Volcanic Lake Sediments as Sensitive Archives of Climate and Environmental Change

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Abstract

In efforts to understand the natural variability of the Earth climate system and the potential for future climate and environmental (e.g., biodiversity) changes, palaeodata play a key role by extending the baseline of environmental and climatic observations. Lake sediments, and particularly sediment archives of volcanic lakes, help to decipher natural climate variability at seasonal to millennial scales, and help identifying causal mechanisms. Their importance includes their potential to provide precise and accurate inter-archive correlations (e.g., based on tephrochronology) and to record cyclicity and high frequency climate signals. We present a few examples of commonly used techniques and proxy-records to investigate past climatic variability and its influence to the history of the lakes and of their biota. This paper is rather a presentation of potentials and limits of palaeolimnological and limnogeological research on crater lakes, than a pervasive review of palaeolimnological studies on crater lakes. We show the importance of seismic stratigraphy for the selection of coring sites, and discuss problems in core chronology. Then we give examples of physical and chemical proxies, including magnetism, microfacies and oxygen and carbon stable isotopes from crater lake deposits mainly located in central and southern Europe. Finally, we present

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the use of air-transported (pollens) and lacustrine biological remains. The continuing need to develop new approaches and methods stimulated us to mention, as an example, the potential of the studies of subsurface biosphere, and the effects of microbiological metabolism on mineral diagenesis in sediments.

Keywords
Paleolimnology · Volcanic lake sediments · Seismic sequence stratigraphy · Dating sediment cores · Oxygen and carbon isotopes · Magnetism · Palynology · Climate and environmental change

1 Introduction

Lacustrine sediments are among the most complete and detailed natural archives, documenting—typically in greater detail than their marine counterparts—the temporal evolution of chemical, physical and biological features of a lake, its catchment and the prevalent climate of the region (Oldfield 2005).

According to Frey (1988), palaeolimnology sets lacustrine sediment studies in a broader context in which the trajectory of the effects of humans and natural changes on lakes requires long-term records of chemical and biological factors, on time scales ranging from the most recent (Holocene) to early geological times (e.g., Permian, Cretaceous, middle Pleistocene). Palaeolimnology studies the origin and the geomorphological history of lake basins and the response of their biocoenoses (plant and animal communities) to variations, for example, in nutrient levels (Guilizzoni et al. 2011), temperature (Battarbee 2000), water levels (Piovano et al. 2002; Giraudi et al. 2011), wind conditions (Brauer et al. 2008), dissolved substances which have occurred throughout time (Meyer 2003), as well as a wide spectrum of other impacts (Smol 2008). The stratigraphic study of sediment cores can provide information linked to local stressors, but also to global phenomena, both on long time scale, such as phases of glaciation (Ramrath et al. 1999; Tzedakis et al. 2001), and on shorter time scales (e.g., ENSO, von Gunten et al. 2012).

Volcanic lakes are particularly interesting for palaeolimnological research. In many regions, such as a large part of Europe and North America, most lakes are formed as a result of glacial activity, and are consequently younger than the last glaciation, or strongly influenced by it. Crater and maar lakes, on the other hand, are located in volcanic areas that are often less influenced by the events related to glaciation (e.g., Eifel Volcanic Field, central and southern Italy, southern France, East Africa, central Mexico, southern Patagonia), and they are "small enough to core easily and old enough to have had a respectable history" (Hutchinson et al. 1970). Volcanic lakes can be very deep and they often lack major in- and outlets which enhance the preservation of the structure of lake bottom sediments often triggering the formation of varves.

Some volcanic lakes are relatively young (less than 10,000 years), but most studies deal with ancient lakes, allowing a number of studies to go back in time up to more than 100,000 years BP, such as for example the dried out lake Valle di Castiglione (Follieri et al. 1988) and Lago Grande di Monticchio (Brauer et al. 2007), both in Italy, or Lac Ribains in France (de Beaulieu and Reille 1992; Rioual et al. 2007). Some palaeolimnological studies on volcanic lakes aim to identify the effect of recent human impact on lake biota, such as fish stocking (Skov et al. 2010) and atmospheric deposition of pollutants in ancient (Schettler and Romer 1988) as well as recent times (Ruíz-Fernández et al. 2007). The relatively small catchment areas of volcanic lakes make them ideal sites to study atmospheric processes and deposition of pollen and other natural air-transported proxies. Human induced changes in land use in the small and sometimes apparently undisturbed catchments of crater and maar lakes should be taken into account, as some of these lakes are strongly affected, even during the Bronze Age (Guilizzoni et al. 2002).

It should be noted that palaeolimnological studies dealing on lake biota or in-lake biogeochemical processes can be strongly influenced by the volcanic nature of the lake itself. For example, endogenous fluids can carry warmer water to the deepest part of the lake, directly affecting the biota, or dissolved carbon dioxide, altering water pH, such as in the case of Lago di Albano and Lago di Bracciano (Carapezza et al. 2010). Furthermore, these lakes can be subject to rapid and pronounced variations in water level (Funiciello et al. 2003) that can also affect lake biota and sediment deposition. Finally, submerged aquifer sources can also carry chemicals to the lake, strongly affecting the biogeochemical cycling of other compounds: for example high Fe concentration can alter the phosphorus concentration by the precipitation of insoluble compounds (Michard et al. 1994).

2 Seismic Sequence Stratigraphy

Most palaeolimnological studies rely on results from a single core that is considered as representative of a uniform, continuous sediment unit throughout a basin. Limnogeology, as envisioned by Kerry Kelts in the early 1980s, refers to a broader approach to study lake systems driven by the progress in ocean research in the context of marine geology, including the study of complex systems and their interactions (Kelts 1987). Modern profiling with various-scale seismic resolution is a good example of a limnogeological approach, since it can provide valuable lithological and geometric information prior to coring (e.g., Ariztegui et al. 2001a), allowing the identification and three dimensional mapping of sediment packages.

Seismic sequence stratigraphy has been widely applied for marine geophysical surveying, and has also been applied in a comprehensive way to lacustrine basins. In analogy to marine studies, when applied to lake systems, seismic stratigraphy can yield unique evidence on lake level fluctuations and rapid changes in the sedimentary system and facies (Mullins et al. 1996). Such changes are commonly due to climatic factors and, furthermore, the responses in lakes are likely to be much faster and more relevant than for ocean margins (Ariztegui et al. 2001a).

Studies of seismic profiling in lakes provide valuable information on the thickness, structure, tectonics, and extent of sedimentary patterns prior to coring. They offer direct support to sediment coring programs in order to select optimal sites for coring long sediment sequences with continuous palaeoclimate records. Seismic profiles allow to identify undisturbed sediment packages that can be used to retrieve continuous cores. They can also be used to correlate distinctive seismic packages among core networks and map the extent of lake level changes (Gilli et al. 2005; Anselmetti et al. 2009). Furthermore, without seismic stratigraphy, it may be difficult to recognize unconformities, slumps, or gaps in spatially limited core sections.

Mapping different seismic facies in volcanic lakes is ideal to distinguish sedimentary packages (Niessen et al. 1993). A succession of high-amplitude, parallel reflections, for example, defines layering within a distinct unit. Strong petrophysical signatures are useful to correlate reflections among coring-sites. Gas-rich zones are not penetrated by the seismic signal and appear seismically transparent. Seismic profiles are important to describe the irregular bottom structure of complex volcanic lakes, such as in the case of Yellowstone Lake (Morgan et al. 2003). Differences in the seismic thickness of sedimentary packages can be exploited in a targeted coring campaign. Thinned or eroded sequences can be cored for maximum age-depth recovery, whereas thicker units may provide higher resolution, or the timing and history of recurring events (Anselmetti et al. 2009).

In Lago Albano (central Italy), for example, the interpretation of high-resolution profiles allows the identification of major lake level changes and is critical for the correlation of different sedimentary cores (Niessen et al. 1993; Chondrogianni et al. 2004). Additionally, seismic information from across the basin provides a unique means to choose the best site for core retrieval in an area of the lake containing parallel reflections. This approach allows the recovery of the entire Holocene and Pleistocene sequence that can be further correlated with geochemical and biological proxies, and can be extended throughout the basin using the geometries determined by seismic profiling (Ariztegui et al. 2001b). Seismic information also allows to discard cores retrieved from the deepest part of the basin, where thick mass-flows or turbidites are detected.

An intensive and multiple seismic survey of Laguna Potrok Aike, southernmost Patagonia, Argentina, has provided critical information prior to the undertaking of a deep drilling program that has recovered ca. 50,000 years of continuous sediments (Anselmetti et al. 2009). Several seismic campaigns were carried out on the lake, as site surveys prior to the drilling, in order to determine (a) the sedimentary architecture of the lacustrine infill; (b) the prevalent geometries to reconstruct lake-level changes; and (c) to confirm the maar origin of the basin (Anselmetti et al. 2009; Gebhardt et al. 2011). While the high-resolution seismic profile was instrumental to reconstruct the most recent lake-level changes (Fig. 1), the air-gun and refraction surveys provide fundamental evidence about the total sedimentary infill and the geometry of the maar (Fig. 2). Thus, Laguna Potrok Aike seismic survey is an excellent example of the use of different seismic arrays and techniques to answer scientific questions pertaining to volcanic lakes and to solve a maximum of uncertainties prior to deep drilling.

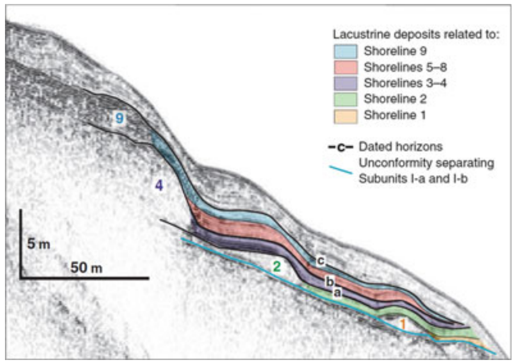

Fig. 1 High-resolution seismic profile from Laguna Potrok Aike with interpreted and numbered palaeoshorelines and identified seismic stratigraphic horizons (a–c). These lacustrine horizons can be linked seismically to palaeoshorelines (a = 2, b = 4, c = 9) allowing determination of palaeo-lake levels (modified from Anselmetti et al. 2009)

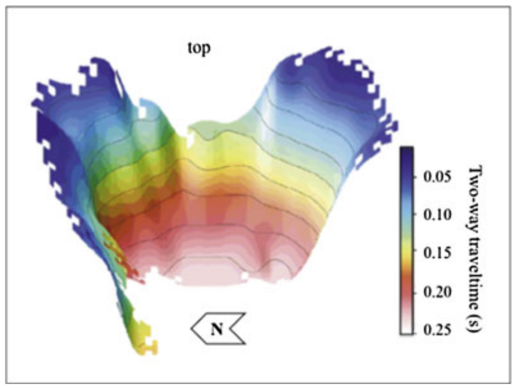

Fig. 2 3D view of the Potrok Aike crater reconstructed using refraction seismic. Depths are given in two-way travel times (modified from Gebhardt et al. 2011)

3 Dating Volcanic Lake Sediment Cores

Dating sedimentary deposits of volcanic lakes ideally follows a multiple dating approach (Fig. 3) encompassing several independent methods including radiometric, incremental and relative dating methods. The most commonly applied method in palaeolimnology is radiocarbon dating of carbon-bearing materials reaching

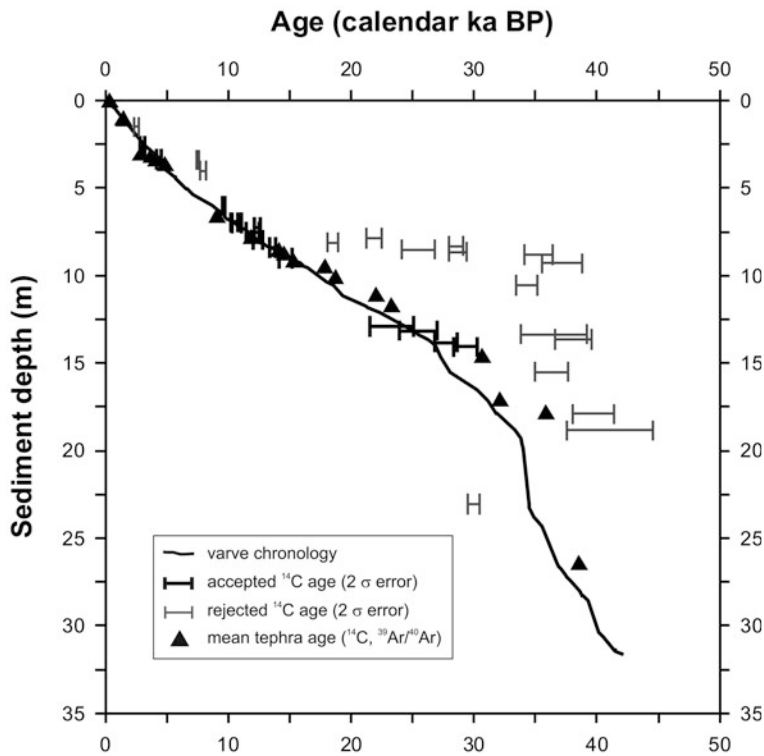

Fig. 3 Comparison of radiocarbon dates, varve chronology and tephrochronology of lake sediments from Lago Grande di Monticchio (southern Italy) for the last ca 40,000 cal years BP (modified after Wulf et al. 2004). ^{14}C dates obtained on bulk sediments and aquatic plant remains (*gray bars*) giving too old ages are rejected, while dates of terrestrial plant material (*black bars*) fit both the varve based age model and the tephrochronology

back in time to ca 40,000 years BP (Lowe and Walker 1997). Accelerator mass spectrometry (AMS) techniques allow dating of small samples (≤1 mg), but there are many inherent sources of errors related to ^{14}C dating in addition to the measurement uncertainty provided in the dating protocols, such as contamination with 'old' or 'young' carbon. Depending on the dated material, the resulting ages may vary significantly (Oldfield et al. 1997) which often is ignored in the error discussion. A particular problem might appear in dating sediments from volcanic lakes, where juvenile volcanic CO_2 rising from sublacustrine springs can be assimilated by submerged macrophytes resulting in too old dates (Hajdas et al. 1998). This problem can be avoided by dating exclusively terrestrial macrofossils, which are, however, rare in sediments taken from the central and deepest parts of volcanic lakes.

A crucial issue of ^{14}C dating is calibration into calendar year time scales. For the dendrocalibration period back to ca 12,500 calibrated (cal) years BP, a robust calibration curve is available (Reimer et al. 2009), but periods of constant radiocarbon ages, the so-called ^{14}C-plateaus, cannot be finely resolved and require additional increment dating, as counting fine annual laminations (varves).

Depending on local climate and lake morphology, varves tend to be rarely formed and preserved in lake sediments. However the typically deep, funnel-shaped maar and crater lake basins favour anoxic deep-water conditions, ideal for the formation and preservation of varves that can be used to establish precise chronologies (Zolitschka 2006). A wide range of different annual laminations, including siliciclastic, organic and evaporitic varves (Brauer 2004) might form, depending on the climate regime and catchment geology. Where they exist, varve counting of undisturbed sediments can be carried out on cleaned surfaces of split cores, photographs, X-radiographs and large-scale thin sections. Micro-facies analyses of thin sections provide crucial information on the seasonal deposition required for reliable recognition of sub-layer boundaries. Typical errors of varve chronologies include missing varves, as a result of erosion and sediment distortion, and counting uncertainties due to poor varve preservation. In the case of sediment sections without any varve preservation, age interpolations have to be carried out based on detailed sedimentation rate determinations in adjacent varved intervals (Zolitschka and Negendank 1996). The most recent decades of varve chronologies can be verified by complementary ^{137}Cs and ^{210}Pb dating (Lami et al. 1994; Alvisi et al. 1996) or historical documented marker layers like, for example, extreme floods or land-use changes. If varves are not preserved in sub-recent sediments, the established varve chronology is considered "floating" and must be anchored to the absolute time scale using isochronous markers such as tephra layers (Brauer et al. 2000).

Explosive volcanic eruptions produce huge amounts of ash material (tephra) which is distributed over large areas and deposited in terrestrial and aquatic environments. A tephra layer from a single, well-defined eruption can be unequivocally identified on the basis of geochemical 'fingerprinting' of volcanic glass using electron microprobe (major elements) and Laser-Ablation-ICP-MS techniques (trace elements) (Lowe 2011). The tephra layer can then be used as an isochronous time marker in sediment archives. The dating of tephra deposits in their proximal settings uses radiometric (^{14}C on buried and intercalated organic material) and radioisotopic techniques (i.e., K/Ar, Ar/Ar, U/Th on phenocrystals or volcanic glass), and the datum obtained can be imported to correlate tephras deposited in other archives.

Volcanic lakes are ideal for recording tephra events due to both the vicinity to active explosive volcanoes and the preservation of tephra layers in largely undisturbed and possibly varved sediments (e.g., Lago Albano, Calanchi et al. 1996; Lago di Mezzano, Ramrath et al. 1999). Combining varve counting and tephra analysis, exceptionally long stratigraphies can be developed for crater and maar lakes in favourable wind position to volcanic sources like, for example, Lago Grande di Monticchio (Wulf et al. 2004), San Gregorio Magno Basin (Munno and Petrosino 2007) and Sulmona Basin (Giaccio et al. 2009) in southern and central Italy.

Varve chronology has demonstrated to be particularly suitable for determining the duration of certain climatic intervals ranging from entire interglacials (Brauer et al. 2007) to short-term climate oscillations (Prasad et al. 2006) and the precise timing of abrupt climate changes (Brauer et al. 2008).

In palaeoclimate research, there is an increasing need to establish a network of key sediment archives from different regions and environments to obtain a more comprehensive picture of past changes. The precise correlation of various well-dated sediment records needs specific synchronisation techniques based on relative dating like biostratigraphy (Litt et al. 2009), palaeomagnetic data (see below) and tephrochronology (Lowe 2011).

4 Micro-Facies as Climate Proxy

Varved lake sediments are key terrestrial archives that provide detailed evidence on past environmental variations in response to climatic change or human impacts (Lamoureux 2001; Zolitschka 2006). While traditional geochemical, physical and biological analyses on discrete bulk samples allow, at best, reconstructions of past changes at decadal to sub-decadal resolution, varve thickness and integrated micro-facies analyses reveal information related to environmental and climatic changes at annual to seasonal scales (Brauer 2004). Microscopic analyses of varve sub-layers on large scale thin sections provide semi-quantitative information on both lake internal processes: for example, diatom blooms and endogenic mineral formation (calcite), as well as catchment processes through composition and structure of detrital matter transported into the lake. In addition, early diagenetic authigenic mineral formation (e.g., pyrite, vivianite) and sedimentological processes like mixing through bioturbation or degassing and internal reworking (slumping) can be traced at great detail. Recently developed µ-XRF element scanning methods provide

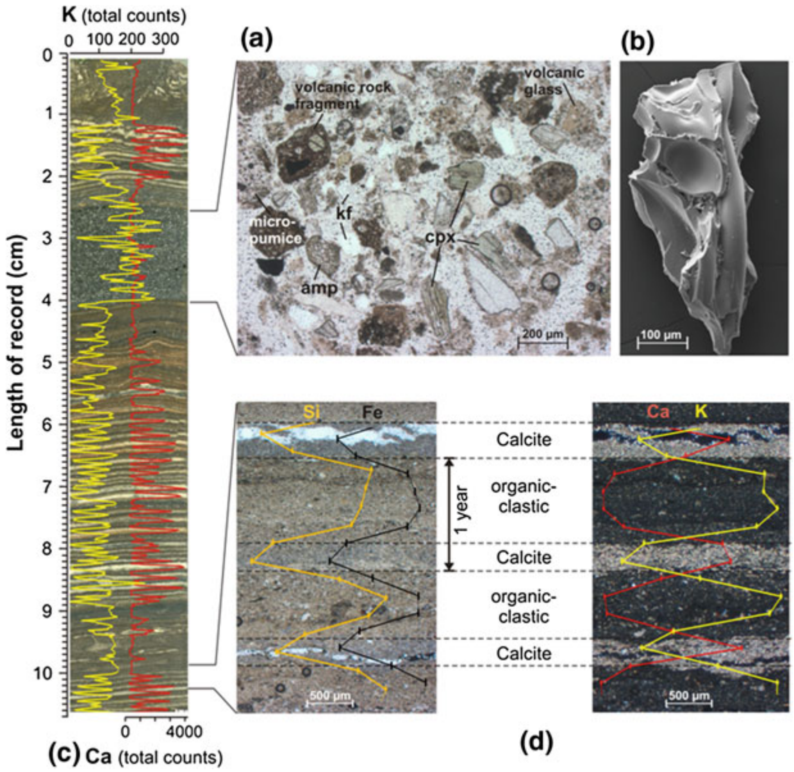

Fig. 4 Microscopic photographs of a varved sediment section from the Lago Grande di Monticchio containing a *tephra layer* from Vesuvius (southern Italy, ca. 35 ka). a Transmitted light photography of tephra components showing juvenile clasts (volcanic glass shards, micro-pumices), rock fragments and phenocrystals (*kf* K-feldspar, *cpx* clinopyroxene, *amp* amphibole). b SEM picture of a typical cuspate shaped volcanic glass shard used for microprobe analysis. c Large-scale thin section (polarized light) showing the elemental distribution of potassium (*yellow line*) and calcium (*red line*) obtained by µ-XRF measurements. Note that the tephra layer in this record (a) is identified by relatively high potassium concentrations. d Transmitted light (*left*) and polarized light (*right*) photographs of individual varves from the lower part of the sediment section. Varves are made up of alternating sublayers of autochthonous calcite precipitates (*summer layer*) and organic-clastic material (*autumn/winter layer*) which are reflected in high calcium concentrations and increased silica, iron and potassium intensities, respectively. *Photo courtesy* K. Wutke, GFZ Potsdam, Germany

complementary geochemical data at comparable sub-millimetre resolution leading to a significant extension of the proxy database and to an improved interpretation of sediment records. In particular, element scanning with vacuum µ-XRF analytical devices on impregnated sediment slabs that have been prepared for thin section fabrication allows precise linking of microscopic observations and high-resolution element data (Brauer et al. 2009). This novel integrative analytical approach allows detailed element profiling across individual varves and precise detection of tephra layers (Fig. 4), as well as other allochthonous sedimentation events like flood layers. Moreover, the detection limits, especially of abrupt climate changes and short to long-term changes in seasonality (Mingram et al. 2004), has significantly improved. Understanding the mechanisms and dynamics of abrupt and high-amplitude climate shifts in the past is crucial for assessing the probability of such events in the future. The onset of the last major climatic oscillation, the Younger Dryas cold phase, is exceptionally well documented in varved sediments from Meerfelder Maar (Eifel, Germany). Here, analysis of the micro-facies at sub-annual resolution, combined with high-resolution element scanning, allows for the identification of the transition from a calm, anoxic lake environment to a seasonally well-mixed and turbulent lake, indicating an abrupt increase in storminess during the autumn to spring seasons (Brauer et al. 2008).

Another key challenge in palaeoclimate research is to decipher changes in seasonality and understanding the driving mechanisms. This is particularly important for strongly seasonal climate regimes like the Asian monsoon systems. Micro-facies analyses and integrated μ-XRF scanning of varved sediments from the Sihailongwan Maar in northeastern China reveal long-term changes in seasonal dynamics controlled by the Southeast Asian monsoon. It is demonstrated that the warm early Holocene is characterized by a more pronounced inter-annual variability compared to the mid- and late Holocene (Mingram et al. 2004), indicating an intensified monsoon as a result of increased northern hemisphere summer insolation.

A future challenge of micro-facies analyses is to integrate comparably precise combinations with biological proxies into the present databases, mainly including sedimentological and geochemical data.

5 Oxygen and Carbon Stable Isotopes

Authigenic carbonates are often a major component of maar lake sediments and they provide material to develop a chemostratigraphy of the sequence with an excellent temporal resolution (Leng and Marshall 2004). Both $\delta^{13}C_{(carbonate)}$ and $\delta^{18}O_{(carbonate)}$ are excellent sources of information concerning lake productivity as well as changes in source of precipitation and hydrological conditions (Nelson and Smith 1966). In addition, the carbon stable isotope composition of the bulk organic matter, $\delta^{13}C_{(OM)}$, can be used to reconstruct changes in both sources of organic matter (Meyers 1994) and lake productivity (Schelske and Hodell 1995).

Changes of water temperature (mean summer) of the Late Glacial transition of Lago Albano (Italy), for example, are estimated using the $\delta^{18}O_{(carbonate)}$ compositions of authigenically precipitated calcite and valves of benthic ostracods (Chondrogianni et al. 2004). These calculated temperatures, however, are generally too high and in conflict with other ecological evidence in the same record. Although diagenetical overgrowths of calcite could not be excluded, an additional source could distort the original isotopic signal. It is proposed that the $\delta^{18}O_{(carbonate)}$ oscillations of authigenic calcite are not simply due to variations in water temperature, but additionally reflect changes in the $\delta^{18}O$ composition of precipitation and consequently of lake water.

To test the above hypothesis, lake-water temperature is also estimated using the oxygen isotopic composition in amorphous silica ($\delta^{18}O_{(opal)}$). These $\delta^{18}O_{(opal)}$ values reveal maximum water temperature changes of 8 °C between oxic and anoxic intervals, with abrupt changes of 4–6 °C occurring within 40–100 years. The trends in $\delta^{18}O_{(opal)}$ generally co-vary with the values of authigenic calcite, but are again in conflict with the ecological data, confirming the assumption of hydrologic variations overprinting the temperature effect, including changes in groundwater hydrology related to climate, human activities and volcanic activity (Telford and Lamb 1999; Funiciello et al. 2003). Changes in $\delta^{18}O$ composition of local precipitation may also occur, due to variations of ambient air temperatures and/or modifications in atmospheric circulation that shift the source of moisture (Fig. 5).

Another example of the application of stable isotopes to lacustrine sediments is Sacred Lake, a closed crater lake occupying a basaltic explosion crater in the humid mountain rain forest of Mount Kenya, East Africa. In this record the carbon isotopic compositions of the bulk organic matter along with those of specific organic compounds (e.g., n-alkanes, phenols) are used to reconstruct past changes in climate and carbon cycling (Street-Perrot et al. 2004).

Organic carbon isotopes are also used to characterize the Late Glacial and Holocene varved sediments of Holzmaar, Germany. They provide an outstanding record of lacustrine

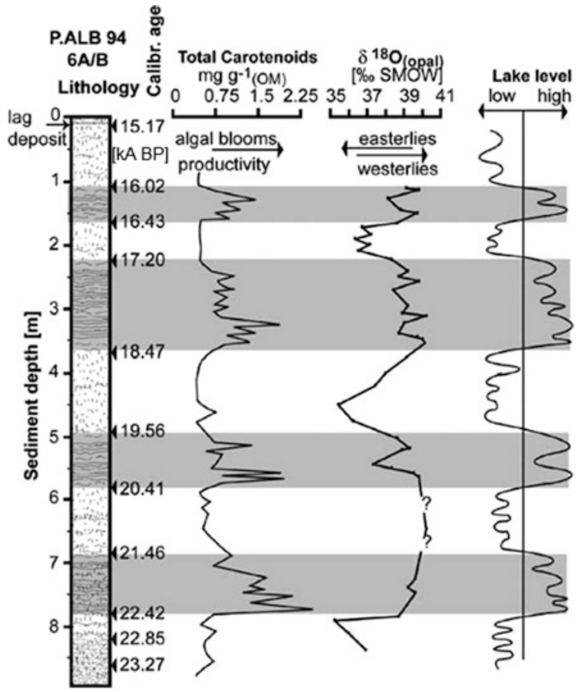

Fig. 5 Multi-proxy palaeoenvironmental records from Lago Albano: lithology, concentration of total carotenoids and $\delta^{18}O_{(opal)}$ as well as interpreted lake level fluctuations from a sediment core encompassing the last deglaciation (modified from Chondrogianni et al. 2004)

palaeoproductivity as well as palaeoenvironmental and palaeoclimatic information (Lücke et al. 2003).

Combined with proxies of lake response and of human activity in the catchments, isotope analysis can help to disentangle the effect on lakes and landscapes of climatic variability and societal development partially stimulated by climate variability itself (Wick et al. 2002; Ryves et al. 2011).

6 Magnetism

Since the application of rock magnetism to environmental disciplines (Thompson and Oldfield 1986), a number of studies demonstrate that the mineral magnetic-palaeoclimatic-environmental linkage reflects the control exerted by climate over magnetic mineral concentration and composition. The supply of magnetic minerals is dominated by catchment sources, but is influenced by weathering and erosion which are mainly under direct climatic control. Environmental magnetism is based on the sensitivity of iron compounds to physical-chemical changes, as iron oxides are among the most sensitive minerals to chemical and thermal transformations of the environment.

Magnetic susceptibility is the main magnetic proxy used for palaeoclimatic reconstruction in volcanic lake sediments. The morphology and depth of these lakes usually allow a rapid and continuous accumulation of sediments, and the drainage input is composed of volcanic sediments that contain a significant amount of iron oxides. Their mineralogy is then able to register the direction of the Earth magnetic field, a key issue for the chronology of the sediment by using the palaeosecular variation record (PSV).

In fact, PSV provides a detailed chronology independent of ^{14}C dating, for the last 10,000–100,000 years or more, and the palaeomagnetic record of volcanic lake sediments are used as a reference for the PSV in different continents. Barton and McElhinny (1981) obtained a master curve by stacking the declination and inclination results of three volcanic lakes for southeast Australia. Several volcanic lakes from Mexico are investigated to retrieve a palaeosecular variation record used for the age model of sediment cores (Chaparro et al. 2008).

The palaeomagnetic data from Lago Grande di Monticchio and Lago di Mezzano, in Italy, record secular variations reaching back 102 and 31 ka BP, respectively (Brandt et al. 1999). The comparison of biogenic and minerogenic sediment accumulation rates, reconstructed for a time window between 34 and 14 ka from both lakes, suggest synchronous periods with increased minerogenic deposition with enhanced erosion and runoff related to the existing hydrological and climatic conditions. Additional data from the late Pleistocene-Holocene sediments of Holzmaar, Germany, record large variations in magnetic mineral concentration through time. The relative contribution of magnetic components, as expressed by magnetic susceptibility, points to a correlation with sediment accumulation rate and non-arboreal pollen content that has been interpreted as representative of cooler conditions (Stockhausen and Zolitschka 1999).

A multi-proxy approach, well supported by palaeomagnetic and rock magnetic data, was used to study the record of cores collected in Lago Albano and Lago di Nemi (Italy, Rolph et al. 1996) as well as in Lac du Bouchet (France, Williams et al. 1996), spanning 30 and 300 ka, respectively. The magnetic signature of the Late-Glacial sediments of Lago Albano exhibits several intervals with low magnetic content, larger grain size and increasing contribution by antiferromagnetic minerals (Rolph et al. 1996, 2004; Vigliotti et al. 2010) (Fig. 6). The correlation with indicators of biological productivity suggests that these intervals were deposited under anoxic conditions driven by bacterial degradation of organic matter in coincidence with increasing lake level that witness short-term warmer climatic conditions occurring during the Late Glacial. The relevant change in magnetic parameters in the varved sediment indicates that these oscillations took place within few decades. Late-Holocene sediments are characterized by higher magnetic susceptibility than catchment rocks, pointing out to the presence of bacterial magnetite (Rolph et al. 1996, 2004; Vigliotti et al. 2010). The reliability of the palaeomagnetic

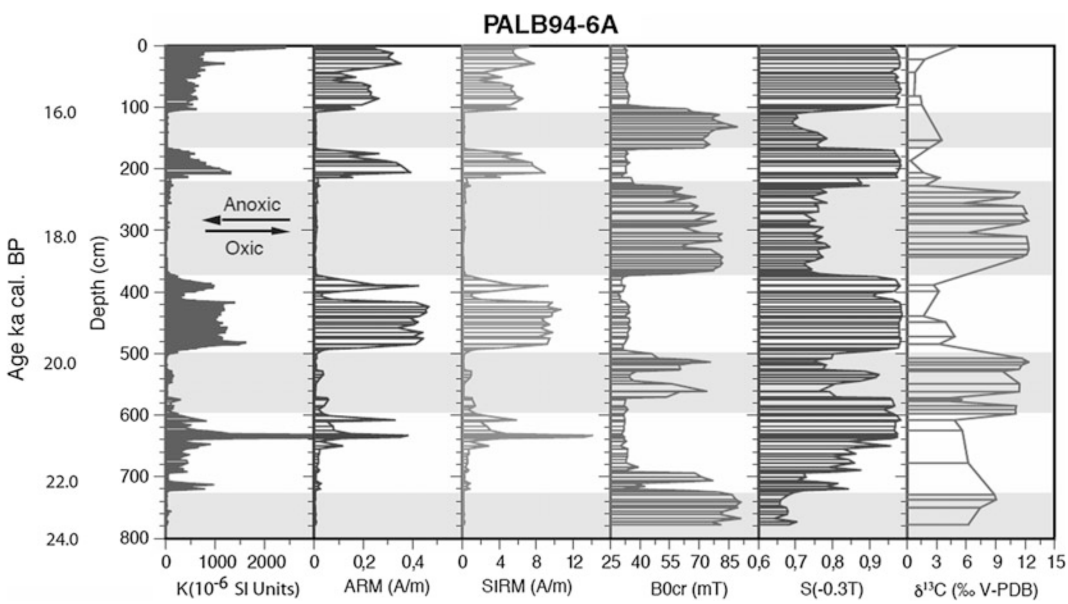

Fig. 6 Stratigraphic variation of bulk magnetic parameters (sediment core PALB94-6A from Lago Albano). *k* low-frequency magnetic susceptibility, *ARM* anhysteretic remanent magnetization, *SIRM* saturation high-field isothermal remanent magnetisation, *B0cr* back field remnant coercivity of the remanence, S(−0.3T): ratio: IRM–0.3T/SIRM, $\delta^{13}C$: deviation of isotopic concentration of ^{13}C (from Vigliotti et al. 2010)

record is also confirmed by Vigliotti (2006), who reports for the neighboring Lago di Nemi, a significant correlation of the PSV record with records obtained from historical lava flows from Etna and Vesuvius volcanoes.

The sediments from Lac du Bouchet are characterized by a detrital magnetic fraction with a composition dominated by titanomagnetite. During interglacials, dilution due to augmented input of catchment materials and diagenetic dissolution resulting from eutrophic conditions causes a decrease in magnetic susceptibility, reflecting climatic variability and strongly correlate with marine $\delta^{18}O$ isotope stages and sub-stages during the last 140 ka (Thouveny et al. 1996). The results from the adjacent Lac de Saint-Front yield a similar trend (Vlag et al. 1996). However, detailed studies of Eemian sediments from both lakes and from Lac Ribains indicate that local processes control the detrital and biogenic input and that variations in ferrimagnetic concentration cannot be interpreted by rock-magnetic results only (Stockhausen and Thouveny 1999).

As already observed by Dearing (1999), magnetic parameters correlate with both glacial-interglacial cycles and arboreal pollen concentration, indicating the role exerted by climate and vegetation on the delivery of the detrital particles to the lake sediments.

In spite of the active diagenesis observed at Lac du Bouchet and Lac de Saint-Front, the palaeomagnetic record is interpreted as representative of relative palaeointensity (Vlag et al. 1996; Williams et al. 1996) with minimum values occurring during the Laschamp, Blake and Iceland Basin geomagnetic excursions.

Maar lake sediments studied in equatorial-tropical Africa also suggest close relationships between climate and magnetic mineral assemblages. For example, Late Quaternary deposits from Lake Magadi (Kenya) yield a magnetic signature indicating the occurrence of dry conditions during the Younger Dryas that led to the separation of Lake Magadi from Lake Natron (Williamson et al. 1993). Mineral-magnetic proxies of erosion/oxidation cycles are observed in the sediments of Lake Tritrivakely (Madagascar): the mineral-magnetic properties are strongly controlled by erosional processes and high-coercivity ferric (oxyhydr)oxides characterize the period of low lake level, corresponding to dry periods, whereas they completely lack the siderite-rich laminated sediments deposited during periods of permanent and stratified water bodies (Williamson et al. 1998). In Lake Massoko (Tanzania), the comparison of sedimentary magnetic signature with catchment material shows three intervals corresponding to humid conditions (high lake level) characterized by increasing pedogenic processes and runoff during the last 45 ka (Williamson et al. 1999).

7 Palynological Studies

Pollen analysis is a central topic in palaeoecological reconstructions. After the pioneering work carried out in central Italy by Frank (1969) and Hutchinson et al. (1970), the first important palynological studies on volcanic lake sediments were undertaken in the late-1980s in Spain (Olot region, Pérez-Obiol 1988), France (Lac Ribains, de Beaulieu and Reille 1992) and Italy (Valle di Castiglione, Follieri et al. 1988). The results from these studies were very promising, as crater and maar lakes have well-defined catchments and little surface inflow, so sediment deposition is rarely disturbed by erosional phenomena. Sedimentation in these lakes is, therefore, fairly uniform, and laminated sediments are often present.

The aim of most palynological studies is to identify pollen evidence of terrestrial vegetation changes, comparing them to climate-driven modifications of lake hydrology and chemistry for the same area. Pollen analysis is intrinsically informative of the plant landscape in the region surrounding the lake. Differences in pollen productivity and dispersal, methods of pollination, past vegetation settings and human disturbance are variables that must be taken into consideration as major factors influencing trends of pollen curves (Faegri et al. 1989). Woodland cover and composition, wetlands, open areas, human environments including cultivated lands, pastures and settlement areas, may be reconstructed based on the observation of pollen percentages, and on objective inferences based on pollen concentration and influx. The pollen influx value is closely related to the abundance of a species around the site where its pollen is found (Berglund and Ralska-Jasiewiczowa 1986), but the calculation of influx requires a robust chronology. A decline in pollen concentration and influx is often interpreted as a signal of increased erosion in the catchment, generally as a result of forest reduction or clearance (Sadori et al. 2011).

At present, palynology of volcanic lakes has spread worldwide (e.g., in Oceania, Lancashire et al. 2002; in Asia, Mingram et al. 2004; in Africa, Ryner et al. 2007; in Europe, Litt et al. 2009 and in South America, Rull et al. 2010), spanning time intervals ranging from the Eocene to the last centuries.

Central and southern Italy is probably the area most covered by palinological studies covering the whole Holocene. From North to South, studied lakes, existing or drained, are: Lago di Mezzano (Sadori et al. 2004), Lagaccione (Magri 1999), Lago di Vico (Magri and Sadori 1999), Stracciacappa (Giardini 2007), Valle di Castiglione (Follieri et al. 1988), Lago Albano and Lago di Nemi (Lowe et al. 1996; Mercuri et al. 2002), Lago di Averno (Grüger and Thulin 1998), and Lago Grande di Monticchio (Watts et al. 1996; Allen and Huntley 2009). For this reason, we use this area as an example in the following discussion.

In Italy, as and in other Mediterranean countries (Wick et al. 2002) and in Africa (Ssemmanda et al. 2005), it can be difficult to discern between natural changes and human impacts. Figure 7 shows the example of two volcanic lakes (Lago Albano and Lago di Mezzano) that record similar vegetation changes at the end of the last Glacial and during the present interglacial (Mercuri and Sadori 2012). Humans have impacted these lakes since the Middle Bronze Age, as documented by archaeological remains of settlements along their shores. Chronologies of the cores have been assessed by several studies (e.g., Ramrath et al. 2000; Rolph et al. 2004) and a stratigraphical marker, the Avellino tephra layer is available in both sediment cores. New studies on the Avellino tephra, dated at 4,200–4,100 years BP in the previous two studies, suggest a younger age for this eruption (3,945 cal. years BP, Sulpizio et al. 2008; Sevink et al. 2011). We take the tephra occurrence as a stratigraphical marker useful for

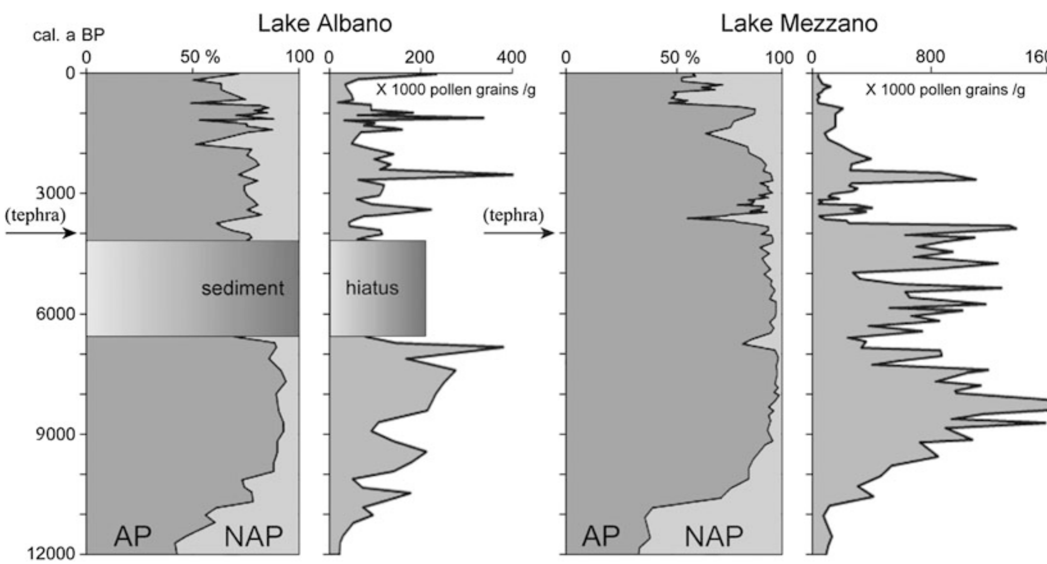

Fig. 7 Pollen records from Lago Albano (Mercuri et al. 2002) and Lago di Mezzano (Sadori unpublished). Pollen percentage (*AP* arboreal pollen, *NAP* non arboreal pollen) and concentration diagrams of Holocene age. The Avellino *tephra layer* is also indicated

core correlation. Few centuries after tephra deposition, a sudden forest change is inferred, indicating drier conditions. It is suggested that climate was the first agent of the shift toward aridity, actually visible in many Mediterranean pollen diagrams at ~4,000 cal. years BP. This is testified by some palynological evidences, such as arboreal pollen concentration that decreased by ca. 80 % in Lago di Mezzano and 60 % in Lago Albano, without any sign of increased fires. Aridity probably pushed human populations to settle along the lake shores, leaving signs of pile dwellings and causing strong modifications in an already open landscape (Sadori et al. 2004).

Since ~3,600 cal. years BP, signs of human activities are evident, such as the cultivation of cereals and legumes, increase in other anthropogenic indicators including *Olea*, forest clearance of selected taxa, fire and grazing activities. Some of these effects are also evident in Lago di Nemi and Lago di Vico. Then, between 2,900 and 2,700 cal. years BP, cultivated trees (*Juglans, Olea* and *Castanea*) spread simultaneously, together with cereals and weeds, suggesting that pre-Roman Iron Age populations had a significant impact on landscape (Follieri et al. 1988; Mercuri et al. 2002). At Lago di Vico, after the forest clearing which occurred during the Bronze Age, the cultivation of trees matches an enhanced forest cover. Finally, a '*Cannabis*-phase', i.e. a hemp pollen peak which followed the peaks of cultivated trees, marked Roman times at Lago Albano and Lago di Nemi, while the 'chestnut landscape' definitively spread at around 700 years BP (Mercuri et al. 2012).

These examples show how the combined interpretation of pollen percentage and influx data can be a robust tool for disentangling climate change and human impact (Sadori et al. 2011). To better identify the relationships between human activity, changes in landscape and in climate and lake response, pollen analysis can be included in multi-proxy analyses of chemical sedimentary parameters (e.g., isotopes) and non terrestrial biotic remains (Guilizzoni et al. 2000; Ryner et al. 2007).

8 Non-terrestrial Biological Records

A number of organisms living in lakes can leave identifiable remains that are used for palaeolimnological studies. A non-exhaustive list includes diatom frustules, algal and bacterial pigments, chrysophyte and dinoflagellate cysts, plant macrofossils, remains of Cladocera and of chironomid larvae, ostracods shells and sponge spicules.

Diatom frustules are the most used remains because they occur frequently, are well preserved, and allow taxonomic identification to species level. The distribution of most species is affected by water pH, salinity, nutrient level and habitat features. In volcanic lakes, diatom analysis is frequently combined with pollen analysis to infer regional climate variability and the consequent lake responses, or to verify and complement the climatic signal with an independent proxy. The presence and abundance of diatom species are used to infer past variability in pH (Lancashire et al. 2002), lake depth (Bradbury 2000; Mayr et al. 2005; Ryner et al. 2007), nutrient levels (Bradbury 2000; Mayr et al. 2005; Stebich et al. 2005), salinity (Gasse et al. 1995; Ryner et al. 2007; Ryves et al. 2011) and the length of winter ice cover (Stebich et al. 2005).

Chironomid head capsules are the second most used biological proxy: their distribution in lakes is influenced by chemical and physical factors, and their presence and abundance is used to infer past lake depth (Manca et al. 1996; Engels et al. 2011), nutrient level (Hoffmann 1993a; Manca et al. 1996; Engels et al. 2011), temperature (Hoffmann 1993a) or salinity (Ryner et al. 2007; Ryves et al. 2011).

Algal pigments are a promising proxy, allowing detailed reconstruction of phytoplankton development and primary productivity. They are surprisingly well preserved in sediments of tens of thousands of years old, although they tend to be degraded compared to the original pool (Leavitt 1993). Promisingly, pigments are used in the palaeolimnology of volcanic lakes (Guilizzoni et al. 2002; Skov et al. 2010).

Other macrofaunal remains, such as ostracod shells (Belis and Ariztegui 2004; Ryner et al. 2007; Gouramanis et al. 2010) or Cladocera head shields, ephippia, or resting eggs (Hofmann 1993b; Manca et al. 1996; Skov et al. 2010), can also be used for inferring past lake depth, salinity or nutrient status.

Alongside these mainly descriptive studies, quantitative inferences of past environmental condition from biotic assemblages are also performed in volcanic lakes: a transfer function, calibrated using data from a set of 30–100 lakes covering an environmental gradient is used along the core to shed light on past lake conditions (Birks 1998).

Specific data sets are developed for volcanic lakes, for example to deduce lake water conductivity from diatom assemblages (Mills and Ryves 2012). However, other regional data sets, not specifically based on volcanic lakes (Gasse and Tokaia 1983; Battarbee et al. 1998), have been used to infer nutrient status (Ryves et al. 1996; Rioual et al. 2007), pH (Barker et al. 2003), salinity (Rioual et al. 2007; Ryves et al. 2011) and lake level and hydrological changes (Rioual et al. 2007) from diatoms, salinity from chironomids (Ryves et al. 2011), ostracods (Gouramanis et al. 2010), and diatoms (Rioual et al. 2007; Ryves et al. 2011) and lake productivity from algal pigments (Guilizzoni et al. 2002).

Combining several biological indicators in a multi-proxy approach can provide a more detailed picture of past lake development. This was first used by Hutchinson et al. (1970) on Lago di Monterosi (Italy), and later by Guilizzoni et al. (2000) on Lago Albano, by Ryner et al. (2007) on Lake Emakat (Empakaai Crater, Tanzania) or by Ryves et al. (2011) on lakes Kasenda and Wandakara (Uganda), to understand the effect of climate variability and human impact on lake ecosystems.

As an example, the multi-proxy study on Lago Albano is summarized in Fig. 8. This study reported strong evidence for aperiodic oscillations in lake biota throughout the period ca. 28–17 ka BP, which can be interpreted as responses to climate forcing through its impact on lake levels and changing aquatic productivity. Productivity peaks can be inferred by the increase in algal pigment concentrations, the abundance of diatoms typical of eutrophic lakes, the presence of sulphur photosynthetic bacteria requiring an anoxic hypolimnion and the high number of animal remains. Chironomid species composition confirms that in these periods lake water was warmer and lake level higher.

9 Subsurface Biosphere

Most published studies in earth sciences dealing with the fast evolving field of geomicrobiology have been carried out in the marine realm. Their results point out the complexity of the chemical reactions associated with microbes that are mostly centered upon changes in redox conditions. These reactions often take place at lithological and geochemical boundaries and result in the formation of diagenetic minerals. The study of these complex interactions is often referred to as the "deep biosphere" and show that the Earth's biosphere extends far below the surface of our planet, including sediments and rocks of the deep ocean. Many microbes in this subsurface biosphere grow extraordinarily slow and under extreme conditions (Konhauser 2007). Studying them is critical in order to obtain a basic understanding of the physiological capabilities and biogeochemical consequences of sub-seafloor life. The source of energy for microbial growing is vast and the exact mechanisms behind them often remain elusive (Konhauser 2007; Inagaki 2010).

In recent years, similar geomicrobiological investigations into lacustrine basins have shown a substantial microbial impact on lake sediments (Jiang et al. 2007). Their study tends to be logistically easier than in their oceanic counterparts, providing analogues to certain marine environments and the ability to investigate a wide range of processes involving extremophiles (Mapelli et al., this issue).

Studies on the subsurface biosphere aim to constrain the physico-chemical conditions of microbially mediated precipitation/dissolution

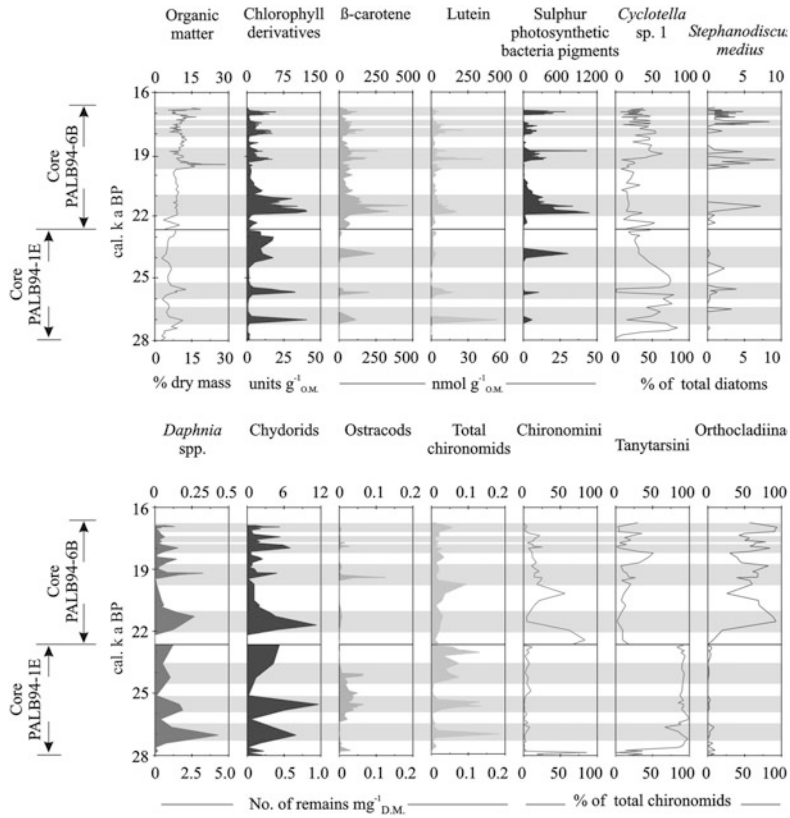

Fig. 8 Biological multi-proxy records at the base of Lago Albano cores PALB94-1E and PALB94-6B. *Dashed grey areas*, based on wide peaks that appear in most proxies, reflect high productivity (indicated by *algal pigments and diatoms*) and higher lake water level intervals. Note the different x-axis scales between the two for cores (from Guilizzoni et al. 2000, with permission)

reactions in the sediments deposited under contrasting and often extreme- environmental conditions (Inagaki 2010). These investigations include living microbial communities in the proximity of fluid/gas seeps and within the sediments to characterize the subsurface biosphere, emphasizing integrated studies of microbiology, geochemistry (pore waters), and mineral authigenesis/diagenesis. Authigenic minerals can be used as signatures of the prevalent conditions during their formation (Manning et al. 1991; Nealson and Stahl 1997).

Standard microbiological methods have been adapted to lake study to detect living microbial communities (e.g., DAPI: 4′,6-diamidino-2-phenylindole, microbial cell count, scanning electron microscopy, etc.). Molecular tools are also used to unambiguously identify the diversity and specific composition of microbial (bacterial and archean) communities. The micro-biota can be further investigated by analyzing the 16S rRNA gene clone library. The results of these investigations allow testing whether microbial communities directly contribute to precipitation and diagenesis of authigenic minerals as well as elemental recycling (Vuillemin et al. 2013).

A 100-m long core taken in Laguna Potrok Aike is used for a detailed geomicrobiological study and sampled in order to address a knowledge gap, related to the lacustrine subsurface biosphere (Vuillemin et al. 2010). The presence of adenosine-5’-triphosphate (ATP) is used as an indication of living organisms within the sediments, as it is not known to form abiotically, and it can be easily detected with high sensitivity and high specificity using an enzymatic assay:

$$\begin{aligned} &\mathrm{ATP} + \mathrm{Luciferin} + \mathrm{O_2} \\ &\quad \rightarrow \mathrm{AMP} + \mathrm{Oxyluciferin} + \mathrm{PPi} + \mathrm{CO_2} \\ &\qquad + \mathrm{Light} \end{aligned}$$

Light is emitted as a result of the reaction, which is detected by a photomultiplier.

The microbial activity in Laguna Potrok Aike sediments provides information on ongoing organic matter mineralization processes, and helps to understand the influence of microbes during early diagenesis (Vuillemin et al. 2013). This procedure could be easily and routinely applied, adding microbiological information, complementary to several standard lacustrine proxies, such as the stable isotope composition of authigenic carbonates and, organic matter, although the sampling protocol should avoid contamination.

10 Conclusions

Sedimentary records from volcanic lakes have the potential for detailed reconstruction of the natural and anthropogenic variability. A number of geographical areas are studied, such as Africa for understanding monsoon history, Mexico for the Southern Oscillation and Australia for phenomena not related to the continental mass of the northern hemisphere. The resulting data are crucial for testing Earth system models (Lenton and Kageyama 2012). In particular, we focussed on central and southern Italy, which represents a tantalizing challenge for palaeoclimatologists, since it is a critical area for understanding the pattern and periodicities of Mediterranean climate, and is affected by impacts of human activities over long timescales.

The combination of a broad range of physical, chemical and biological proxies is required to synthesise and compare lacustrine archives in order to decipher both the pattern and amplitude of climatic forcing and the response of aquatic ecosystems.

Volcanic lakes are interesting study sites to understand small scale climate variability using changes in pollen profiles and rock magnetic properties, whereas the lake response and human disturbance is reflected by limnic biota.

New techniques are continuously improving the ability to utilize lake sediments to deduce past lake conditions. For example, the subsurface biosphere studies, applied to a maar lake in Patagonia, provide information about diagenetic processes and organic matter mineralization processes occurring in the sediments, filling the gap in the knowledge of the role of microbial metabolism in these processes.

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