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Invited review

Deglaciated areas of Kilimanjaro as a source of volcanic trace elements deposited on the ice cap during the late Holocene

P. Gabrielli [a,b,*], D.R. Hardy [c], N. Kehrwald [d], M. Davis [a], G. Cozzi [e], C. Turetta [e], C. Barbante [d,e,f], L.G. Thompson [a,b]

[a] Byrd Polar Research Center, The Ohio State University, 108 Scott Hall, 1090 Carmack Road, Columbus, OH 43210, USA
[b] School of Earth Sciences, 275 Mendenhall Laboratory, The Ohio State University, 125 South Oval Mall, Columbus, OH 43210, USA
[c] Department of Geosciences, 611 North Pleasant Street, 233 Morrill Science Center, University of Massachusetts, Amherst, MA 01003-9297, USA
[d] Dipartimento di Scienze Ambientali, University Ca'Foscari of Venice, Dorsoduro 2137, 30123 Venice, Italy
[e] Istitutoper la Dinamica dei Processi Ambientali-CNR, Dorsoduro 2137, 30123 Venice, Italy
[f] Accademia Nazionale dei Lincei, Centro B. Segre, Via della Lungara 10, 00196 Rome, Italy

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ABSTRACT

Ice fields on Kilimanjaro (5895 m a.s.l., Tanzania) are retreating and 85% of the ice cover has been lost since 1912. The degree to which this recession is exceptional during the Holocene is uncertain, as age control of the entire ice stratigraphy exists only for the very shallow and very bottom ice of the Northern Ice Field. This empirical evidence suggests that the Kilimanjaro ice cover may be a persistent Holocene feature, while a model based on maximum possible extent and a constant shrinkage rate of the summit glaciers suggests a cyclic decay time on the order of one to two centuries. Today the mass balance of these ice fields is negative and no persistent ice accumulation zones are observed over multiannual scales. The expanding deglaciated area within the Kilimanjaro caldera should act as an increasingly larger and productive source of volcanic-origin aeolian dust that is quickly deposited onto the surface of the adjacent ice fields, particularly in the seasonal absence of caldera snow cover. Variations in the local dust influx may directly influence albedo and the energy balance of these ice fields. Investigating the characteristics of insoluble material entrapped in the ice remnants of Kilimanjaro can thus provide insights into the extent of ice and/or continuity of the summit snow cover through time. Here we report the trace element composition linked to the insoluble particles entrapped in Holocene Kilimanjaro ice in the context of the current understanding of the past ice accumulation processes (including solid precipitations and ablation) contributing to build the horizontal caldera ice fields. For this purpose we analysed an ice core drilled to bedrock from the Northern Ice Field thought to span the late Holocene (2200 BC–1950 AD). The ultra low trace element concentrations recorded in this Kilimanjaro core are consistent with a generally low volcanic dust source availability (i.e. limited exposure of the deglaciated area in the caldera) and fairly continuous ice accumulation during the late Holocene. In contrast, the maximum concentrations for most of the trace elements recorded in the surface ice section suggest that the current lack of ice accumulation on the Kilimanjaro ice fields is unusual over the last ∼4 ka.

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1. Introduction

Kilimanjaro is the highest mountain and volcano in Africa and is one of the few high altitude sites on this continent that still hosts glaciers. However, ice fields on Kilimanjaro are retreating and the caldera has lost 85% of its ice cover since 1912 (Thompson et al., 2010; Cullen et al., 2013). The existing glacial relicts are the remaining fringe of an ice cap that covered most of the whole summit area of Kilimanjaro in the late 19th century (Meyer, 1900). Today the mass balance of these ice fields is generally negative and no ice accumulation zones are observed. Rather, horizontal (Mölg and Hardy, 2004), sloping (Mölg et al., 2009), near-vertical (Winkler et al., 2010), and basal (Hardy, 2011) surfaces of old ice are ablating due to a combination of melting and sublimation.

Low-latitude/high-altitude glaciers are valuable archives of past environmental processes. Ice cores extracted from glaciers in the Andes, European Alps and the Himalaya provide compelling

* Corresponding author. Byrd Polar Research Center, The Ohio State University, 108 Scott Hall, 1090 Carmack Road, Columbus, OH 43210, USA.
E-mail address: gabrielli.1@osu.edu (P. Gabrielli).

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records of past environmental variability (Thompson et al., 1998; Barbante et al., 2004; Hong et al., 2009). In 2000 a team of researchers from the Byrd Polar Research Center at The Ohio State University (BPRC OSU) drilled ice cores to bedrock on Kilimanjaro: three on the Northern Ice Field, two on the Southern Ice Field and a core on the Furtwängler glacier (Fig. 1). The Kilimanjaro cores include the only African ice fields drilled to bedrock and provide the only opportunity to retrieve a high elevation environmental history from this continent (Thompson et al., 2002).

The degree to which the recession of the Kilimanjaro ice fields is exceptional over the Holocene is under debate (Mölg et al., 2010; Thompson et al., 2010). Radiocarbon (^{14}C) dates determined from a few organic particles found in several of the ice cores extracted from the Northern Ice Field suggest that the Kilimanjaro ice cover is a persistent Holocene feature that has expanded and contracted in concert with climate change including alternating humid periods and droughts in Eastern equatorial Africa over a time scale of several millennia (Thompson et al., 2002). In contrast, a conceptual model based on maximum possible extent, a constant shrinkage rate, and current observations of physical processes, suggests a short decay time of ~165 years for the summit glaciers (Kaser et al., 2010).

Today, the summit of the Kilimanjaro caldera (up to 2.4 km in diameter) is largely deglaciated and free of snow through most of the year, containing only remnants of the former ice cap (Fig. 2) (Hardy, 2011). The extensive deglaciated upper section is currently an increasingly large and likely productive source of aeolian dust of volcanic origin that can be deflated, transported and quickly deposited onto the surface of the adjacent ice fields. Investigating the characteristics of insoluble material entrapped in the ice remnants can thus provide insights into the past role of the deglaciated areas of Kilimanjaro as potential sources of aeolian dust of volcanic origin and, indirectly, indications of the degree of deglaciation and continuity of the snow cover of the caldera through time. In light of the current understanding of the processes that could have influenced past ice accumulation on the ice cap, here we report new trace element data from a Kilimanjaro ice core describing volcanic dust deposition on the Northern Ice Field during the late Holocene. These results suggest the rarity of the current recessional phase of these ice fields.

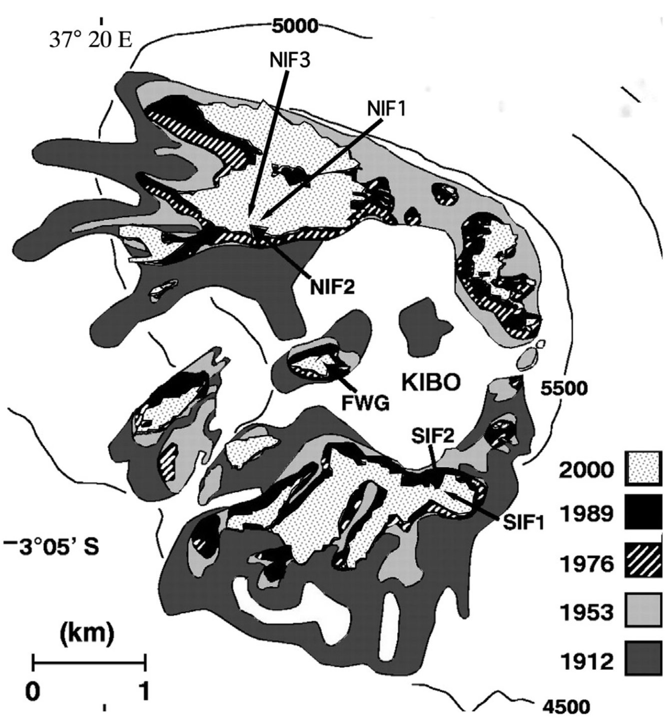

Fig. 1. Map of the Kilimanjaro ice fields on the Kibo caldera at the time of the 2000 drilling operation (adapted from Thompson et al., 2002). The locations of the drill sites on three ice fields (Northern Ice Field (NIF), Southern Ice Field (SIF), and the Furtwängler Glacier (FWG)) are shown. The 1912–1989 ice areas are from Hastenrath and Geischar, 1997, 2000 is after Thompson et al., 2002).

Fig. 2. The Northern Ice Field and the nearby caldera as seen during drilling operations in 2000. The arrow indicates the drilling dome (Photo by Lonnie Thompson).

2. Kilimanjaro study site

Kilimanjaro (5895 m a.s.l., Tanzania) is located on the border between Kenya and Tanzania, ~370 km from the equator and at an equivalent distance from the Indian Ocean. The closest large city is Nairobi, ~240 km to the north. The last significant volcanic activity occurred around 150–200 ka BP and formed the present summit crater of Kibo and the linear parasitic volcanic belts, comprised of numerous Strombolian-type isolated cones on the NW and SE slopes (Nonnotte et al., 2008). Today Kilimanjaro is considered dormant rather than extinct, because steam and sulphur fumaroles (Kent, 1944) are still present. This activity has possibly continued since the last eruptive phase as supported by the extensive nature of fumarolic alteration and deposited sulphur. This quiescent activity is intermittent over periods of months to years, yet current data are inadequate to provide firm conclusions on the variability through time (Downie and Wilkinson, 1972).

While there are several slope glaciers on Kilimanjaro, in this paper we focus only on the summit ice fields and their processes. There are currently three main ice fields atop of Kilimanjaro and all are characterized by vertical cliffs and negligible or absent horizontal flow because the limited thickness (10–50 m) of these ice fields does not allow substantial deformation. These ice fields are: the Northern Ice Field (NIF), which is the largest remaining ice field which covered only a total area of 0.95 km^2 in 2007 (Thompson et al., 2010), the Southern Ice Field and the Furtwängler Glacier (Fig. 1). The two rainy seasons (March to May and November to December) account for 70–90% of annual precipitation on the mountain slopes as well as in the summit zone (Coutts, 1969; Mölg et al., 2009; Hardy, 2011). On the summit the mean annual temperature is −7 °C and precipitation (250–500 mm y^{-1} of water equivalent (w.e.)) occurs entirely as snow or graupel (snow pellets) (Mölg et al., 2009; Hardy, 2011). However, this accumulation typically completely ablates over a few days to a few years, resulting in a negative net ice mass balance for these glaciers. As there are currently no ice accumulation zones, we have no modern analogue to infer how the Kilimanjaro ice cap formed during the past. This past formation remains a major topic of glaciological and paleoclimatic research.

3. Holocene ice-accumulation

Glaciers build up over periods of centuries to millennia in regions where snow accumulates at a faster rate than ablation. This glacial growth occurs in cold regions such as those at high latitudes and on the highest mountains of the tropics and mid-latitudes. Typically, the surface layers are gradually compacted by the accumulating snow to become denser firn, which is then further compressed at depth to form ice. The mass accumulation rate at any location on a glacier can be defined in terms of *specific mass balance* that generally is the result of the total snow deposited minus the ablation that occurs over a given year and can be expressed as centimetres of w.e. While the total snow (or other forms of solid precipitation) deposited in a given area depends on mean air temperature and annual precipitation rate, ablating processes such as melting and sublimation are linked to the glacier's *energy balance*. This is controlled by the sum of three components: 1) radiative fluxes (downward/upward shortwave and longwave radiation), ii) turbulent exchange of sensible heat between the glacier surface and the atmosphere, and iii) turbulent exchange of latent heat.

Currently the annual mass balance of the Kilimanjaro ice fields is negative and generally no multi-annual net snow accumulation is observed (Mölg et al., 2009; Hardy, 2011), ultimately resulting in the observed ongoing shrinkage of these ice fields (Thompson et al., 2010; Cullen et al., 2013). Due to the lack of annual resolution in the ice core record (Thompson et al., 2002), it is difficult both to obtain information on the past ice accumulation rates and to place modern climatic conditions on Kilimanjaro in perspective with past conditions. In this section we review the current understanding of the processes thought to have governed past ice accumulation rates including precipitation (sub-section 3.1), ablation (3.2), ice characteristics including ice formation (3.3) and stratigraphy (3.4) on the Kilimanjaro ice cap during the late Holocene.

3.1. Past precipitation

Due to exceptionally prolonged dry conditions during the Younger Dryas (12,900–11,500 BP) (Verschuren et al., 2009), the Kilimanjaro ice fields may have been extinct at the end of this period. With the beginning of the Holocene (~11,500 BP), wet conditions in Eastern equatorial Africa were favourable to build up the ice cap during the African Humid period (deMenocal et al., 2000). This idea of a transition from a possibly deglaciated to a glaciated Kilimanjaro is supported by the maximum age of the bottom ice of the NIF (~11,700 BP) (Thompson et al., 2002). A sediment record (Verschuren et al., 2009) from the nearby Lake Challa indicates that monsoon rainfall in this region varied at half-precessional intervals (~11,500 years), in phase with orbitally controlled insolation forcing. From this record high precipitation rates were inferred at the beginning of the Holocene (between ~11.500 and ~8000 years BP) and lower rates during the late Holocene.

The second part of the Holocene (after ~8000 years BP) was less favourable than the early Holocene to the formation and expansion of the ice cap. A particularly dry period was inferred from a thick dust layer observed in a NIF ice core which was dated ~4 ka BP (Thompson et al., 2002). A sediment record from Lake Naivasha (Kenya; north west of Kilimanjaro) indicates drier conditions than

Fig. 3. Abundant aeolian dust deposited on the Upper Rebmann Glacier, at ~5800 m (southern rim of the Kilimanjaro's caldera, October 2013). In this particular case dust visible on the horizontal surface may have been mobilized by trekkers transiting on a nearby trail and transported onto the glacier by the prevailing easterly flow. Dust at the glacier surface decreases albedo, leading to an increase in absorption of solar radiation (Photo by Doug Hardy).

today in equatorial East Africa during the Medieval Warm Period (AD 1000–1270) and a wetter climate during the Little Ice Age (LIA; AD 1270–1850) (Verschuren et al., 2000). This finding of a wetter LIA is corroborated by another Lake Challa sediment record, although over a shorter period than previously suggested (AD 1680–1765) (Tierney et al., 2013).

Over a multidecadal time scale, the Indian Ocean drives East African precipitation variability by influencing the local effects of the Walker circulation. Humid conditions and low pressure in coastal east Africa were associated with cold sea surface temperature and high atmospheric pressure in the eastern Indian Ocean. In this context, the high precipitation inferred in coastal East Africa during the LIA occurred contemporaneously with the lowest values in the Indo Pacific sea surface temperature during the past millennium (Tierney et al., 2013).

As the LIA is consistently indicated as a relatively humid period by the nearby sediment records (Verschuren et al., 2000; Tierney et al., 2013), this suggests a higher total snow deposition on the summit over this period. A combination of measurements and backward energy and mass balance modelling of a slope glacier on Kilimanjaro suggests a 160–240 mm w.e. higher mean annual precipitation, 2–4% higher mean relative humidity and 3–5% higher mean cloud cover in the 19th century wet interval than today (Mölg et al., 2009). Subsequent drier conditions started concomitantly with the observed retreat of the Kilimanjaro ice fields (Meyer, 1900; Thompson et al., 2010; Cullen et al., 2013). In particular, likely as a result of the modern global climatic change, Indian Ocean warming during the last few decades may be driving the observed disruption in moisture supply from the ocean (Funk et al., 2008).

3.2. Ablation processes

Ablation processes on the summit glaciers of Kilimanjaro are intimately linked to their energy balance. Recent meteorological measurements and modelling indicate that radiative energy, governed by variations in net shortwave radiation, dominates the energy fluxes at the ice field surfaces (Mölg and Hardy, 2004; Hardy, 2011). The most important factor controlling glacier ablation on the horizontal surfaces is albedo, as it governs the net shortwave radiation receipt (Mölg and Hardy, 2004) that provides most of the energy needed to allow the ice to change phase (see below). Albedo depends on solid precipitation amount and frequency, and the flux/accumulation of aeolian micro-particles to the glacier surface (Fig. 3). Hence Kilimanjaro glaciers should have been very sensitive to changes in solid precipitation and possibly dust deposition/exposure during the past.

The second most important contribution to the energy balance is the turbulent latent heat flux, which in many parts of the glaciers is typically directed away from the glacier surface and causes sublimation. Melting also occurs at the glacier surface sometimes, even at air temperatures below 0 °C, due to abundant energy provided by shortwave radiation (Kuhn, 1987; Mölg and Hardy, 2004; Mölg et al., 2009; Kaser et al., 2010). The amount of melting on Kilimanjaro is locally constrained by sublimation, because this process employs energy that would otherwise be available for melting. Thus, the role of melting in the ablation processes varies seasonally and spatially – even on a diurnal basis – and also depends on the amount of refreezing of meltwater within the glacier body (Mölg and Hardy, 2004), a process called "internal accumulation". During the drilling operations in 2000, meltwater was observed flowing on the glacier surface and down from the vertical ice cliffs of glacial margins, ultimately infiltrating into the volcanic ash on the caldera floor. However, the amount of past and even modern water runoff from the summit should be highly variable, as it was also observed to be extremely brief and insignificant in other circumstances (Kaser et al., 2004). Clearly even the modern variability of diurnal, seasonal and inter-annual runoff remains very uncertain.

An energy-balance model validation using eddy covariance data (i.e., a direct measurement of the turbulent latent heat flux and sublimation) over a few days showed that mass loss by melting is less important than sublimation on the horizontal glaciated surfaces during a dry period (Cullen et al., 2007). However, the agreement between the Kilimanjaro ice core stable isotope ratios and the meteoric water line does not support sublimation as an important factor during past times of ice accumulation (Thompson et al., 2011). Frequent melting features observed in the Kilimanjaro ice cores (e.g. the cumulative thickness of the ice lenses observed in the NIF3 ice core span up to ~47% of its length) indicate melting as a very common and intense process during the history of this ice cap. Importantly, model runs of Mölg et al. (2009) suggest that melting was confined to the shallowest glacier layers and mostly occurred during the wet season. Essentially no melting was simulated below ~100 cm of depth at 5750 m during the modern dry period and/or below ~200 cm during a LIA wet interval. These results and ice core observations point to a process of internal accumulation over time, due to meltwater percolation through firn and refreezing within the shallowest layers. We note that this process in itself does not cause a net loss in ice mass on horizontal or quasi-horizontal surfaces such as the drilling sites and also implies the conservation of the constituents dissolved in the glacier (see below).

The turbulent exchange of sensible heat plays a minor contribution in the modern energy balance (Mölg and Hardy, 2004; Mölg et al., 2009) because of the small temperature gradient between the glacier surface and the air at subfreezing atmospheric temperatures. However, the influence of past local air temperature variations on ice ablation over time is not known, as high elevation atmospheric temperature data for Kilimanjaro are unfortunately not available before 2002 and temperature reanalysis data seems unsuitable for documenting temperature changes at such a local spatial scale during the most recent past. Sediment records from Lake Tankanyika indicate that, at low elevation, temperature in this region was lower during the LIA and the current warming is unprecedented over the last 1500 years (Tierney et al., 2010). We note that this warming is consistent with both current global anthropogenic warming trends and the modern increase in the radiative energy influx due to the recent decade-long decline in East African rainfall (Lyon and DeWitt, 2012). This illustrates the difficulty of interpreting low-elevation air temperature changes and of disentangling/quantifying the roles of the various factors that influenced the past recessional phases on the Kilimanjaro ice cap.

Thompson and co-workers hypothesized that the recent increase in *global* atmospheric temperature plays a significant role in explaining the modern recession of the Kilimanjaro ice fields, consistent with the ongoing retreat of most of the glaciers around the world (Thompson et al., 2009). Kaser/Mölg and co-workers, building on previous work (e.g., Hastenrath, 2001), have proposed the reduction in local and regional precipitation since the end of the 19th century and the associated increase in absorbed shortwave energy as local drivers (Mölg et al., 2003; Kaser et al., 2004). Both viewpoints do not necessarily contradict one another if global atmospheric warming (not increase in local air temperature) is considered the main driver of glacier recession on Kilimanjaro. Snowfall in the summit zone (and its impact on the energy balance through surface albedo) certainly has a strong control on ice mass balance variability. However, global warming may alter precipitation patterns in the tropics, and thus large-scale warming can be a driver of precipitation characteristics in the Kilimanjaro region (Mölg et al., 2009). Clearly, linkages between local/regional climatic conditions on Kilimanjaro and global warming remain a topic of current research.

3.3. *Past ice formation*

A growth mechanism of the horizontal ice fields on the summit of Kilimanjaro has been proposed by Kaser and co-workers suggesting that a major snowfall season, followed by a series of exceptional wet seasons, may cause a persistent snow cover over the deglaciated areas of the caldera. The resulting albedo increase would allow a tabular ice body to grow. These studies argue that multiple wet and dry periods inferred from lake sedimentary level at lower elevations (see section 3.1) may imply ice field growth and contraction over a timescale of 100–200 years (Kaser et al., 2010). We note that this concept still needs to be supported by empirical data. Precise dating of the relicts of the existing tabular ice bodies should provide indications on the lifetime of the Holocene glacial remnants and whether they result from the growth of individual ice fields or the ablation of a unified ice cap (Thompson et al., 2011).

Currently, it is unknown whether in the past any persistent firn layer existed on top of the Kilimanjaro ice surface(s), and if snow was ever altered to ice through the firnification process. No firn was observed in any of the boreholes during the 2000 ice core drilling program (Thompson et al., 2002). Melting and refreezing cycles have been noted since the end of the 19th century (Meyer, 1900) and affect the surface of the Kilimanjaro ice fields to the present (Mölg et al., 2009). Such cycles were particularly noted to have strongly affected the uppermost part of the NIF to a depth of ~65 cm (Thompson et al., 2002). However, multiple layers of transparent ice throughout all the Kilimanjaro cores indicate that melting and refreezing cycles routinely occurred in these ice fields in the past. The model runs of Mölg et al. (2009) surmise that refreezing cycles occur only within the shallowest (100–200 cm depth) layers. Depending on the snow accumulation and melting intensity, ice formation by both superimposition and firnification is possible, as indicated by the presence at various depths of observed thick transparent lenses and ice sections that are rich in air bubbles.

A low and uniform ice accumulation rate of 12 mm y^{-1} w.e. on Kilimanjaro during the Holocene was deduced based on a ^{36}Cl spike at 1.6 m depth (interpreted as evidence of the fallout from the 1953 nuclear testing program), along with several assumptions on the timing of notable stable isotope depletion events during the LIA (Thompson et al., 2002). Although the current range of precipitation on Kilimanjaro is relatively low (250–500 mm y^{-1} w.e.), a high mean annual ablation rate is necessary in order to reach such low accumulation value. This would require considerable sublimation and meltwater runoff together removing ice mass from a past unified ice cap.

As it is difficult to estimate the uncertainty of the past ice accumulation rate, we simply assume that the modern annual range of precipitation is the upper limit of the past ice accumulation rate. While the modern cumulative amount of snow deposited over one year on Kilimanjaro is likely lower than during the Little Ice Age and the African Humid period, significant ablation, caused primarily by intense solar radiation at this latitude, likely resulted in a past net accumulation rate within or below the modern range of annual precipitation.

3.4. Ice stratigraphy

Due to the lack of distinguishable annual ice layers and absence of age controls in the middle part of the ice cores, the degrees of uncertainty in the Kilimanjaro chronologies remain difficult to evaluate. The influence of past post-depositional processes (including sublimation, melting, percolation and internal refreezing) on the concentrations of the various chemical species is also difficult to assess. Linking concentration data from the Kilimanjaro ice cores to past ice accumulation and depositional characteristics of atmospheric species is therefore challenging. While the uncertainty in the chronology of the Kilimanjaro cores was already discussed in detail (Kaser et al., 2010; Thompson et al., 2011), in this paper we focus on the variations and origin of trace elements in Kilimanjaro ice in order to obtain information on past ice accumulation and depositional/post-depositional processes in the context of the glaciation/deglaciation history of the former ice cap.

Visible annual layers and annual cycles of physical and chemical parameters in the Kilimanjaro cores are not identifiable (Thompson et al., 2002). While multiple layers of transparent ice indicate that melting and refreezing cycles routinely occurred in these ice fields during the past, there is no obvious evidence of post-depositional overprinting of the chemical species in the already available NIF stable isotopes, major ions, micro-particle concentrations records (Thompson et al., 2002). Even soluble chemical components such as major ions occur in variable concentrations and seem reproducible to some degree when comparing the corresponding records from different Kilimanjaro ice cores (Thompson et al., 2002). If meltwater percolation had overprinted the entire vertical profiles, the chemical–physical record of the various parameters would show limited variability and reproducibility. This overprinting seems to be the case only for the thinner and smaller Furtwängler glacier where a water-saturated core was extracted (Thompson et al., 2002).

We explain this persistently high variability in the chemical species by considering that any melting, percolation and refreezing that occurred in the NIF during the Holocene was limited to the shallowest layers of the glacier at any given time, as suggested from modelling runs (Mölg et al., 2009). We argue that, while these processes have likely caused a local mobilization of the chemical species in the ice, they should have also prevented complete washout and a net removal of the chemical species and have therefore likely conserved a coarser variability.

4. Ice core trace elements study

In this work we investigate trace element (TE) concentration variations in one of the Kilimanjaro ice cores (NIF2, 50.8 m in length). We use a continuous series of 98 ice sections obtained from the NIF2 core that were cut at an average of ~50 cm in length and ~200 g of mass. The NIF2 timescale was previously reconstructed by matching distinctive features of the oxygen isotopic ratio record ($\delta^{18}O$) with that from the reference core NIF3 (Thompson et al., 2002). The timescale for NIF2 spans ~4 ka, and at 1.6 m depth was dated at approximately 1950 AD (Thompson et al., 2002) and thus most of the recent snow accumulation should have been removed by ablation. Each of the 98 NIF2 ice sections, from the

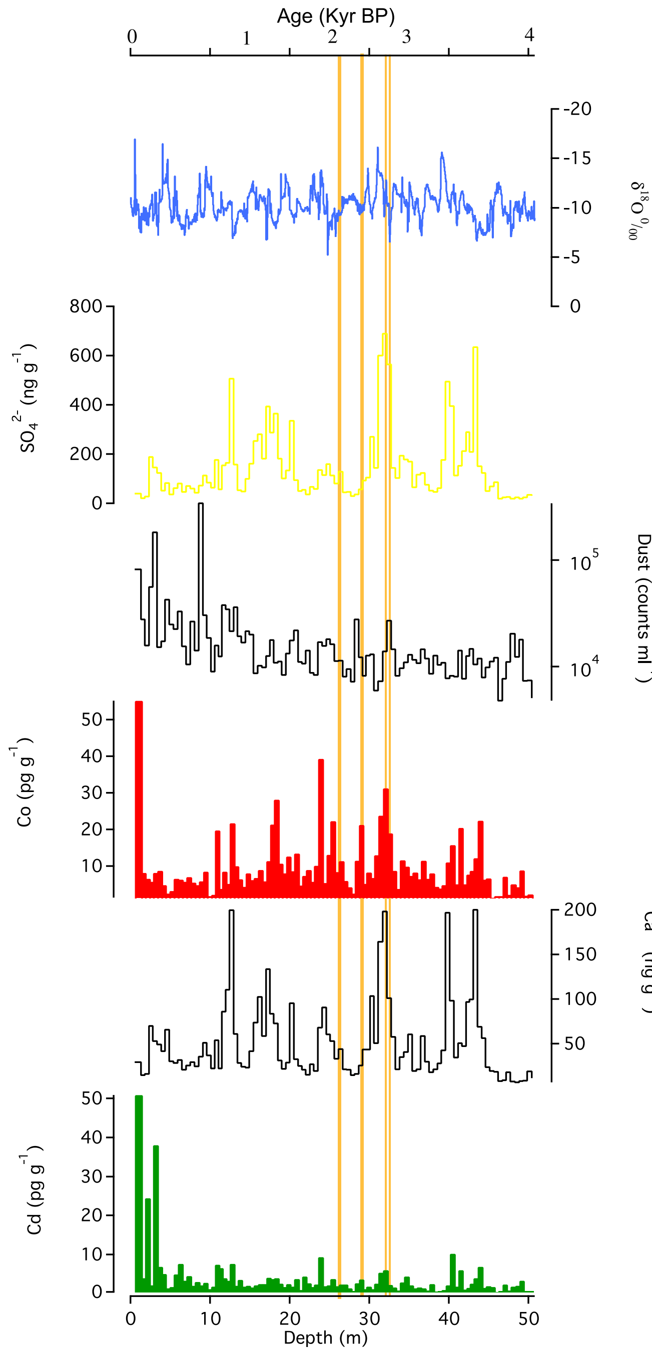

Fig. 4. Comparison of measured parameters in the NIF2 core. Profiles of $\delta^{18}O$, SO_4^{2-}, dust microparticle concentration, Co (a refractory metal that in this case can serve as a proxy of volcanic dust contribution), Ca^{2+} (a typical proxy of crustal dust) and Cd (a volatile trace element) as determined in the NIF2 core are shown. Vertical bars highlight the four visible dust layers observed between 25 and 31 m of depth.

Table 1
Main statistics of trace element concentrations as determined in the Northern Ice Field core 2. The mean concentrations are compared with values determined by using comparable methodologies in Antarctic and low latitude ice cores from other continents.

Kilimanjaro							Coats Land[a] (Antarctica)		Sajama[b] (Andes)		Everest[c] (Himalaya)		Colle Gnifetti[d] (Western Alps)	
	Skewness	Minimum	Maximum	Median	Std. dev.	Mean	Holocene backgr.	Industrial	Holocene backgr.	Industrial	Holocene backgr.	Industrial	Holocene backgr.	Industrial
		(pg g^{-1})	(pg g^{-1})	(pg g^{-1})	(pg g^{-1})	(pg g^{-1})	(pg g^{-1})	(pg g^{-1})	(pg g^{-1})	(pg g^{-1})	(pg g^{-1})	(pg g^{-1})	(pg g^{-1})	(pg g^{-1})
Ag	1.4	0.6	7.3	2.0	1.3	2.4	0.1	0.2	11.0	9	–	–	–	–
As	3.7	1.9	155	15	20	21	–	–	1405	1399	36	40	19	94
Bi	5.2	0.07	13	0.64	1.5	1.1	0.015	0.051	11	13	2.2	5.4	1.3	4.1
Cd	5.5	0.4	51	2.3	7	4	0.28	0.25	25	27	–	–	3.5	70
Co	2.8	1.4	55	7	8.2	9.7	0.5	0.76	205	77	26	36	16	29
Cr	6.5	4.1	296	16	33	23	1.7	2.2	–	–	77	95	60	85
Cu	4.6	12.2	553	41	71	59	1.3	2.6	2550	1053	–	–	75	300
Mo	2.2	3.9	110	16	19	22	–	–	–	–	2.3	2.9	–	–
Pb	5.2	3.6	718	49	86	69	0.5	2.5	691	688	–	–	311	3600
Rb	3.1	14	1719	217	242	274	–	–	1134	748	–	–	64	89
Sb	4.0	0.3	18	1.5	2.4	2.3	–	–	–	–	1.9	2.3	–	–
Sn	2.6	2.8	44	7.8	7	10	–	–	–	–	8	16	–	–
Tl	4.3	0.06	10.5	2.5	1.3	1.2	–	–	–	–	1.2	1.7	–	–
U	2.8	1.5	148	19	23	25	0.020	0.037	32	19	6	19	3.6	18
V	2.9	3.7	236	26	37	38	0.7	0.6	593	224	74	97	36	213
Zn	2.2	92	3638	392	716	684	1.9	2.1	1716	1325	–	–	54	363
		(ng g^{-1})	(ng g^{-1})	(ng g^{-1})	(ng g^{-1})	(ng g^{-1})	(ng g^{-1})	(ng g^{-1})	(ng g^{-1})	(ng g^{-1})	(ng g^{-1})	(ng g^{-1})	(ng g^{-1})	(ng g^{-1})
Al	4.3	4.4	1076	88	136	124	–	–	–	–	37	40	28	38
Fe	3.3	3.6	179	21	27	29	–	–	–	–	55	58	24	26
Mn	2.4	0.14	7	1.2	1.3	1.5	0.0104	0.0150	–	–	1.3	1.7	0.79	1.3
Ti	2.5	0.19	19	0.83	3.1	3.4	–	–	–	–	3.4	4.6	0.094	0.2

[a] Mean trace elements concentrations in firn blocks dated 1830s–1880s and 1890s–1990 AD (Planchon et al., 2002).
[b] Mean trace elements concentrations in ice cores dated 8400 BP–1700 AD and 1825–1988 AD (Hong et al., 2004).
[c] U, Bi, Tl, V, Cr, Co, Al, Fe, Ti, Mn median concentrations in ice cores dated 1650–1800 AD and 1950–2002 AD (Kaspari et al., 2009); Mo, Sn, Sb and As mean concentrations in ice cores dated before 1900 AD and 1900–2002 AD (Hong et al., 2009).
[d] Mean Holocene concentrations in ice cores dated pre-20th century and 20th century (Gabrieli, 2008).

surface to bedrock, encompasses approximately 40 years in accordance with this timescale.

This is the first study of TE concentrations in any African ice core. These chemical constituents can reveal the origin and composition variation of the insoluble particles entrapped in the ice (e.g. Gabrielli et al., 2010). Concentrations were determined for the trace elements Ag, Al, As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Rb, Sb, Sn, Ti, Tl, U, V and Zn, covering a time period of ~4 ka. The procedures used to process the ice samples and to perform the TE determination by ICP-SFMS are presented in the supplementary information.

4.1. *Trace elements results*

TE concentrations are low but variable throughout the NIF2 ice core (Fig. 4 and Fig. S1). Mean concentrations range between 1.1 pg g^{-1} for Bi and 124 ng g^{-1} for Al. Very low average concentrations were obtained for Tl (1.2 pg g^{-1}), Sb (2.3 pg g^{-1}) and Ag (2.4 pg g^{-1}) while much higher levels were observed for Mn (1.4 ng g^{-1}), Ti (3.4 ng g^{-1}) and Fe (29 ng g^{-1}). Minimum concentrations are below 1 pg g^{-1} for Sb (0.3 pg g^{-1}), Cd (0.4 pg g^{-1}) and Ag (0.6 pg g^{-1}) while Rb (1.7 ng g^{-1}) and Zn (3.6 ng g^{-1}) are above the 1 ng g^{-1} level. Maximum Al concentrations were determined at the 1.1 μg g^{-1} level (Table 1).

Mean TE concentrations in Kilimanjaro ice are generally at about the same level or lower than those in ice cores extracted from other preindustrial Holocene sections of low latitude glaciers and analysed using comparable methods (Table 1). We determined 4 pg g^{-1} of Cd in NIF2 compared to 25 pg g^{-1} and 3.5 pg g^{-1} in Sajama (Bolivia) and Colle Gnifetti (Swiss–Italian Alps), respectively (Hong et al., 2004; Gabrieli, 2008). We detected a mean Pb value of 69 pg g^{-1} in NIF2, while higher concentrations were observed in the Sajama (691 pg g^{-1}) and Colle Gnifetti (311 pg g^{-1}) ice cores. In contrast, the mean U concentration is higher in NIF2 (25 pg g^{-1}) than in Colle Gnifetti (3.6 pg g^{-1}). Mean TE concentrations in NIF2 are consistently higher than values recorded in recent Antarctic snow. Firn studies from Coatsland, West Antarctica (Planchon et al., 2002) show mean Co and V values of 0.5 pg g^{-1} and 0.7 pg g^{-1}, respectively, while Kilimanjaro ice concentrations are 9.7 pg g^{-1} of Co and 38 pg^{-1} of V (Table 1).

TE concentrations do not demonstrate distinctive trends by depth along the NIF2 ice core (Fig. 4 and Fig. S1). We observe the highest concentrations of most TEs in the uppermost sample (0–0.54 m depth): Al (1076 ng g^{-1}), Ti (18.5 ng g^{-1}), Rb (1719 pg g^{-1}), Pb (718 pg g^{-1}), Cu (553 pg g^{-1}), Cr (296 pg g^{-1}), As (155 pg g^{-1}), U (148 pg g^{-1}), Mo (110 pg g^{-1}), Co (55.2 pg g^{-1}), Cd (50.9 pg g^{-1}), Tl (10.5 pg g^{-1}) and Ag (7 pg g^{-1}). These values are most probably influenced by the insoluble particles deposited and concentrated on the ablating ice surface. The upper 15 m of the core contain peaks in Cu (up to 327 pg g^{-1}), Cr (110 pg g^{-1}), Cd (38 pg g^{-1}), Sb (18.5 pg g^{-1}) and Bi (12.6 pg g^{-1}). The Cd peaks (24 and 38 pg g^{-1}) in the shallow core sections exceed the range of Cd values throughout the rest of the core (3 ± 2 pg g^{-1}). The Cu, Cr, Sb and Bi peaks in the upper core section are high but not the highest of the entire NIF2 record (Fig. S1).

Four visible dust layers are observed between ~25 m and ~31 m of depth (Fig. 4) and are proximal to several peaks in concentrations for Al (up to 595 ng g^{-1}), Fe (179 ng g^{-1}), Ti (16 ng g^{-1}), Mn (7.2 ng g^{-1}), Rb (1236 pg g^{-1}), Pb (387 pg g^{-1}), V (236 pg g^{-1}), Cu (206 pg g^{-1}), U (119 pg g^{-1}), Mo (57 pg g^{-1}), As (55 pg g^{-1}), Co (39 pg g^{-1}), and Tl (6.0 pg g^{-1}). Other TEs show high values near the base of NIF2: Zn (up to 3.6 ng g^{-1}), Mo (79 pg g^{-1}) and Sn (44 pg g^{-1}) (Fig. S1).

As all the TE concentrations correlate with each other (0.01 level, 2-tailed *t*-test), we used more descriptive statistical treatments to highlight less obvious linkages. A Ward hierarchical analysis applied to the matrix of the first five principal components (with a cumulative explained variance of nearly 90%), extracted from the ranked concentrations (Gabrielli et al., 2008), separates the TEs into three groups (Fig. S2). The first group contains Mn, Co, Fe, Ti, U, Al, Rb, Ag and V; the second Tl, As, Pb, Bi, Mo and the third Sn, Zn, Sb, Cr, Cd and Cu. The first and the second group are closely linked and also show high Spearman correlation coefficients when calculated between the TEs of each single group (mean $r_1 = 0.84$, $SD_1 = 0.10$ and $r_2 = 0.83$, $SD_2 = 0.07$, respectively). The third group is clearly separate and its TEs have lower Spearman correlation coefficients with each other (mean $r_3 = 0.63$, $SD_3 = 0.09$). The TEs from the first group are characterized by refractory moderately-volatile geochemical behaviour while those from the second and the third have more volatile characteristics.

4.2. *Trace element variability in Kilimanjaro ice*

Trace elements can be depleted or enriched in adjacent ice layers as a consequence of melting and refreezing (Gabrielli et al., 2009). As these kinds of processes likely occurred only within 100–200 cm below the glacier surface (Mölg et al., 2009), TE and other species should have been depleted/enriched only within this active ice layer while the overall mass budget of trace elements across the entire core length should have not been affected. In this case, a degree of TE coarser depositional variability was preserved when surface layers were transferred by the vertical flow to greater depths that were unlikely affected by further post depositional processes.

To support the chronology and the substantial integrity of the Kilimanjaro ice cores as recorders of past depositional variability, the $\delta^{18}O$ time series from NIF2 was compared with various local environmental archives (Thompson et al., 2011). To the best of our knowledge, no independent regional TE records exist for direct comparison with the corresponding NIF2 concentrations. We note that the four visible dust layers in NIF2 correspond to some degree to TE concentration peaks (e.g. Co and Cd in Fig. 4). However, the NIF2 TE profiles do not significantly correlate with the records of major ions, microparticle concentrations and stable isotopes determined in the same core (Fig. 4). We also note that no significant correlation exists between the microparticle and the Ca^{2+}/Mg^{2+} records (e.g. Ca^{2+} in Fig. 4) that are typically considered proxies of aeolian dust (Thompson et al., 2002). We explain this anomalous lack of correlation between TE and the other parameters

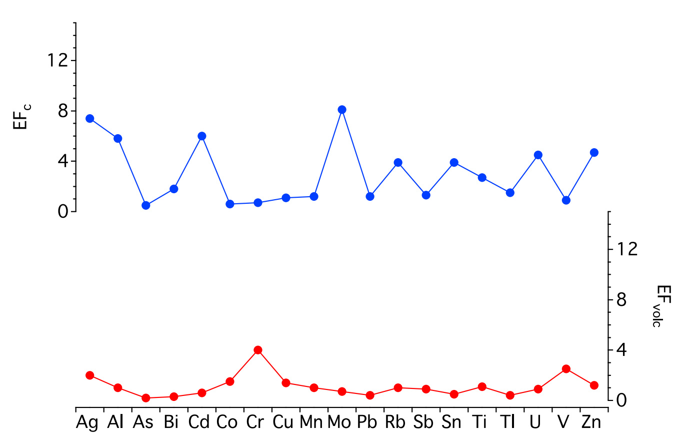

Fig. 5. Median trace element enrichment factors of the NIF2 ice core samples calculated with respect to the composition of loess from the Tibetan Plateau [EF_c] (blue line) and the composition of dust collected from the caldera of Kilimanjaro [EF_{volc}] (red line).

in NIF2 by assuming that a small-scale (<1 m) heterogeneity of the impurities within the ice matrix must have been produced at any given time by the local post depositional processes within the shallowest layers of NIF and then transferred to greater depth. This heterogeneity could also be differently recorded by the large (200 g) and small (20 g) ice samples used for trace elements and major ions determinations, respectively.

We conclude that melting, percolation and refreezing that occurred at any time within the shallowest NIF layers represent the main factors explaining the <1 m spatial variability of TEs in NIF2. However, because TEs were routinely concentrated/diluted only within the surface layers as the ice accumulated, the total TE burden entrapped in the NIF (i.e. NIF2 total mean TE concentrations) should have been substantially preserved. The likely lack of further post depositional processes at greater depth should have contributed to the conservation of the TE variability at larger spatial scales (>1 m) that would still represent a depositional history, although probably smoothed at centennial-millennial time scales. For this reason we will discuss these data only in terms of possible long term temporal variations during the late Holocene.

4.3. Trace element compositions

Radiocarbon (^{14}C) dates determined in a few small organic particles within the NIF3 core (drilled ~77 m apart from NIF2) suggest that the NIF is composed of thousands of years of Holocene-age ice (Thompson et al., 2002). If TEs (i.e. their reciprocal mass ratios) were conserved after the various past post-depositional processes occurred within the shallowest glacier layers, their relative composition would generally indicate the overall micro-particle characteristics during the Holocene. In this case, the principal sources of those TEs that were not fractionated (e.g. TEs permanently entrapped in the mineral structure of insoluble dust particles) can be inferred.

In order to assess the origin of TEs in Kilimanjaro ice, we calculated the crustal enrichment factor (EF_c) (Gabrielli et al., 2006) as $\{[TE]/[Fe]\}_{ice}/\{[TE]/[Fe]\}_{loess}$, where $\{[TE]/[Fe]\}_{loess}$ is the mass ratio between a TE and Fe in our crustal reference material derived from loess collected from the Tibetan Plateau (see supplementary information) while $\{[TE]/[Fe]\}_{ice}$ is the corresponding mass ratio in the ice. We initially assumed Fe is entirely of crustal origin. Median EF_c (Fig. 5) deviates from the loess composition for Ag (7.4), Al (5.8), Cd (6), Mo (8.1), Rb (3.9), Sn (3.9), U (4.5) and Zn (4.7) while the EF_c is closer to unity for As (0.5), Bi (1.8), Co (0.6), Cr (0.7), Cu (1.1), Mn (1.2), Pb (1.2), Sb (1.3), Ti (2.7), Tl (1.5) and V (0.9).

In contrast, when we use the TE composition of dust ($\{[TE]/[Fe]\}_{volc}$) collected from the Kilimanjaro caldera (instead of $\{[TE]/[Fe]\}_{loess}$; see supplementary information) to evaluate the TE composition in the ice core, we obtain a volcanic enrichment factor (EF_{volc}) between 0.3 and 2.5 (average = 1.1; median = 1.0; Table S2) for all the TEs determined in this study except Cr, which has a EF_{volc} of 4 (Fig. 5). The correspondence between the caldera dust and the ice core TEs composition is a robust indication that TEs entrapped in NIF2 originate from volcanic material deflated from the deglaciated areas of Kilimanjaro and dry-deposited on the NIF. This also suggests that volcanic TE mass ratios, rather than concentrations in NIF2, are substantially conserved despite any post depositional processes that occurred during the Holocene.

Several TEs demonstrate more variable EF_{volc} with large maximum values for Bi (31), Cd (150), Cr (6), Cu (14), Mo (41), Sb (9), Sn (30), V (9), and Zn (64) (Fig. S2). Most of these elements occur within the third group highlighted by the cluster-PCA analysis (Cd, Cr, Cu, Sb, Sn and Zn) and are characterized by moderate to highly volatile behaviour. Cu and Cd contain EF_{volc} peaks (up to 14 and 150, respectively) only in the upper 15 m of the ice core. As previously discussed, these upper sections contain the highest Cu and Cd concentrations of the entire record.

These high EF_{volc} values may result from other volcanic sources. Volcanic gas emissions can be enriched in Cr, Zn, Cu and Cd (Mather et al., 2012), suggesting that a volcanic gaseous origin is also possible for these peaks in the NIF2 core. Quiescently degassing products/condensates from Kilimanjaro may have fractionated these volatile TEs (Hinkley et al., 1999) resulting in the occasional fallout of enriched volcanic aerosol onto the NIF. Another possibility is that the TE composition of Kilimanjaro was influenced by the volcanic activities from Chyulu Hills (e.g. in 1855 AD) or Meru (e.g. in 1910 AD) (Siebert and Simkin, 2002) or Ol Doinyo Lengai, three volcanoes that are within ~200 km of Kilimanjaro. A final possibility is that concentrations of these volatile TEs are more sensitive than others to post-depositional processes due to their gaseous phase transport and deposition.

4.4. Past trace element source strength

Low-latitude drilling sites that are located farther from their local TE sources (e.g. soil dust) than Kilimanjaro is from the caldera sediments often contain TE concentrations at the same level or higher than those recorded in NIF (Table 1). As the other low-latitude locations likely have larger or comparable mass accumulation rates than NIF (assumed to be up 250–500 mm w.e. y^{-1}), such as 200–400 mm w.e. y^{-1} on Colle Gnifetti (Jenk et al., 2009), 400 mm w.e. y^{-1} on Sajama (Hong et al., 2004) and 300–800 mm w.e. y^{-1} on Everest (Kaspari et al., 2008), the comparison between the TE concentrations in NIF2 and in the other cores provide a first order assessment of the different TE depositional characteristics at the various sites.

The similar or lower mean TE concentrations in NIF2 compared with remote high-altitude/low-latitude glaciers are difficult to reconcile with the current high proximity and essentially same elevation of the NIF to the mostly ice free and dusty caldera (Fig. 2). Fine volcanic dust can be easily mobilized and quickly deposited by dry deposition on the adjacent ice fields. In contrast, the drilling sites of Colle Gnifetti and Everest are surrounded by extensive glaciated areas and the closest ice free surfaces that are suitable for dust deflation and transport to the drilling site are located several kilometres away and 1000–2000 m lower in elevation. The Sajama ice cap is located on the top of an isolated and extinct volcano in Bolivia. The summit is entirely glaciated and the flanks of this volcano are the closest potential dust source; however, unlike on Kilimanjaro this source is located ~1000 m below the summit of the ice cap. Nevertheless, the crustal trace element concentrations in the Sajama core are typically between several factors and up to an order of magnitude higher than in NIF2.

Assuming that millennially-smoothed TE depositional records are preserved in NIF2 (Section 4.2), the low mean TE concentrations reflect the average depositional characteristics of Kilimanjaro dust and snow accumulated on the NIF during the late Holocene. TE concentration variability can thus be interpreted by two factors: 1) centennial/millennial variations of the deglaciated areas of Kilimanjaro (e.g. the caldera) and 2) centennial/millennial changes in ice accumulation rates. We note that variations in the deglaciated areas also depend on changes in the ice accumulation rate. Thus it is not possible to disentangle these two factors from the TE concentrations that reflect both of these variables.

The low mean TE values during the late Holocene are consistent with a generally limited aerial extent of the adjacent deglaciated caldera during this period. In turn, these concentrations are also consistent with a large extension of the Kilimanjaro ice cap and/or greater magnitude or duration of seasonal and/or perennial snow cover within the caldera during the late Holocene (before 1950 AD), suggesting that the current lack of multiannual snow accumulation atop the Kilimanjaro is unusual over the last 4 ka.

This idea is supported by: 1) the maximum TE concentrations recorded in the top NIF2 ice section (indicative of the TE values on the exposed NIF ice at the surface) and 2) by the thick dust layer (4 cm) observed in the NIF3 core which is dated ~4 ka BP (Thompson et al., 2002). The low EF_{volc} in the NIF2 surface sample (0–0.54 m) indicates that the corresponding high TE concentrations are due to dust deposition from Kilimanjaro during the modern period and are consistent with negative annual mass balances and a progressive deglaciation of the caldera. Today, increasing amounts of volcanic dust are likely routinely deflated from the deglaciating caldera and deposited on the NIF where the current process of ablation contributes to the accumulation of volcanic dust on the surface.

To find a possible analogue of strong depositional conditions we need to go back ~4 ka when the 4 cm thick dust layer discovered in the NIF3 core (Thompson et al., 2002) and its REE determination (Gabrielli, unpublished results) indicate that the deglaciated area of Kilimanjaro was also the source of this dust layer. Remarkably, the age of the bottom section of the NIF2 core (~4 ka) is consistent with the age of this event of thick dust accumulation. It is likely that, due to dry climatic conditions that followed the African Humid period, extreme deglaciation eradicated the ice at the location of NIF2 around 4 ka BP, but not at the more interior NIF3 drilling site (Fig. 1) (Thompson et al., 2002). This difference between the two sites, which are only 77 m apart, is consistent with the idea that the current aerial shrinking of NIF is governed by ablation through the lateral recession of its near-vertical ice margins (Mölg et al., 2003; Kaser et al., 2010; Winkler et al., 2010). A subsequent phase of positive mass balance resulted in ice accumulation atop the ~4 ka dust layer, building the younger extension of NIF that now includes the location where NIF2 was drilled.

5. Conclusions

During the Holocene, ice accumulation on Kilimanjaro likely varied substantially, with maximums during the African Humid Period and the Little Ice Age. The modern lack of accumulation on these ice fields has at least one possible past analogue, dated ~4 ka BP. While the causes of the modern retreat are thought to be the product of global climatic changes, which are manifested by lack of ice accumulation and consequent dry conditions atop of Kilimanjaro, the uniqueness during the Holocene of the current reduced areal extent of the Kilimanjaro ice cap remains controversial.

Regardless of the relative but still undetermined importance of factors such as melting and sublimation in assessing the condition of the Kilimanjaro ice cap during its history, changes in albedo most likely played the most important role in determining variations in the energy budget and thus the ice accumulation. The most critical influences on the albedo were the frequency and amount of snowfall and probably the amount of aeolian dust deflated from the adjacent caldera that was deposited on the ice surface.

In this study we provide the first information on variability and deposition of volcanic dust from the deglaciated areas of Kilimanjaro on the Northern Ice Field. Trace element concentrations determined in the 50.8 mNIF2 ice core indeed reveal that microparticles entrapped in the Northern Ice Field during the late Holocene originate from the ice-free areas of the adjacent caldera. These particles were (and are) entrained by middle tropospheric circulation and quickly dry-deposited on the ice.

Post-depositional processes such as surface melting, percolation and refreezing played a role in diluting/concentrating the volcanic trace elements in the ice matrix. These processes routinely took place during the time period during which the ice in the NIF2 core accumulated. A model developed by Mölg and co-workers suggests that melting and refreezing could occur at any time, but only within the uppermost layers of the ice. In this case, internal accumulation occurred within the shallowest depths (0–200 cm), implying no significant ice mass loss and the conservation of the total trace elements burden (i.e. mean concentrations) during the late Holocene in the Northern Ice Field.

Given the current close proximity and mere ~50 m difference in elevation between the caldera (the primary source of trace elements) and the largest ice field, the NIF2 concentrations are comparable to or lower than levels found in other low-medium latitude ice cores. This seemingly paradoxical comparison persists in spite of the remote locations of the other sites with respect to their respective trace element sources, and their comparable or higher mass accumulation rates than Kilimanjaro. A consistent positive ice accumulation rate throughout the late Holocene, along with the consequent limited exposed surface of the deglaciated caldera, are proposed to reconcile the low mean TE concentrations with the current proximity of the ice fields to their volcanic source. Further investigations of the corresponding modern processes of intermittent snow accumulation and volcanic dust deposition on the Northern Ice Field will be essential to better understand the history of the ice fields on the summit of Kilimanjaro.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.quascirev.2014.03.007.

References

Barbante, C., Schwikowski, M., Doring, T., Gaggeler, H.W., Shottered, U., Tobler, L., Van de Velde, K., Ferrari, C., Cozzi, G., Turetta, A., Rosman, K., Bolshov, M.A., Capodaglio, G., Cescon, P., Boutron, C.F., 2004. Historical record of European emission of heavy metals to the atmosphere since the 1650s from alpine snow/ice cores drilled near Monte Rosa. Environ. Sci. Technol. 38, 4085–4090.

Coutts, H.H., 1969. Rainfall in the Kilimanjaro area. Weather 24, 66–69.

Cullen, N.J., Molg, T., Kaser, G., Steffen, K., Hardy, D.R., 2007. Energy-balance model validation on the top of Kilimanjaro, Tanzania, using eddy covariance data. Ann. Glaciol. 46, 227–233.

Cullen, N.J., Sirguney, P., Mölg, T., Kaser, G., Winkler, M., Fitzsimons, S.J., 2013. A century of ice retreat on Kilimanjaro: the mapping reloaded. Cryosphere 7, 419–431.

deMenocal, P., Ortiz, J., Guilderson, T., Adkins, J., Sarnthein, M., Baker, L., Yarusinsky, M., 2000. Abrupt onset and termination of the African Humid Period: rapid climate responses to gradual insolation forcing. Quat. Sci. Rev. 19, 347–361.

Downie, C., Wilkinson, P., 1972. The Geology of Kilimanjaro. Dept. of Geology, University of Sheffield, Sheffield.

Funk, C., Dettinger, M.D., Michaelsen, J.C., Verdin, J.P., Brown, M.E., Barlow, M., Hoell, A., 2008. Warming of the Indian Ocean threatens eastern and southern African food security but could be mitigated by agricultural development. Proc. Natl. Acad. Sci. U. S. A. 105, 11081–11086.

Gabrieli, J., 2008. Trace Elements and Polycyclic Aromatic Hydrocarbons (PAHs) in Snow and Ice Sampled at Colle Gnifetti, Monte Rosa (4450 m), During the Last 10,000 Years: Environmental and Climatic Implication (PhD thesis), Department of Environmental Science. University of Venice, Venice, p. 178.
Gabrielli, P., Cozzi, G., Torcini, S., Cescon, P., Barbante, C., 2008. Trace elements in winter snow of the Dolomites (Italy): a statistical study of natural and anthropogenic contributions. Chemosphere 72, 1504–1509.
Gabrielli, P., Planchon, F., Barbante, C., Boutron, C.F., Petit, J.R., Bulat, S., Hong, S., Cozzi, G., Cescon, P., 2009. Ultra-low rare earth elements content in accreted ice from sub-glacial Lake Vostok, Antarctica. Geochim. Cosmochim. Acta 73, 5959–5974.
Gabrielli, P., Plane, J.M.C., Boutron, C.F., Hong, S., Cozzi, G., Cescon, P., Ferrari, C., Crutzen, P., Petit, J.R., Lipenkov, V.Y., Barbante, C., 2006. A climatic control on the accretion of meteoric and super-chondritic iridium–platinum to the Antarctic ice cap. Earth Planet. Sci. Lett. 250, 459–469.
Gabrielli, P., Wegner, A., Petit, J.R., Delmonte, B., De Dekker, P., Gaspari, V., Fisher, H., Ruth, U., Kriews, M., Boutron, C.F., Cescon, P., Barbante, C., 2010. A major glacial–interglacial change in aeolian dust composition as inferred from Rare Earth Elements in Antarctic ice. Quat. Sci. Rev. 29, 265–273.
Hastenrath, S., Geischar, L., 1997. Glacier recession on Kilimanjaro, East Africa, 1912–89. J. Glaciol. 43, 455–459.
Hastenrath, S., 2001. Variations of East African climate during the past two centuries. Clim. Change 50, 209–217.
Hardy, D.R., 2011. Kilimanjaro. In: Singh, V.P., Singh, P., Haritashya, U.K. (Eds.), Encyclopedia of Snow, Ice and Glaciers. Springer, Dordrecht, The Netherlands, pp. 672–679.
Hinkley, T.K., Lamothe, P.J., Wilson, S.A., Finnegan, D.L., Gerlach, T.M., 1999. Metal emissions from Kilauea, and a suggested revision of the estimated worldwide metal output by quiescent degassing of volcanoes. Earth Planet. Sci. Lett. 170, 315–325.
Hong, S., Barbante, C., Boutron, C.F., Gabrielli, P., Gaspari, V., Cescon, P., Thompson, L.G., Ferrari, C., Francou, B., Maurice-Bourgoin, L., 2004. Atmospheric heavy metals in tropical South America during the past 22,000 years recorded in a high altitude ice core from Sajama, Bolivia. J. Environ. Monit. 6, 222–226.
Hong, S., Lee, K., Hou, S., Hur, S.D., Ren, J., Burn, L.J., Rosman, K.J.R., Barbante, C., Boutron, C.F., 2009. An 800-year record of atmospheric As, Mo, Sn, and Sb in central Asia in high-altitude ice cores from Mt. Qomolangma (Everest), Himalayas. Environ. Sci. Technol. 43, 8060–8065.
Jenk, T.M., Szidat, S., Bolius, D., Sigl, M., Gäggeler, H.W., Wacker, L., Ruff, M., Barbante, C., Boutron, C.F., Schwikowski, M., 2009. A novel radiocarbon dating technique applied to an ice core from the Alps indicating late Pleistocene ages. J. Geophys. Res. 114.
Kaser, G., Hardy, D.R., Mölg, T., Bradley, R.S., Hyera, T.M., 2004. Modern glacier retreat on Kilimanjaro as evidence of climate change: observations and facts. Int. J. Clim. 24, 329–339.
Kaser, G., Mölg, T., Cullen, N.J., Hardy, D.R., Winkler, M., 2010. Is the decline of ice on Kilimanjaro unprecedented in the Holocene? Holocene 20, 1079–1091.
Kaspari, S., Hooke, R.L., Mayewski, P., Kang, S., Hou, S., Qin, D., 2008. Snow accumulation rate on Qomolangma (Mount Everest), Himalaya: synchroneity with sites across the Tibetan Plateau on 50–100 year timescales. J. Glaciol. 54, 343–352.
Kaspari, S., Mayewski, P.A., Handley, M., Osterberg, E., Kang, S., Sneed, S., Hou, S., Qin, D., 2009. Recent increases in atmospheric concentrations of Bi, U, Cs, S and Ca from a 350-year Mount Everest ice core record. J. Geophys. Res. 114. D04302.
Kent, P.E., 1944. Kilimanjaro: an active volcano. Nature 153, 454–455.
Kuhn, M., 1987. Micro-meteorological conditions for snow melt. J. Glaciol. 33, 24–26.
Lyon, B., DeWitt, D.G., 2012. A recent and abrupt decline in the East African long rains. Geophys. Res. Lett. 39, L02702.
Mather, T.A., Witt, M.L.I., Pyle, D., Quayle, B.M., Aiuppa, A., Bagnato, E., Martin, R.S., Sims, K.W.W., Edmonds, M., Sutton, A.J., Ilyinskaya, E., 2012. Halogens and trace metal emissions from the ongoing 2008 summit eruption of Kılauea volcano, Hawaii. Geochim. Cosmochim. Acta 83, 292–323.
Meyer, H., 1900. Der Kilimandscharo. Reimer–Vohsen, Berlin.
Mölg, T., Cullen, N.J., Hardy, D.R., Winkler, M., Kaser, G., 2009. Quantifying climate change in the tropical midtroposphere over East Africa from glacier shrinkage on Kilimanjaro. J. Clim. 22, 4162–4181.
Mölg, T., Hardy, D.R., 2004. Ablation and associated energy balance of a horizontal glacier surface on Kilimanjaro. J. Geophys. Res. 109, D16104.
Mölg, T., Hardy, D.R., Kaser, G., 2003. Solar-radiation-maintained glacier recession on Kilimanjaro drawn from combined ice-radiation geometry modeling. J. Geophys. Res. 108, 4731.
Mölg, T., Kaser, G., Cullen, N.J., 2010. Glacier loss on Kilimanjaro is an exceptional case. Proc. Natl. Acad. Sci. U. S. A. 107, E68.
Nonnotte, P., Guillou, H., Le Gall, B., Benoit, M., Cotton, J., Scaillet, S., 2008. New K-Ar age determinations of Kilimanjaro volcano in the North Tanzanian diverging rift, East Africa. J. Volcanol. Geotherm. Res. 173, 99–112.
Planchon, F., Boutron, C.F., Barbante, C., Cozzi, G., Gaspari, V., Wolff, E.W., Ferrari, C., Cescon, P., 2002. Changes in heavy metals in Antarctic snow from Coats Land since the mid-19th to the late-20th century. Earth Planet. Sci. Lett. 200, 207–222.
Siebert, L., Simkin, T., 2002. Volcanoes of the World: an Illustrated Catalog of Holocene Volcanoes and Their Eruptions. In: Global Volcanism Program Digital Information Series, GVP-3. Smithsonian Institution.
Thompson, L.G., Brecher, H.H., Mosley-Thompson, E., Hardy, D.R., Mark, B.G., 2009. Glacier loss on Kilimanjaro continues unbated. Proc. Natl. Acad. Sci. U. S. A. 106, 19770–19775.
Thompson, L.G., Brecher, H.H., Mosley-Thompson, E., Hardy, D.R., Mark, B.G., 2010. Response to Mölg et al.: glacier loss on Kilimanjaro is consistent with widespread ice loss in low latitudes. Proc. Natl. Acad. Sci. U. S. A. 107, E69–E70.
Thompson, L.G., Davis, M.E., Mosley-Thompson, E., Sowers, T., Henderson, K.A., Zagorodnov, V.S., Lin, P.N., Mikhalenko, V.N., Campen, R.K., Bolzan, J.F., Cole-Dai, J., Francou, B., 1998. A 25,000-year tropical climate history from Bolivian ice cores. Science 282, 1858–1864.
Thompson, L.G., Mosley-Thompson, E., Davis, M., Mountain, K., 2011. A paleoclimatic perspective on the 21st-century glacier loss on Kilimanjaro, Tanzania. Ann. Glaciol. 52, 60–68.
Thompson, L.G., Mosley-Thompson, E., Davis, M.E., Henderson, K.A., Brecher, H.H., Zagorodnov, V.S., Mashiotta, T.A., Lin, P.N., Mikhalenko, V.N., Hardy, D.R., Beer, J., 2002. Kilimanjaro ice core records: evidence of Holocene climate change in tropical Africa. Science 298, 589–593.
Tierney, J.E., Mayes, M.T., Meyer, N., Johnson, C., Swarzenski, P.W., Cohen, A.S., Russell, J.M., 2010. Late-twentieth-century warming in Lake Tanganyika unprecedented since AD 500. Nat. Geosci. 3, 422–425.
Tierney, J.E., Smerdon, J.E., Anchukaitis, K.J., Seager, R., 2013. Multidecadal variability in East African hydroclimate controlled by the Indian Ocean. Nature 493, 389–392.
Verschuren, D., Laird, K.R., Cumming, B.F., 2000. Rainfall and drought in equatorial east Africa during the past 1,100 years. Nature 403, 410–414.
Verschuren, D., Sinninghe Damste, J.S., Moernaut, J., Kristen, I., Blaauw, M., Fagot, M., Haug, G.H., 2009. Half-precessional dynamics of monsoon rainfall near the East African Equator. Nature 462, 637–641.
Winkler, M., Kaser, G., Cullen, N.J., Moelg, T., Hardy, D.R., Pfeffer, W.T., 2010. Land-based marginal ice cliffs: focus on Kilimanjaro. Erkunde 64, 179–193.