Micro-XRF-inferred depositional history of the Orakei maar lake sediment sequence, Auckland, New Zealand

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Abstract Lake sediment records offer insights into past climate and environmental changes. There are, however, few continuous lake sediment records from the Southern Hemisphere mid-latitudes that span the last glacial interval (LGI) and have the requisite chronological control and sampling resolution. Orakei maar paleolake in the Auckland Volcanic Field, New Zealand, is an exception, as it contains a high-resolution record of continuous lacustrine sedimentation from its formative phreatomagmatic eruption ~ 130 ka, until post-glacial sea-level rise breached the crater tuff rim and connected the lake to the sea ~ 9 ka. We used micro-XRF core scanning, dry bulk density, loss-on-ignition and visual facies descriptions to investigate the depositional history of Orakei maar lake as a response to regional and global drivers of climate change, and to erosional events in the lake catchment. The climate history of the lake was divided into six depositional phases: (I) Early warming with frequent in-wash events, followed by climate fluctuations coeval with marine isotope stages (MIS) 5e to mid-5c, (II) Warm, quiescent depositional conditions during mid-MIS 5c to 5a, (III) A colder, windier interval during MIS 4, (IV) Warmer conditions with dominantly autochthonous sedimentation during MIS 3, (V) Cold conditions followed by a slow temperature increase and the onset of sea-level rise during late MIS 2, (VI) Warm conditions that culminated in formation of a peat unit at the top of the Orakei lacustrine sediment sequence, which was terminated by an influx of massive marine muds into the basin at 9.75 ka. Comparison of the inferred climate evolution at Orakei with climate inferences from the global marine benthic MIS record during LGI shows general agreement, though inferred climate changes consistently occur earlier at Orakei than in the MIS. There is also general agreement in temperature changes inferred from the Orakei record and from other regional lake sediment records, but more detailed comparison requires additional proxy climate data such as pollen, organic geochemistry and biomarkers, to better understand discrepancies between some records. This study demonstrated the great potential of the Orakei record for paleoclimate inference and the applicability of micro-XRF core scanning data for addressing questions about paleoclimate and paleoenvironment. It also highlighted past intervals that require further study.

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Introduction

Late Quaternary terrestrial paleoclimate reconstructions are crucial to form a complete picture of events, processes, and drivers of the global climate system. In this context, the mid-latitudes of the Southern Hemisphere are an important, but insufficiently studied part of the global climate system and are influenced by both tropical and polar climate conditions (Alloway et al. 2007; Augustinus et al. 2012). Investigating past terrestrial environmental changes in the Southwest Pacific is intrinsically difficult, as large landmasses are few. However, maar lake basins in the Auckland Volcanic Field (AVF) of northern New Zealand contain the necessary sedimentological, climatological and environmental archives, spanning at least the last two glacial cycles (Augustinus et al. 2012; Shane and Sandiford 2003). Sediment cores retrieved from these deep, small-diameter lakes, with catchments essentially restricted to the crater rim, contain records of past climate and environmental changes as well as volcanic activity throughout the North Island of New Zealand (Molloy et al. 2009; Stephens et al. 2012a; Hopkins et al. 2015).

This study focused on Orakei Basin, a former maar lake that contains a complex sequence of rapidly deposited, continuous and finely laminated sediment that spans the whole Last Glacial Interval (LGI; Peti et al. 2020; Peti and Augustinus 2019). Here we describe geochemical variability recorded by high-resolution micro-XRF scanning of the sediment sequence of Orakei maar and present a reconstruction of regional climatic and local environmental conditions contained in the Orakei maar sediment sequence. This represents the first study of its type from a New Zealand lake sediment sequence that spans the whole Last Glacial Interval and demonstrates the utility of micro-XRF core scanning for reconstruction of sedimentological and climatic conditions archived in lake sediment.

The AVF is located in Auckland City, on the North Island of New Zealand (Fig. 1). The study site, Orakei Basin, is one of more than 50 volcanic centres of the AVF and one of at least six maars to have hosted a deep lake throughout its history (Augustinus 2016; Molloy et al. 2009; Peti and Augustinus 2019). Orakei Basin is presently a tidal lagoon, connected to the sea through sluice gates that artificially control the inflow and outflow, enabling regulation of water levels and periodic flushing (Fig. 1). The Orakei maar sediment infill records lacustrine conditions from the time of formation ~ 130 ka until ~ 9.75 ka (Peti et al. 2020), when post-glacial sea-level rise breached the crater rim, allowing mass influx of tidal mud (Hayward et al. 2008).

Materials and methods

Sediment core retrieval from Orakei maar and the construction of the composite stratigraphy and event-corrected depth for the sequence (ECD, m) are described in Peti and Augustinus (2019). The Orakei chronology (Fig. 2) is based on Bayesian age modelling of radiocarbon dates, tephra ages, luminescence ages and fine-tuning of relative paleointensity variations of the Earth magnetic field, manifested in magnetic properties (natural remanent magnetisation/anhysteretic remanent magnetisation). The detailed age-depth model is described in Peti et al. (2020).

Sediment dry bulk density (DBD) and loss-on-ignition (LOI%) were measured with a mean sampling resolution of ~ 4.5 cm, yielding on average ~ 7.3 samples per ka. DBD was acquired by drying a known volume of wet sediment and relating the dry mass to the volume (g/cm³). LOI%, as an indicator of organic matter, was acquired by baking a known mass of sediment at 550 °C and relating the mass loss to the initial mass (in %; Gale and Hoare 1991).

Micro-XRF core scanning

A micro-XRF, multi-element core scanner was used to irradiate split core surfaces with an X-ray source, generating energy-dispersive radiation from which relative element intensities and relative variations in coherent and incoherent radiation scattering were obtained. Micro-XRF core scanning records down-core elemental variation in the range Al to U (on the Mo X-ray tube) rapidly, non-destructively, and with very little sample preparation (Croudace et al. 2006; Croudace and Rothwell 2015).
Orakei maar lake sediment cores examined in the present study were scanned using an Itrax micro-XRF core scanner (Cox Analytical Systems, Gothenburg, Sweden) at the School of Environment, University of Auckland, New Zealand. Data were acquired for all cores with the Mo X-ray tube (at 30 kV, 55 mA) at 1 mm spatial resolution and 10 s exposure time/measurement interval. Selected Orakei sediment cores, representing all sediment facies types, were also scanned with the same Itrax core scanner, fitted with a Cr X-ray tube to enhance detection of light elements. A comparison of the scanning output using both anodes is presented in Electronic Supplementary Material (ESM) Figs. S1, S2. All subsequent analyses
described here are based only on the complete dataset obtained using the Mo X-ray tube.

Statistical techniques applied to the multi-element micro-XRF core scanning results

The Itrax output-dataset includes elemental intensities in the range from Al–U, depending on their presence and abundance in the sediment core. Many elements, however, may be dominated by noise and/or carry little environmental significance. We used the following elements for statistical analyses: Al, Si, P, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Zn, Br, Rb, Sr, Zr, Ba, as well as the inc/coh ratio. In lacustrine studies, Al, Si, K, Ti, Rb and Zr are often used as indicators of detrital input (Aufgebauer et al. 2012; Kämpf
et al. 2012; Kylander et al. 2011), whereas the inc/coh ratio is traditionally used as an organic matter indicator (Burnett et al. 2011; Jouve et al. 2013), though problems with this indicator have been identified (Woodward and Gadd 2019). Fe and Mn can indicate detrital input, but are more commonly used to indicate reducing conditions (Fe) or oxygenation of lake bottom water (Mn), most commonly as the Fe/Mn ratio (high = reducing conditions; Cuven et al. 2011; Haberzettl et al. 2007). P indicates nutrient enrichment (Corella et al. 2012), whilst S indicates aquatic productivity, dependent on trophic status, as well as sulphide production in anoxic bottom waters (Evans et al. 2020; Urban et al. 1999). Cl is prominent in marine salt and can thus indicate marine influence on the chemistry of the lake basin, such as via windblown salts (Nishri et al. 1999; Ruecker et al. 2014). A more detailed consideration of these elements and ratios, and their paleoenvironmental interpretation in the context of the Orakei maar lake record, is presented in the Discussion.

The DBD and LOI% datasets were linearly interpolated onto the micro-XRF dataset to match the downcore position of datapoints and enable application of statistical techniques without gaps in the joint dataset. The joint dataset was then linearly interpolated to 10-year steps to enable the computing-intensive techniques described below. All steps were performed in R version 4.0.2 (R Core Team 2021).

Stratigraphically constrained CONISS clustering

CONISS (constrained cluster analysis by the method of incremental sum of squares) clustering is commonly used on datasets for paleoenvironmental or paleoclimate reconstructions, including those produced by micro-XRF core scanning (Dietze et al. 2016; Evans et al. 2019). CONISS is a hierarchical clustering method with a further stratigraphic constraint developed specifically for stratigraphic research (Grimm 1987). Clusters are formed based on similarity of neighbouring samples and thus, clusters can only be constructed using contiguous depths. This is the data-driven equivalent of forming lithostratigraphic units from observed characteristics, as in Peti and Augustinus (2019), and was implemented in R package rioja 0.9–21 (Juggins 2017). The number of clusters that best represent the geochemical variation of the Orakei sediment sequence was determined from the broken-stick plot (Fig. S3).

Principal component analysis

Principal component analysis (PCA) performs a rotation of the variables, defining the multivariate data-set in such a way that the new axes (principal components) are orthogonal to each other. The principal components successively correspond to dimensions of maximum variance of the scatter of the data points (Borcard et al. 2018). The results can be visualised in a biplot in which covarying elements plot close to each other. Similar samples (measurement positions) cluster together and close to the dominant variables. The centralised log-ratio transformation was applied to all elemental counts before PCA to eliminate non-linear matrix effects, constant-sum constraints and obtain normally distributed data, following Weltje and Tjallingii (2008) and Weltje et al. (2015). PCA was then performed on scaled clr (centralised log ratio)-transformed elemental intensities in R with the prcomp function (R Core Team 2021) and visualised with the R package ‘factoextra’ (Kassambara and Mundt 2017).

Results

Downcore elemental variation in the Orakei sediment sequence

Sediment organic matter content (LOI%) mostly ranges between ~5 and 15% (Fig. 3). An increase from low values at the core base is followed by short-duration peaks at ~120 ka and 111 ka. LOI% displays high-frequency variability until the onset of a sustained decrease at ~70 ka (Fig. 3). LOI% values remain low before a sharp increase at 58 ka, with maxima of ~20% attained by 50 ka. A long-term decrease in LOI%, accompanied by high-frequency fluctuations, continues to the top of the studied section (~18 ka; Fig. 3). The variation in the inc/coh ratio resembles LOI%, although the high-resolution micro-XRF core scanning introduces more high-frequency fluctuations, resulting in some deviations between these records. This similarity between LOI% and inc/coh gives credibility to inc/coh being used as a first-order organic matter indicator (Burnett et al. 2012; Kylander et al. 2011).
but should only be used for broad inferences (Woodward and Gadd, 2019). Inc/coh was extended to the top of the Orakei sediment sequence, beyond the LOI% record, and highlighted a marked, step-wise increase in organic matter content starting at ~ 18 ka (Fig. 3).

Despite high-frequency downcore variability in DBD, some broad patterns can be identified (Fig. 3). DBD values are relatively high up to ~ 99 ka (Fig. 3), followed by abrupt reduction to lower values until ~ 70 ka, when a sharp increase in DBD is followed by higher DBD values until a sudden reduction at ~ 58 ka. Up to ~ 38 ka, DBD is very low, followed by highly fluctuating values and a steady increase from ~ 26 to 20 ka, after which a drop towards the top of the investigated section follows (~ 18 ka; Fig. 3).

Laminated facies units 10, 8, and 4 show consistently elevated log(Fe/Ti) values, whereas the silty units 11 and 9, as well as facies units 7 to 5, and 3 to 1 show lower log(Fe/Ti) values (Fig. 3). log(Rb/Sr) shows a strong increase from the core base into facies unit 13, followed by relatively steady values and another increase starting in facies unit 11 (Fig. 3). High log(Rb/Sr) values reached in facies unit 10 persist until the top of facies unit 9, then increase to a peak at ~ 40 ka. A relatively sharp decrease in log(Rb/Sr) leads to a distinct low around ~ 27 ka, coinciding with facies units 7 to 5, and subsequently increases steadily towards the top of the Orakei sequence (Fig. 3). From the core base up until ~ 115 ka, log(Cl/K) is relatively constant, followed by an increase to a maximum at ~ 105 ka in facies unit 11 (Fig. 3). High-frequency variability in log(Cl/K) persists up until ~ 40 ka (facies unit 8), fluctuating around a relatively stable mean value, with a steady increase to the top of the Orakei lacustrine sequence starting at ~ 40 ka and punctuated by an abrupt increase at ~ 27 ka (Fig. 3). Log(S/inc) is low at the core base, but increases abruptly at ~ 130 ka, followed by a steady decrease until ~ 97 ka (Fig. 3). Elevated log(S/inc) values persist until ~ 71 ka, when a sudden decrease is observed. Log(S/inc) remains low until a sharp increase between ~ 60 and 58 ka (Fig. 3). A long-term decrease in log(S/inc) until ~ 12 ka is interrupted by oscillations in the interval ~ 36 to 32 ka (Fig. 3).

CONISS clustering

Seven clusters were established in the stratigraphically constrained hierarchical clustering using the broken stick model (Bennett 1996) (Fig. S3). The stratigraphic extent of these seven clusters only aligns with the lithostratigraphic units of the Orakei sediment sequence (Peti and Augustinus 2019) in a few cases, in part a consequence of the different numbers of clusters/units (7 vs. 14), but also because of changes in sediment geochemistry that are independent of visual changes, and because of visual changes accompanied by insignificant chemical changes. Cluster 1 spans all of facies units 1 to 7, as well as parts of unit 8a (Fig. 3). The short cluster 2 relates to a section within facies unit 8a, not separated by the visual facies units. Cluster 3 spans the remainder of facies unit 8, with its lower boundary almost aligning with the facies unit 8/9 boundary. Cluster 4 spans most of facies unit 9 and parts of unit 10, whereas cluster 5 spans the remainder of facies unit 10, with the CONISS cluster and facies unit boundary aligned at ~ 98 ka (Fig. 3). Cluster 6 includes several facies units, reaching from the top of unit 11 to the base of facies unit 13, whilst cluster 7 spans unit 14 to the base of the Orakei sediment sequence (Fig. 3).

Principal component analysis

PCA reveals geochemical elements that display similar trends and enables dimensionality reduction of the complex dataset. Principal component (PC) 1 explains 23% of the overall variance contained in the Itrax micro-XRF dataset and is dominated by LOI% (negative) with Ti, Si, Zn, K, Rb, Zr being dominant in the positive direction of PC1 (Fig. 4). This observation suggests that PC1 predominantly records a difference between organic (PC1 negative) and inorganic (PC1 positive) sediment components. PC2 explains an additional 16% of the overall variance contained in the Itrax micro-XRF dataset, with Sr, Zr, Rb and Cl dominantly negative on PC2. Mn, Fe and Cr are dominant positive elements on PC2 (Fig. 4). This observation suggests that PC2 predominantly differentiates...
between allochthonous (PC2 negative) and autochthonous (PC2 positive) sediment (Fig. 4).

The cluster association of the seven CONISS clusters with geochemical elements can also be investigated in the PCA biplot (Fig. 4). Cluster 1 shows a large spread in the biplot, with approximately one half of it strongly negative on PC1 and highly correlated with LOI and DBD, whereas the other half plots close to the centre of the biplot (Fig. 4). Cluster 2 is positive on PC1, tends to be mostly positive on PC2, and is mainly associated with elements such as Mn, S, and Fe, which indicate sedimentation dominated by in-lake processes. Cluster 3 is approximately neutral on PC1, but strongly positive on PC2 and highly associated with Cr, thereby indicating a dominance of autochthonous sedimentation during this cluster. The spur of datapoints in the upper left quadrant of the biplot relates to the short interval of cluster 3 that covers the uppermost part of facies unit 9 (Figs. 3, 4), which appears to be chemically different from the rest of the cluster. Cluster 4, being very similar to cluster 6 and 7, is slightly positive on PC1 and negative on PC2, indicating mostly inorganic, allochthonous sedimentation, defined by clusters dominated by the detrital elements Sr, Ca, Zr, Rb, K, and Ni (Fig. 4). Cluster 5, in turn, is similar to clusters 2, 3 and dominated by autochthonous sedimentation.

Consequently, it appears that the Orakei sediment sequence can be separated into three sediment types (Fig. 4): (1) detrital, inorganic, in-washed sediment (dominant in clusters 4, 6, 7); (2) inorganic, autochthonous sediment (dominant in clusters 2, 3, 5) and (3) highly organic sediment (younger part of cluster 1).

Discussion

Micro-XRF datasets as paleoclimate and paleoenvironmental proxies

Micro-XRF datasets have been used widely for paleoclimate and paleoenvironmental inference, with many elements or elemental ratios used as indicators of a variety of processes or conditions, depending on the study context and location (Davies et al. 2015; Evans et al. 2020; Kaboth-Bahr et al. 2019; Kemp et al. 2020; Kylander et al. 2011). Drawing on studies and observations similar to those in the micro-XRF dataset from Orakei maar, we used four elemental ratios, as well as the first two principal components (PC), to reconstruct the sedimentation history of the Orakei maar lake sequence.

Unkel et al. (2010) and Fernández et al. (2013) used the Rb/Sr ratio to indicate dominance of chemical weathering over physical weathering, since Rb is associated with detrital input (Kylander et al. 2011), whereas Sr tends to be more mobile under warm, moist conditions and can be precipitated in situ as SrCO₃ (Burn and Palmer 2014). Chemical weathering is favoured over physical weathering in warmer and moister conditions, and hence, we interpret the log(Rb/Sr) ratio predominantly to indicate a difference between warm and moist conditions (high) and cool and dry conditions (low). A common indicator for redox conditions is the Fe/Mn ratio (Corella et al. 2012; Cuven et al. 2011; Davies et al. 2015). We follow the interpretation of Aufgebauer et al. (2012), in that Ti is a relatively immobile element of detrital origin, whereas Fe forms relatively stable FeS mineral phases under reducing conditions, given sufficient S availability. As with Lake Prespa (Aufgebauer et al. 2012), S is present in Orakei maar and correlates relatively well with the log(Fe/Ti) ratio (Fig. 3). Hence, we consider high log(Fe/Ti) ratios to indicate reducing/anoxic bottom-water conditions, implying little or no mixing of the water column, with low log(Fe/Ti) ratios indicating opposite conditions. Thus, we interpret high log(Fe/Ti) ratios to indicate a deep lake and/or reduced windiness.

Cl can indicate organic matter content (Hahn et al. 2014), but in the Orakei record has little or only a very weak correlation with LOI% (Fig. 4). This behaviour suggests an alternative source for Cl in the Orakei sediments, which could be volcanic deposits or marine salts (Nishri et al. 1999; Ruecker et al. 2014). The most likely source for Cl is salts in sea spray from adjacent Waitemata Harbour (Fig. 1c). Contrary to Evans et al. (2019), we consider higher Cl to indicate increased sea-spray influence and normalized Cl to the detrital element K. Therefore, higher log(Cl/K) appears to indicate either higher sea-level, hence a closer shoreline to
the Orakei maar lake, and/or increased windiness to transport Cl-containing salts into the lake basin in the form of sea spray. Since S indicates aquatic productivity, depending on trophic status (Evans et al. 2020; Urban et al. 1999), we consider high log(S/inc) ratios to indicate high nutrient availability in the Orakei maar lake, a stable water column and anoxic bottom-water conditions. The striking resemblance of the log(S/inc) curve to the reconstructed global temperature variations over the studied time interval (Fig. 5) suggests that nutrient availability is driven primarily by temperature changes, so that the log(S/inc) record serves as a temperature proxy.

PC1 differentiates between organic (negative) and inorganic (positive) material. The Orakei sediment sequence is only highly organic in its top part (~12 ka and younger), dominated by a peat deposit with abundant macroscopic plant remains and a very dark brown colour. Whereas PC1 predominantly reflects the distinction between lacustrine sediment and peat, it may also indicate warmer temperatures, which favour accumulation of organic-rich sediment. PC2 differentiates allochthonous (negative) from

![Figure 5](image-url)  
**Fig. 5** PC1, PC2, important micro-XRF ratios (grey) with 100-point running mean (red; equivalent to approximately 140 years) and their interpretation alongside the CONISS clusters from Orakei maar with six depositional phases and interpreted environmental and climate conditions. MIS: Marine Isotope Stages from Lisiecki and Raymo (2005). Blue and red shading indicates time intervals of cooler and warmer conditions, respectively, referred to in the text. Sea surface temperature (SST) centred around a zero mean from Shakun et al. (2015). Relative sea level (RSL) variation compared to today from Rohling et al. (2009)
autochthonous (positive) modes of sedimentation in the Orakei maar lake as described above. Hence, we interpret PC2 to reflect predominantly sedimentation dynamics, which may be controlled by local, regional or global climate factors.

Stratigraphy of the Orakei maar lake sequence as a response to catchment evolution and climate change

The Orakei sediment sequence was separated into six depositional phases based on the CONISS clusters, as well as down-core geochemical and sedimentological variability (Fig. 5). The chemical composition, as well as visual and physical properties of the sediment, enabled a broad-scale reconstruction of the depositional history of the Orakei maar lake and sediment sources, which in turn enabled interpretation of climate conditions at the time of sediment deposition. In conjunction with the age-depth model from Peti et al. (2020), first-order paleoenvironmental reconstructions are provided and compared to global and regional climate records. These reconstructions and comparisons are expected to be further refined with forthcoming results from ongoing pollen, stable isotope, biomarker and high-resolution micro-facies investigations.

Phase I (~130–97 ka)

The earliest phase of deposition on top of the basaltic ejecta and pieces of country rock from the creation of Orakei maar at ~130 ka (Peti and Augustinus 2019) was dominated by low lake level (oxic conditions, no laminations in facies unit 14), little biomass production (low LOI%, Fig. 2), and comparatively cooler and drier conditions, followed by strong warming at ~130 ka (Fig. 5). At the transition from facies unit 14 to 13 (~128 ka), the sharp onset of laminations suggests abrupt lake deepening and development of anoxic or sub-oxic bottom water, concomitant with highest temperatures (based on log(S/inc)) of the studied record at ~127–125.5 ka (Fig. 5). High-frequency variability in log(Fe/Ti) and negative loadings on PC2 suggest that allochthonous sedimentation, sourced mainly from the crater rim, caused frequent mixing and thus recurring oxygenation of the bottom waters.

The interval 111–97 ka was characterized by frequent coarse-grained bands, inferred to result from high-energy sediment influx events, and comparatively cooler and drier conditions accompanied by marine influence on the lake sediment chemistry, in the form of wind-blown salts (Fig. 5). Greater windiness at this time can explain the input of Cl into the lake basin, since cool temperatures suggest a lower sea level at that time. Increased windiness during likely drier and cooler climates may also be the reason for increased allochthonous sediment input. Since the catchment boundary for Orakei maar was essentially limited to the tuff ring, mass-flow deposits from the rim were favoured by the reduced presence of stabilizing plant growth combined with storm-driven sediment influx.

Phase II (~97–73 ka)

The transition to phase II was characterized by warming and an abrupt change to autochthonous deposition and sub-oxic to anoxic bottom-water conditions (Fig. 5). The mode of sedimentation in this phase was uniform until ~73 ka and was dominated by high autochthonous biological productivity under anoxic bottom-water conditions (PC 2 positive, high log(Fe/Ti), high log(S/inc) and fine laminations). Despite a higher sea level, the marine influence in the form of wind-blown salts (log(Cl/K)) was low, indicating reduced windiness that enabled persistence of anoxic bottom waters, associated with a deep, stable, lake water column (Fig. 5).

Phase III (~73–60 ka)

The onset of phase III aligned with an abrupt change in dominant sediment geochemistry from autochthonous to allochthonous (Fig. 5). Phase III resembled the later stage of phase I, with dominant in-wash from the crater rim slopes caused by cooler and drier conditions (reduced stabilizing plant cover) and increased windiness inferred from elevated sea spray (log(Cl/K)). These indicators supported water column mixing, lower lake level and more oxic bottom-water conditions in Orakei maar lake over this period (Fig. 5).

Phase IV (~60 ka–31 ka)

Phase IV resembled phase II, with dominantly anoxic bottom-water conditions, warmer inferred
temperatures, and little marine influence apparent in the Orakei sediment record. However, the mode of sedimentation was dominantly autochthonous in phase IV and associated with higher nutrient availability and warmer and/or more humid conditions (Fig. 5) compared to phase II. A more varied interval of geochemical composition in the Orakei sediments occurred towards the end of phase IV, coinciding with CONISS cluster 2 (~37.5–33 ka), which is characterized by greater variability in the micro-XRF-based geochemical signatures and a short interval of sediment in-wash with no visible change in lithology (facies unit 8a, Fig. 5). This event marked a temperature decline and an onset of increased sea spray (higher log(Cl/K), Fig. 5).

Phase V (~31–18 ka)

Phase V was dominated by cold conditions, with coldest temperatures at ~29 to 26 ka (blue in Fig. 5). Warming followed until ~21 ka, before cold temperatures returned until 18 ka (blue in Fig. 5) Intervals of slightly warmer temperatures in this phase correlated with increased sea spray (Fig. 5) although we cannot exclude an erosional signature influencing the log(Cl/K) ratio during facies unit 3, which is characterized by fluvial sedimentation associated with Pourewa Stream breaching the crater rim (Fig. 1). In facies unit 3, a large amount of sediment (6.85 m thickness) was deposited rapidly, and associated with significant shallowing of the Orakei lake basin. At the transition from facies unit 3 to 2 (~17.9 ka), it appears that the Pourewa Stream either changed course or dried up, as dominantly coarse-grained sedimentation ceased abruptly (Peti and Augustinus 2019).

Phase VI (~18–9.8 ka)

The onset of phase VI was marked by an abrupt change from inorganic to highly organic sediments, based on a sudden change from positive to negative PC1 and alignment with the base of facies unit 2 (massive sediment with some signs of bioturbation; Peti and Augustinus 2019). Increasing marine influence and warmer temperatures from ~18 ka onwards are commensurate with rising sea level. This trend agrees with Termination I at 18 ka and subsequent glacio-eustatic sea-level rise. Throughout phase VI, Orakei maar lake became increasingly oxic, indicating decreasing lake water depth and water-column mixing, driven by sediment infill during the latter part of Phase V. By ~12.5 ka the hydrosere succession from a freshwater aquatic system to a terrestrial environment had reached its maximum, with the terrestrial peat of facies unit 1 (PC1; Fig. 5). After depositional phase VI, post-glacial sea-level rise caused a sudden breach of the crater rim ~9.75 ka, depositing 18.6 m of marine mud in the Orakei maar and opening its present-day connection with Waitemata Harbour (Fig. 1).

Comparison with global and regional paleotemperature records.

Paleoclimate records that span a similar time frame and occur in the same or nearby climate zones to Orakei Basin are few. Consequently, we undertook comparisons with both global and regional records of paleotemperature.

Marine isotope stages (MIS), based on benthic δ18O values, are used widely, even in non-marine settings, as a global reference for the timing and magnitude of glacial, interglacial, stadials and interstadials (Lisiecki and Raymo 2005). Hence, we compared the relative temperature reconstruction at Orakei maar paleolake (based on the log(S/inc) and log(Rb/Sr) ratios), using the age model established in Peti et al. (2020), to the MIS with their respective ages (Lisiecki and Raymo 2005; Fig. 5).

Okarito Pakihi in South Westland (Fig. 1a) is a >10-m-deep, moraine-impounded peat bog on the South Island of New Zealand, beyond the limits of LGM ice advance (Vandergoes et al. 2005). A basal age for the Okarito Pakihi record during MIS 6 is assumed, based on a deepest datable point of 127 ± 29 ka and a lithological change interpreted to have been the result of a strong climate shift, such as a glacial/interglacial transition (Vandergoes et al. 2005). Hence, it matches closely the age range of the Orakei maar record—though possesses far lower resolution. The location of Okarito Pakihi, west of the Southern Alps and in the direct path of the westerly winds, as well as its proximity to glaciers, provides an environmental setting different from that of Orakei. However, given the sparsity of terrestrial records in

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New Zealand that cover this age range, a comparison between Orakei and Okarito Pakihi is warranted.

Onepoto and Pupuke maars in the AVF have histories similar to Orakei maar (Fig. 1). Both maars are older than Orakei, but Pupuke is the only AVF maar that is an extant lake (Augustinus et al. 2006; Shane and Sandiford 2003; Stephens et al. 2012a). Onepoto was breached by post-glacial sea-level rise at a time similar to that for Orakei maar (Augustinus et al. 2011, 2012). Because of chronological difficulties, dating the Onepoto and Pupuke sequences beyond the radiocarbon limit of ~50 cal ka meant that for the most part only the well-dated <45-ka sections of the sediment sequences contained in these two maars have, as yet, been the focus of paleoclimate analyses (MIS 4 and younger in Onepoto; ~45 ka (above the Rotoehu tephra) to present in Pupuke).

MIS 5 (130–71 ka)

Phases I and II at Orakei align approximately with MIS 5 (Fig. 5). Warmer temperatures at Okarito Pakihi during MIS 5 were inferred from pollen taxa indicating forest expansion, with two intervening intervals of more dominant montane-subalpine shrubland indicating cooling. Vandergoes et al. (2005) interpreted these oscillations to represent the subdivisions of the marine isotope record into substages 5e to 5a. Generally warmer temperatures for MIS 5 are also inferred at Orakei maar based on log(S/inc), but the a-e substages do not stand out as clearly as at Okarito (Fig. 5).

Considering uncertainties in dating, the peak of MIS 5e at 123 ka aligns with the inferred warmest temperatures at Orakei at ~127–125.5 ka (Fig. 5). MIS 5e is considered to have been warmer than today and certainly the warmest interval of the last 130 ka, until the early Holocene (Lunt et al. 2013), which agrees with the Okarito temperature interpretations (Fig. 5). The peak of MIS 5d at 109 ka centres approximately on a cooler interval between 112 and 104 ka at Orakei (Fig. 5). The peak of MIS 5c at 96 ka aligns with a temperature peak, based on log(S/inc), during generally warmer conditions between ~97.5 and ~88 ka (Fig. 5). Three additional temperature peaks that occur during this warmer interval do not appear to be related to a MIS peak, although they are of similar magnitude (Fig. 5). The peak of MIS 5b at 87 ka occurs within a relatively uniformly cooler interval at Orakei from ~88 to 84 ka (Fig. 5). The peak of MIS 5a at 82 ka aligns again with a small peak in temperature at Orakei, based on log(S/inc), but warmer and more persistent warm conditions occurred in the outgoing MIS 5a, between ~76 and 73 ka (Fig. 5).

Additionally, the apparent five subdivisions of MIS 5 give further credibility to log(S/inc) as a suitable temperature proxy in this setting and time-frame, but require refinement using more reliable temperature proxies derived from pollen, i.e., pollen-inferred mean annual air temperatures (Wilmshurst et al. 2007), and from biomarkers, e.g., GDGTs (glycerol diakyl glycerol tetraethers; Zink et al. 2010).

MIS 4 (71–57 ka)

Phase III aligns relatively well with the colder stadial MIS 4 (Fig. 5). MIS 4 to MIS 2 are dominated by cold temperatures, with frequent ice advances at Okarito Pakihi (Vandergoes et al. 2005). Similarly, in Onepoto, temperatures cooler than today were inferred for the period between 76 and 26 ka (latest MIS 5 to earliest MIS 2) based on pollen assemblages lacking warm-indicator Holocene taxa (Shane and Sandiford 2003). These general conditions align broadly with the temperature reconstruction for Orakei (Fig. 5). A thermal minimum at Onepoto is inferred at ~64.4–60.5 ka (darker blue in Fig. 5; Shane and Sandiford 2003), which agrees with low temperatures at Orakei during MIS 4, although the joint log(Rb/Sr)- and log(S/inc)-inferred temperature reconstruction for Orakei shows a division in two of MIS 4, with especially cold conditions from ~72 to 69 ka and from ~66 to 61 ka (lighter blue in Fig. 5). Pollen studies at Orakei and higher-resolution work at Onepoto will shed light on whether this discrepancy is real, reflects the imprecision of the XRF-based temperature inferences, or whether the simple, linear-interpolation age model in Shane and Sandiford (2003) is inadequate for such comparisons.

MIS 3 (57–29 ka)

Phase IV aligns approximately with the warmer interstadial MIS 3 (Fig. 5). Some climate amelioration during generally cool conditions is evident in increased tree pollen during MIS 3 at Okarito Pakihi (Vandergoes et al. 2005), similar to that inferred from
the Orakei temperature record. The maximum for tree pollen was reached around 52 ka at Okarito Pakihi (red in Fig. 5). At Orakei, the log(S/inc) indicates slight cooling at that time, with the log(Rb/Sr) indicating a very minor change towards warmer/wetter conditions, but a warmer interval ~50 ka (Fig. 5).

**MIS 2 (29–14 ka)**

Phase V aligns closely with the glacial MIS 2, but MIS 2 extends approximately halfway into the warm phase VI (Fig. 5). MIS 2 was still dominated by cold temperatures with frequent ice advances at Okarito Pakihi (Vandergoes et al. 2005). Alloway et al. (2007) defined the last glacial coldest period (LGCP), which lasted from 28 to 18 ka, as the coldest period of the last glacial-interglacial transition and postglacial/Holocene periods, including the LGM sensu strictu, in the North and South Island of New Zealand. The LGCP from 28.8 to 18 ka (blue in Fig. 5) was also observed at Pupuke (Stephens et al. 2012b) and Onepoto (Augustinus et al. 2011, 2012). This interval of cold, dry and windy conditions aligns well with cold phase V at Orakei (Fig. 5). Additional short-term climate fluctuations were identified at Pupuke, with coldest conditions inferred at 27.8–26 ka and 22–19 ka (darker blue in Fig. 5, Stephens et al. 2012b). These colder phases also stand out in the Orakei log(Rb/Sr) record, but are not clearly apparent in the log(S/inc) record (Fig. 5). Between 25 and 23 ka, somewhat warmer interstadial conditions were inferred at Onepoto (Augustinus et al. 2011; Sikes et al. 2013), which are not supported by the XRF record from Orakei, where only a slight recovery could be observed between the intervals of coldest temperatures from 26 to 22 ka (light blue in Fig. 5).

**MIS 1 (19–0 ka)**

The current interglacial MIS 1 aligns with the remaining phase VI, with the MIS 2/1 boundary marked by a sudden increase in nutrient availability and thus likely a sudden temperature increase at Orakei (red in Fig. 5). Post-Termination I climate amelioration at ~18 ka occurred at Okarito, Onepoto and Pupuke as well as at Orakei. A warmer interval from 18 to 10.2 ka (red in Fig. 5) was also observed at Pupuke (Stephens et al. 2012b), in agreement with observations at Onepoto and Orakei. A climate reversal during generally warming conditions (red in Fig. 5) was observed at Pupuke at 14.5–13.8 ka, coeval with the Antarctic Cold Reversal (ACR; blue in Fig. 5; Stephens et al. 2012b). A decrease in log(S/inc) immediately followed the time interval of the ACR in the Orakei record (Fig. 5) and may indicate cooling. However, given the chronological uncertainties, it is possible that the reduction in log(S/inc) indicates the ACR at Orakei, though this possibility needs refinement with independent pollen and/or biomarker-based temperature reconstructions. Furthermore, the age models from Pupuke and Onepoto maar lakes were developed with older radiocarbon calibration curves and tephra ages that are currently being refined. A more detailed comparison of these intervals in the post-Termination I interval is only worthwhile after all records are aligned using the same chronological foundation.

Throughout the Orakei record, the depositional phases commenced earlier than the MIS, even considering the uncertainty of the Orakei age model, which shows a mean 95% confidence range of 1.43 ka and reaches a maximum 95% confidence range of 3.23 ka at 59.23 m ECD (Peti et al. 2020). These offsets have several possible explanations: (1) Subjectivity in deciding where to place boundaries between depositional phases—though they were generally chosen to align with abrupt micro-XRF-based geochemical changes, (2) Problems with the age model established in Peti et al. (2020). However, if this were the case, the offset should be much smaller in the section younger than ~45 ka, which has much greater age resolution than the older section, which should show much higher offsets between onsets of the Orakei depositional phases and the MIS, (3) New Zealand may consistently record climate changes earlier than other locations, as occurs for the Last Glacial Maximum (LGM) when cooling was observed at 29 ka, several ka before it was evident in the marine record (Barrell et al. 2013; Newnham et al. 2007; Vandergoes et al. 2005).

Offsets in the nature, magnitude, and timing of climate changes between the South and North Island of New Zealand have been observed previously and are well documented (Shulmeister et al. 2019). These authors attribute spatio-temporal differences in extent of glaciations between the North and South Island to precipitation changes caused by a northward shift of the westerly winds. Whether such offsets are
supported by our observations, in this case the South Island (Okarito Pakihi) leading the North Island (Orakei) in climate changes, or whether this stems from the imprecise nature of the micro-XRF-based temperature interpretation, cannot be resolved at present. Ongoing pollen and biomarker-inferred paleo-temperature studies at Orakei are expected to shed light on this issue.

Conclusions

The Orakei maar lake sediment study highlights the power of multi-variate statistical investigation of micro-XRF core scanner elemental output for reconstruction of lake depositional dynamics and paleoclimate. Stratigraphically constrained clustering and principal component analysis have proven useful for disentangling the environmental and sedimentological history of the Orakei maar paleo-lake in a way not possible using simple facies descriptions.

Through careful interpretation of the observed geochemical variability and sediment facies changes linked to the Orakei age model (Peti et al. 2020), we were able to reconstruct the paleo-environmental, paleoclimatic, and depositional history of Orakei maar paleo-lake in six phases: (I) ~130–97 ka: Following the maar-forming phreatomagmatic eruption, a deep lake developed rapidly in the new crater under warming, but variable conditions. Frequent coarse-grained in-wash dominated the first half of MIS 5 (MIS 5c to MIS 5c, ~130–96 ka), likely caused by or aggravated by strong wind or storm events. (II) ~97–73 ka: Quiescent sedimentation occurred in a deep lake dominated by high in-situ biological productivity, with a near absence of in-wash events under warm, but variable conditions during the second half of MIS 5 (MIS 5c to 5a, ~96–71 ka). (III) ~73–60 ka: Aligning with MIS 4 (71–57 ka), cold temperatures prevailed, and in-wash events became dominant as a consequence of reduced protective vegetation cover and increased windiness. (IV) ~60–31 ka: Relatively stable, warm conditions in Orakei and the return of quiet deposition dominated by in situ processes during this phase, which correlated approximately with MIS 3 (57–29 ka). (V) ~31–18 ka: Broadly aligning with MIS 2 (29–14 ka), a thermal decline was followed by a gradual temperature increase at ~18 ka, as commonly observed in New Zealand and globally coincident with the onset of sea-level rise. (VI) ~18–9.8 ka: The sea-level rise and warm temperatures of the outgoing MIS 2 and early MIS 1 (14 ka and younger) end in a peat deposit at the top of the lacustrine section of the core before sea level rise breached the protective crater rim and Orakei maar lake became connected to the sea at ~9.75 ka.

The temperature record from Orakei is based primarily on variability in log(S/inc) and shows first-order similarities with the global marine isotope record as well as with the Okarito lake sediment record from South Island, New Zealand, and other AVF maar lakes. However, discrepancies in climate evolution and timing are also observed and need further investigation with pollen and/or biomarker-based paleo-temperature and paleoprecipitation studies, as well as improvements in the age models for these sediment records.

This study demonstrates the power of the multi-variate, micro-XRF core-scanning approach for rapid paleoenvironmental investigation of lake sediment records. This approach can be used to assess the quality of an archive as well as target sections of the sediment sequence for more traditional and time-consuming approaches to paleoclimate reconstruction.

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Data availability The micro-XRF data of this study can be found here: https://doi.pangaea.de/10.1594/PANGAEA.933144. The LOI and DBD data of this study can be found here: https://doi.pangaea.de/10.1594/PANGAEA.933122. The supplementary material includes a comparison of the Mo- and Cr-X-ray tube data as well as the R code used for the presented analyses.

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