary Ca and Di-pH correlated significantly, four samples with high Ca between 5.5 and 5.0 ky BP were outliers in the linear regression (Figure 4). Short-term changes in the geochemical and mineralogical composition that were combined with low water temperatures during climate deteriorations, as well as subsequent snowmelt with high flushing rates, could be the main reasons for the decoupling. Schmidt et al. (2002) suggested melt-water impact in Unterer Landschitzsee to be responsible for a continued low pH at the transition from cold to warm periods. Thus, the rapid succession of cold (snow-rich) and warm (snow-melting) phases during 6–5 ky BP kept the pH low. Additionally, outwash of humic acids during wet phases could have lowered pH. Enhanced $Ca^{++}$ availability from weathering and leaching (minerals from physical weathering, e.g. Ca-feldspars) could have forced alkalinity generation during warming (Sommaruga-Wögrath et al. 1997), thus explaining the initial Di-pH peaks, which followed the cold and wet periods at ObLAN (10.8, 9.2, 7.6, 5 ky BP).

The two phases of increased weathering followed by erosion from melt-waters fit to marked minerogenic incursions and changes in the pollen succession observed in the pre-glacier Rotmoos (Tyrol) (Gams 1962; Bortenschlager 1970). Fritz and Ucik (2001) related increased weathering and erosion in the Tauern area to the 'Rotmoos complex'. The warm period of ObLAN around 5.2 ky BP, which separates the two phases of increased weathering, coincided with a ca. 200-years period of glacier retreat in the E-Alps (Nicolussi and Patzelt 2000).

Snow-rich conditions (low *A. viridis*) were probably prevailing during the younger part of DZ5. Melting gained, however, in importance when compared with the climate deteriorations of the former period, as indicated by the marked increase in quartz (Figure 5) and the higher level in median and coarse grain-size (Figures 2 and 3). The increase in LOI and As probably resulted from eroded organic matter during melting and/or from increased production. High organic matter and more stable lake summer stratification probably caused hypolimnetic oxygen depletion resulting in increased sulphur contents. Earlier Di-$A_{mix}$ (Figure 2) may indicate colder (earlier freezing) and/or wetter autumns that caused pronounced weathering and surface run-off. We suppose that seasonal climate developed differently: wet and mild (*Abies* + *Fagus* expansion) winters and cool autumns (earlier Di-$A_{mix}$) contrasted with warm summers (Di-pH increase). Jalut et al. (2000) described for Spain a step-like Holocene expansion of the Mediterranean climate northward. Adriatic pollen records of the evergreen oak (*Quercus ilex*), which is characteristic for the eu-Mediterranean belt, fit this pattern. The evergreen oak expanded on the SE Dalmatian coast (Isle of Mljet) after the end of the early-Holocene pluvial period (Jahns 1991; Wunsam et al. 1999), whereas in the north (Isle of Cres) the mass expansion occurred later, dated at about 4.5 ky BP (Schmidt et al. 2001). The hypothesis of changes in seasonal patterns also fit the observations of an increase in oceanic conditions in the Pyrenees found by Pla and Catalan (2005).

From ca. 5 ky BP onward, for the first time low pollen percentages of Chenopodiaceae, *Plantago lanceolata*, *Urtica*, *Rumex acetosa*-type, and *Cirsium* appeared (summarised as anthropophytes in Figure 3). These pollen types indicate the presence of Neolithic humans at ObLAN, which probably used the alpine meadows for pasturing (sheep?). Their occurrence resembles the results from other high-alpine sites in the Austrian Alps (Öggl 1994). The most famous evidence for the presence of Neolithic occupation at high alpine sites was the finding of the Iceman in the Austrian central Alps, at the border between North and South Tyrol, dated at 5.3 ky BP (Bortenschlager and Öggl 2000). At ObLAN, this date corresponded with a short but marked warm period (latest Di-$A_{mix}$) followed by climate deterioration. This climate pattern corresponded with climate inference by Baroni and Orombelli (1996).

## Conclusions

(1) The early-Holocene climate warming was followed by a cool and wet phase, which probably

correlated with the 'Preboreal Oscillation'. The following temperature lowering culminated during a cool and wet climate oscillation at ca. 10.2 ky BP. It was separated by a warm period from another cool and wet phase between 9.5 and 9.2 ky BP. Generally, the interval from 11 to 9.2 ky BP indicated a transition from an early Holocene continental climate to wetter (snow-rich) conditions. Climate warming from ca. 9.2 to 8.7 ky BP separated the older period with low Di-$A_{mix}$ from the younger climate deteriorations between 8.7 and 7.6 (7.0) ky BP. During this interval, two cooler and wetter phases were separated by a warmer and drier phase. The older of these climate deteriorations was discussed in the context of the 8.2 ky cooling event. By 7 ky BP, climate warming most probably caused the disappearance of perennial snow-fields in the catchment of ObLAN. The warm period from 7 to ca. 6.8 ky BP differed from the period 6.5 to 6 ky BP by less snow-rich conditions. A climate oscillation followed around 6 ky BP. The interval from 6 to 5 ky BP indicated two phases with intensified snowfall and weathering that were divided by a short, but intense, period of climate warming. The period from 5 to 4 ky BP indicated strong seasonal divergences; snow-rich, but in contrast to the period 6.5–6 ky BP mild winters and cool/wet autumns, most probably contrasted warm summers.

(2) Taking into account slight $^{14}C$ uncertainties, the cool and wet 'phases 15 to 10' from Magny (2004) of the interval 12–6 ky BP seem to coincide with those reconstructed from ObLAN. This could indicate a dominant and common Atlantic climate influence. The establishment of the present Mediterranean climate between 5 and 4 ky BP seems to have, however, forced its influence to the southern slopes of the Alps. South of the main Alpine ridge, winters probably became milder (oceanic) and autumns cooler and wetter. Additionally, 'dipole' conditions might have weakened climate correlations with areas north of the Alps.

(3) Decreasing air temperatures, coupled with increased precipitation, which resulted in cold ground- and surface-water flows and the formation of snowfields, were probably the main reasons for early (low) Di-$A_{mix}$. 'Under-cooled' lakes appear to be ultra-sensitive to climate warming as was expressed by the marked Di-$A_{mix}$ change at 7 ky BP.

(4) When vegetation cover developed in the catchment and $A_{mix}$ was late (high), Di-DOC was at its highest, indicating that prolonged warm summers with increased productivity were the main reasons for increased DOC.

(5) The long-term trend in Di-pH was related to vegetation and soil development superimposed by climate. When climax-vegetation had established during the mid-Holocene, the long-term pH decline stopped and fluctuated within a narrow range around the present pH. Cold and snow-rich climate oscillations caused low pH, whereas warm and dry summers increased pH, both following the hypothesis of a climate-driven pH control (Psenner and Schmidt 1992; Koinig et al. 1998). However, melt-waters with high flushing rates decreased pH. They also caused outliers in the significant correlation between sedimentary Ca and Di-pH. The negative climate oscillations opposed the loss in cation availability and forced in-lake alkalinity generation during the subsequent lake warming (initial Di-pH peaks).

(6) In sum, our multi-proxy study suggested a complex climate pattern and processes within different time-scales (long-term trends, climate oscillations, seasonality) that were influenced by Atlantic climate forces and Mediterranean climate development.

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