Large variability of trace element mass fractions determined by ICP-SFMS in ice core samples from worldwide high altitude glaciers

Chiara Uglietti [a], Paolo Gabrielli [a,b,*], John W. Olesik [b], Anthony Lutton [b], Lonnie 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, The Ohio State University, 275 Mendenhall Laboratory, 125 South Oval Mall, Columbus, OH 43210, USA

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ABSTRACT

We quantified leaching and mass fractions of trace elements in melted acidified ice core samples measured by Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS). This assessment was conducted using nine ice core sections retrieved from various high-altitude drilling sites in South America, Africa, Asia and Europe.

Twenty trace elements (Ag, Al, As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Rb, Sb, Sn, Ti, Tl, U, V and Zn) were determined. During a 1½ month acid leaching period our assessment shows distinct increases in the concentration of various trace elements (10% for Cd; 30% for Pb; 50–80% for As, Cu, Mo, Mn, Tl and U; 80–90% for Bi, Rb, Sb, Sn and Zn; 100–160% for Al, Cr, Co, Ti and V; 200% for Fe). The exception is Ag, which shows a 50% decrease. We found that the observed relative increases in trace element concentrations are: (i) independent of the absolute trace element concentrations and micro-particle levels/size of the samples, and (ii) unlikely to affect reconstructions of the crustal/non-crustal origin of trace elements based on the use of the crustal enrichment factor.

After 1½ months of leaching, the measured trace element concentrations were found to be only a fraction of the estimated total concentration and that the mass fractions determined vary largely from element to element (on average 80–90% for As and Mn; 50–70% for U, Fe, Ti and Tl; 20–50% for Al, Cd, Co, Cr, Cu, Mo, Pb, Rb, V and Zn; 15% for Bi and 2% for Ag). These observations imply: (i) a significant underestimation of the mass fluxes of these trace elements to high altitude glaciers and (ii) a likely dependency of the mass fractions on the typical crystallographic position of each trace element within the micro-particles contained in the ice core samples.

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1. Introduction

Human and natural processes introduce large amounts of trace elements into the atmosphere (Nriagu, 1989; Pacyna and Pacyna, 2001), thus influencing its chemical composition. Trace elements can be transported in various phases (gaseous, liquid, solid), deposited on the surface of high altitude glaciers and ultimately entrapped in the ice (Gabrielli and Vallelonga, in press). When trace elements were determined in snow and ice cores, they have proven to be valuable proxies of past climate and environmental processes (Gabrielli et al., 2010; Kaspari et al., 2009; Planchon et al., 2002). In particular, these studies allowed better understanding of the past and modern human-influenced pathways of trace

elements from the various reservoirs to the sinks (Barbante et al., 2004; Hong et al., 1994; Krachler et al., 2008).

Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) is recognised as the most sensitive and accurate technique for the quantification of ultra-trace element concentrations in ice cores (Barbante et al., 1997; Gabrielli et al., 2004; Krachler et al., 2005). Typically, ICP-SFMS analyses of melted ice core samples are performed after acidification by ultrapure HNO_3 (Gabrielli et al., 2005; McConnell et al., 2002; Planchon et al., 2002). This process is crucial to dissolve trace elements in microparticles (such as crustal dust) into the solution (Gabrielli et al., 2010; Ruth et al., 2008). Importantly, only trace elements dissolved in solution or included in sufficiently small particles are vaporised in the plasma, converted into elemental ions and ultimately detected by ICP-SFMS (Horner et al., 2008; Olesik and Gray, 2012).

Edwards and Sedwick determined Fe by flow injection analysis in East Antarctic snow/ice and observed significant increases in meltwater Fe concentrations for up to 3 months following a slight 0.1% v/v HCl acidification (Edwards and Sedwick, 2001; Edwards

et al., 2006). They defined the Fe concentration obtained after 3 months as total-dissolvable Fe and made the hypothesis that most of the Fe contained in polar snow and ice samples was rendered soluble under mildly acidic conditions, with the exception of that contained within the lattice of highly refractory alumino-silicate particles.

Successive studies (Gabrielli et al., 2010; Gaspari et al., 2006; Ruth et al., 2008) demonstrated that only a fraction (30–65%) of crustal elements such as Fe, Al and Rare Earth Elements (in terms of estimated total concentration) is determined by ICP-SFMS in simply acidified (1% v/v HNO$_3$) polar ice core samples which are characterised by very low dust content. Clearly, this same effect could be important also for other trace elements, especially when determined in dust laden ice core samples from high altitude glaciers located at mid to low latitudes. Recently Rhodes and co-workers tested the leaching over time of trace elements using mineral dust standards at 10 µg g^{-1} concentration and dissolved in acidified (1% HNO$_3$) ultrapure water as surrogates for melted ice core samples (Rhodes et al., 2011). This test resulted in significantly increasing recoveries of trace elements over time.

In this paper we quantify trace element leaching and mass fraction when determined directly in a variety of real ice core samples by employing both simple acid and full acid digestions. We note that our ice samples are substantially different from the synthetic samples used in the Rhodes' experiment. While acidified dust standards in ultrapure water are characterised by a single and uniform mineralogy, real ice core samples contain both complex natural water matrices and mineralogies of the leached micro-particles (Gaudichet et al., 1988). So far the results of Rhodes and co-workers have been initially tested by determining trace element leaching (but not the mass fraction) in a single polar (low-dust) snow sample (Koffmann et al., 2014). In this context the quantification of both trace element leaching and mass fractions in a variety of dust laden ice core samples is necessary.

To fully evaluate the efficiency of the simple HNO$_3$ acidification of melted ice core samples, we have quantified by ICP-SFMS the leaching and the mass fraction of twenty trace elements (Ag, Al, As, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Rb, Sb, Sn, Ti, Tl, U, V, and Zn) during 1½ months of leaching. For this test, we procured nine ice core sections extracted from high altitude glaciers in South America, Europe, Asia and Africa.

Studying the ultimate trace element mass fraction that can be obtained by simple acidification of real ice core samples is important, as large deviations from the total may severely hamper both the calculation of the mass fluxes of atmospheric trace elements to high altitude glaciers and the comparison of trace element levels in samples processed using different methodologies. In particular, if relative increases in trace element concentrations over time were strongly dissimilar, classic interpretative tools based on elemental mass ratios, such as the crustal enrichment factor (e.g. Boutron et al., 1991; Gabrielli et al., 2004; McConnell and Edwards, 2008) would be affected, potentially introducing biases in the interpretation of the origin of trace elements.

2. Methodology

2.1. Locations and samples

We selected nine ice core sections retrieved from nine high altitude drilling sites: Dasuopu (central Himalaya, China); Dunde (Qilian Shan, China); Quelccaya (Cordillera de Vilcanota, Peru); Mt. Ortles (South Tyrol, Italy); Puruogangri (western Tanggula Shan, China); Col of Huascarán (Cordillera Blanca, Peru); Guliya (western Kunlun Shan, China); Northern Ice Field (Kilimanjaro, Tanzania); and Naimona'nyi (western Himalaya) (Table 1).

These sites, which have distinct lithological backgrounds, are the most likely potential source areas for the micro-particles contained in the corresponding samples. Kilimanjaro is a dormant volcano, characterised by a mildly alkaline series (i.e. alkali olivine basalts, tephritic lavas) (Williams, 1969). Mt. Ortles is composed mainly of sedimentary rocks (dolomites and limestones) (Desio, 1967). The bedrock below the Quelccaya and Huascarán glaciers is composed of andesite (Mercer and Palacios, 1977) and granodiorite (Evans and DeGraff, 2002), respectively. The Tibetan Plateau and the Himalayan chain consist mainly of uplifted sedimentary and metamorphic rocks (Liu, 1988; Sun et al., 2007).

Because of the variety of locations and geological backgrounds from which these samples come, we were presented with an array of complex micro-particle mineralogies for our test. For instance, microanalyses performed on the Dunde ice core using a scanning electron microscope with an energy dispersive X-ray system revealed the presence of quartz, feldspars, carbonates, biotite and iron oxides (Mary Davis, personal communication), which is a mineralogy similar to that of dust in the nearby Qaidam Basin (Li et al., 2013)

2.2. Materials and reagents

Large mouth low density polyethylene (LDPE) bottles (60 mL, Nalgene) were used to store both the standard solutions and the melted samples during the test. All the items that came in contact with the samples, including the stainless-steel forceps used for rinsing, were pre-cleaned by prolonged immersion in a series of acid baths of decreasing concentration and increasing HNO$_3$ purity accordingly to well established procedures (Boutron, 1990). Ultrapure MilliQ water (RiOs™ 16, Millipore, Billerica, MA) was produced in the Class 100 clean room at the Byrd Polar Research Center (BPRC) and used for rinsing labware, washing ice samples and preparing diluted standard solutions for external calibration. All the samples and standards were acidified using Optima grade HNO$_3$ (Fisher Scientific).

2.3. Preparation of the simply acidified samples

Using a band saw in a cold room laboratory at BPRC, a block of ~165 g was cut from a section of ice core from each of the nine sites listed in Table 1. All the ice samples were decontaminated in our Class 100 clean room by triple rinsing with ultrapure water using stainless-steel forceps (Wei et al., 2008). The average mass of the washed samples was ~110 g, and they were thawed in pre-cleaned large mouth 1 L LDPE bottles (Nalgene) at room temperature, poured in pre-cleaned 60 mL LDPE bottles and frozen for a week. These samples were then melted and acidified (2% v/v) using Optima grade HNO$_3$ and kept at room temperature (23 °C). The strength of the acidification (2% v/v) was chosen in consideration of the relatively high dust content which is typical of mid-low latitude ice core samples and on the basis of past experience acquired during the ICP-SFMS analysis of similar samples (Gabrielli et al., 2008).

In our leaching experiment, the first session of analyses (day 1) was performed 24 h after the acidification (day 0). A second session was performed one day after the first analysis (day 2) followed by analyses after one week (day 8), two weeks (day 15) and six weeks (day 43) after the acidification (Fig. 1). As the most suitable benchmark for comparison we chose the concentrations obtained on day 1, as the 24 h interval has previously been adopted as the most common between the acidification and the analysis of discrete samples (Rhodes et al., 2011).

Here we note that the significance of this experiment lies mainly in the evaluation of trace element leaching in discrete samples that are acidified at least one day before the analysis.

Table 1
Descriptions of the nine ice core sections used in the analytical test. Dust concentration, standard deviation and size mode were determined in the nine ice sections (this study).

Sample	Drilling site	Elevation (m a.s.l.)	Sample depth (m)	Year (AD)	Dust (ng g⁻¹)	SD Dust (ng g⁻¹)	Dust mode (μm)	Reference
1	Dasuopu, central Himalaya, China	7200	65	1951	4050	250	5	Thompson et al. (2000)
2	Dunde, Qilian Shan, China	5325	87	~1150	10,870	535	10	Thompson et al. (1989)
3	Quelccaya, Cordillera de Vilcanota, Peru	5600	30	1983–1984	50	4	3	Thompson et al. (2013)
4	Mt. Ortles, South Tyrol, Italy	3859	55	~1900	615	41	8	Gabrielli et al. (2012)
5	Puruogangri, western Tanggula Shan, China	5961	81	~1450	1180	80	6	Thompson et al. (2006)
6	Col of Huascarán, Cordillera Blanca, Peru	6048	86	1916	195	13	12	Thompson et al. (1995)
7	Guliya, western Kunlun Shan, China	6710	20	1921	11,660	700	8	Thompson et al. (1997)
8	Northern Ice Field, Kilimajaro, Tanzania	5795	17	~800	65	6	6	Thompson et al. (2002)
9	Naimona'nyi, western Himalaya, China	6030	36	~1860	885	56	10	Kehrwald et al. (2008)
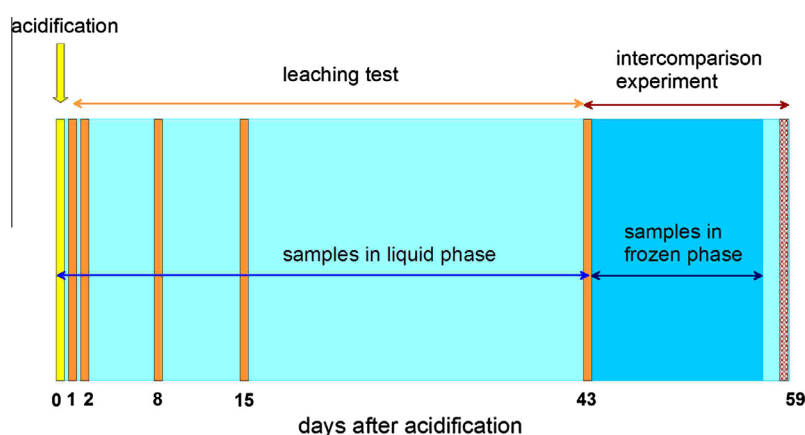
Fig. 1. Scheme of the analyses performed during the test period (vertical filled bars, Byrd Polar Research Center; gridded bar, School of Earth Science).

However, our test can provide limits of trace element concentrations and fractions determined by means of continuous analyses as performed with a melter system coupled directly with the ICP-SFMS (Knüsel et al., 2003; McConnell et al., 2002). In this latter case, the sample stream is combined with HNO_3 a few seconds before its introduction into the ICP-SFMS and therefore the leaching can occur over a very short period of time.

Immediately prior to each session of analysis, ~5 mL sub-aliquots were poured from the original 60 mL sample bottle into pre-cleaned polypropylene (PP) vials (10 mL, Sarstedt) for a single measurement. The vials were placed in a rack and agitated manually at least one half hour before the analysis. They were not agitated again prior to analysis to allow the largest micro-particles to settle. During the analysis the auto sampler probe was set at 1.8 cm above the bottom of the PP vials in order to decrease the possibility of large particle aspiration, which may obstruct the capillary during the transfer of the sample solution to the introduction system of the ICP-SFMS. In this way we increased the chances for the analysis of the most homogenous solution possible. These details were crucial to obtain an excellent reproducibility of the analysis of ice core samples characterised by significant micro-particle content.

To produce a procedural blank, a large mouth 1 L LDPE bottle was filled with ultrapure water. Aliquots were poured into three LDPE 60 mL bottles. The remaining water (about 0.6 L), was frozen in the 1 L LDPE bottle in a horizontal position to simulate a half

cross section of an artificial "ice core". This ice sample was treated exactly like the real ice core sections and ultimately yielded three additional 60 mL aliquots. The averages of the three blank replicates before and after the artificial ice core processing were computed and their difference was taken as a net procedural blank that accounts for the possible contamination that occurred during sample preparation.

2.4. ICP-SFMS analysis

Determination of trace elements was carried out in the ultra-trace ice core laboratory at BPRC, which is equipped with an ICP-SFMS (Element 2, Thermo Scientific, Bremen). Temperature (23 °C) and humidity (40–60%) are constant in this laboratory which is maintained in clean condition by means of (i) multiple high-efficiency HEPA filters mounted on the ceiling and (ii) constant overpressure with respect to the external office environment, which is connected through a dual-entry vestibule. An additional HEPA filter is placed directly above the sample introduction area of the instrument. The ICP-SFMS is coupled with a desolvation system (Apex Q, ESI) for sample introduction. A low resolution mode (LR) was used for the detection of ^{85}Rb, ^{95}Mo, ^{109}Ag, ^{111}Cd, ^{120}Sn, ^{121}Sb, ^{205}Tl, ^{208}Pb, ^{209}Bi and ^{238}U, medium resolution mode (MR) for ^{27}Al, ^{48}Ti, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{63}Cu, and ^{64}Zn, and high resolution mode (HR) for ^{75}As. Detailed instrumental conditions

used during the analyses are reported in the Supplement (Table S1).

Standard solutions were prepared in order to bracket the sample concentrations. External calibrations were performed at the beginning and at the end of every analytical session using standards obtained by mass dilution from a multi-elemental custom-made stock solution (CPI International) (1 µg/mL for Ag, Bi, Cd, Sb, Tl; 10 µg/mL for As, Mo, Sn, U; 100 µg/mL for Cr, Cu, Co, Mn, Pb, Rb, V, Zn; and 1000 µg/mL (for Al, Fe, Na, Ti). Different concentrations of the multi-stock solution are used to mimic the relative levels of the average crustal abundances and allow appropriate calibration ranges to be obtained. Standard concentrations ranged between 1 and 20 pg g^{-1} for Ag, Bi, Cd and Sb; 2 and 200 pg g^{-1} for As, Mo, Sn and U; 20 and 2000 pg g^{-1} for Co, Cr, Cu, Mn, Pb, Rb, V and Zn; and 200–20,000 pg g^{-1} for Al, Fe and Ti. The instrumental standard deviation of the standard concentrations varied between 2% and 10%. Slopes and correlation coefficients (r, which averaged 0.996 ± 0.022) were calculated with the weighted linear regression method using the Element 2 software.

Stability of the instrumental signal was checked in LR, MR and HR modes every five samples using a 1 ng g^{-1} In solution. Stability was typically within 8%, with an intensity of the In signal of approximately 3×10^6 counts per second in LR.

Procedural blanks (Table S2) range from 1% to 5% of sample concentrations (compared to the typically lowest sample concentrations on day 1 of the leaching test) for all elements except Cd, Cu, Sb, Sn and Zn, for which procedural blanks range between 20% and 40% of the lowest values. No significant trend for the procedural blank samples was observed over the entire leaching period, indicating a negligible trace element contribution from the 60 mL LDPE bottles to the liquid samples.

Accuracy and precision were routinely evaluated during every phase of analysis. Accuracy was assessed by using a certified material solution (TM Rain 95, Environment Canada), which was diluted by a factor of ~20 to obtain concentrations comparable to sample values. This solution was determined with an accuracy within 5–10% for Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Sb, Sn, Tl, U, V; 20% for As and 40% for Bi. Long-term precision was estimated as relative standard deviation of the concentrations determined in the diluted certified material during the entire test period (1½ months) and varied from 5% to 10% for Co, Bi, Cd, Cu, Fe, Mn, Mo, Sb, Sn, Tl, U, V and Zn to 15% for Cr, Rb, Pb and Ti. A lower precision was found
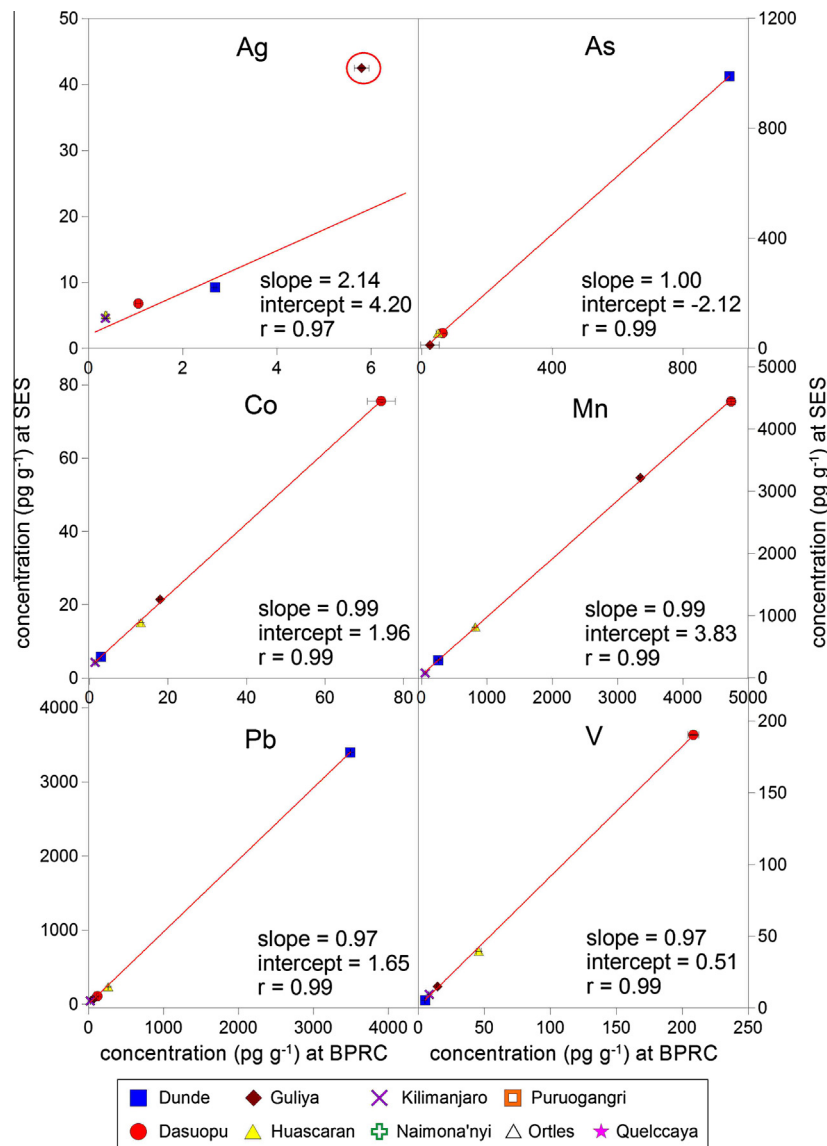

Fig. 2. Scatter plots of trace element concentrations determined at the Byrd Polar Research Center (BPRC) (day 43) and at the School of Earth Sciences (SES) (day 59). The Ag determination in the sample from Guliya (circled) is considered an outlier and is not included in the correlation.

for Ag, Al and As (30%). Detection limits were calculated as three times the standard deviation of 10 determinations of a 2% HNO_3 ultrapure water solution and ranged from 0.02 pg g^{-1} for Bi to 200 pg g^{-1} for Al. Typical quality assessment parameters are also detailed in Gabrielli et al. (2014).

2.5. ICP-SFMS inter-comparison

In order to better constrain the trace element concentrations obtained after 1½ months of leaching and to further asses the quality of our analysis, we utilised two essentially identical instruments (Element 2, Thermo Scientific, Bremen) located at BPRC and at the School of Earth Sciences (SES) of The Ohio State University. These two instruments are equipped with identical micronebulizers, although mounted on two different sample introduction systems (a desolvation system at BPRC and a conventional quartz spray chamber at SES; Tables S1 and S3).

At the end of the leaching experiment (day 43), the nine ice core samples were frozen for two weeks. Afterwards, they were melted and analysed. Concentrations determined at BPRC (day 43) versus those determined at SES (day 59) show very high correlation coefficients (Figs. 2 and S1; weighted linear regressions), spanning between 0.90 and 0.99 for all the trace elements except Bi (0.47).

The slopes vary between: 0.9 and 1.1 for Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Rb, Sb, Tl, U, V, Zn; 0.76 for Bi. The lowest and the highest slopes were 0.65 for Sn and 2.14 for Ag. The intercepts were not significant for most of the trace elements except Ag (4 pg g^{-1}), Bi (12 pg g^{-1}), Cd (2.4 pg g^{-1}) and Sn (16 pg g^{-1}), possibly indicating a significant instrumental background for these elements determined at SES.

2.6. Full digestion of samples and analysis

Additional sub-aliquots of about 10 mL from each sample were prepared by microwave (Ethos EZ, Milestone, Bergamo, Italy) full
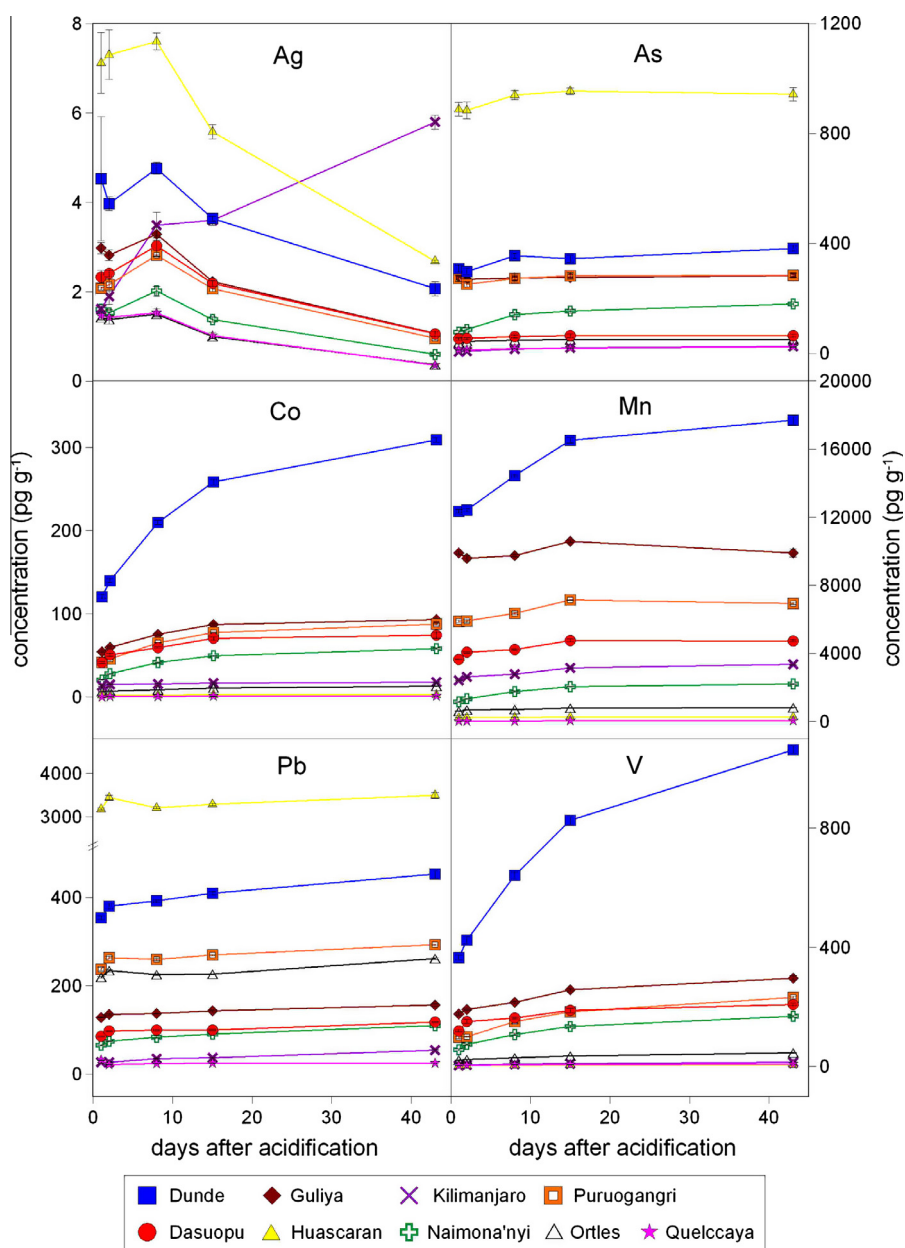
Fig. 3. Examples of changes in trace element concentrations over time after acidication. The error bars indicate the instrumental standard deviation (when these are not visible this indicates that they are smaller than the symbol used).

acid digestion at the BPRC in order to estimate the total trace element concentrations which are useful for calculating the mass fraction determined by analysing the 2% HNO_3 sample solutions. The samples from the Dunde and Guliya ice caps presented particular complications since they contained a few large visible particles (on the order of ~0.1 mm), which could not be dissolved completely by full acid digestion. For this reason, only the supernatant solution in all the original 60 mL bottles was prepared by full digestion. After the 60 mL bottles were agitated, they were allowed to rest for 15 min in order to allow the largest particles to settle. Afterwards, 9 mL of supernatant sample solution were pipetted (Eppendorf Research plus) into acid pre-cleaned polytetrafluoroethylene (PTFE) pressure vessels (100 mL, TFM™ PTFE, Milestone).

Each sample was acidified by adding a 1 mL mixture of Optima grade acids (0.8 mL of HNO_3; 0.2 mL of HF), then irradiated by microwave (Gabrielli et al., 2010). Analyses of these samples were performed by ICP-SFMS at BPRC by using an HF resistant Teflon® (PFA) spray chamber and the same method as for the 2% HNO_3 sample solutions. Procedural blanks were obtained by processing

ultrapure water and artificial ice core samples in the same way (Table S2). In general, the average concentrations of the trace elements in procedural blanks are 1–8% of the average concentrations for all the trace elements, except Co, Cr, Cu, Mo, Sn and Zn (blanks up to 20%), possibly due to some contamination that occurred during the digestion procedure. While procedural blanks are within the instrumental error and thus are adequate to determine most of the trace elements in most of the samples, their levels are typically 30–40% of the concentrations for all the trace elements determined in the cleanest ice core samples (i.e. Quelccaya and Huascarán), which indicates the difficulty of obtaining very accurate trace element concentrations in clean ice core samples by means of full acid digestion.

2.7. Micro-particle determinations

Before the acidification, a 10 mL sub-aliquot from each sample was poured into a 15 mL pre-cleaned LDPE bottle where micro-particle concentrations were determined using a Coulter
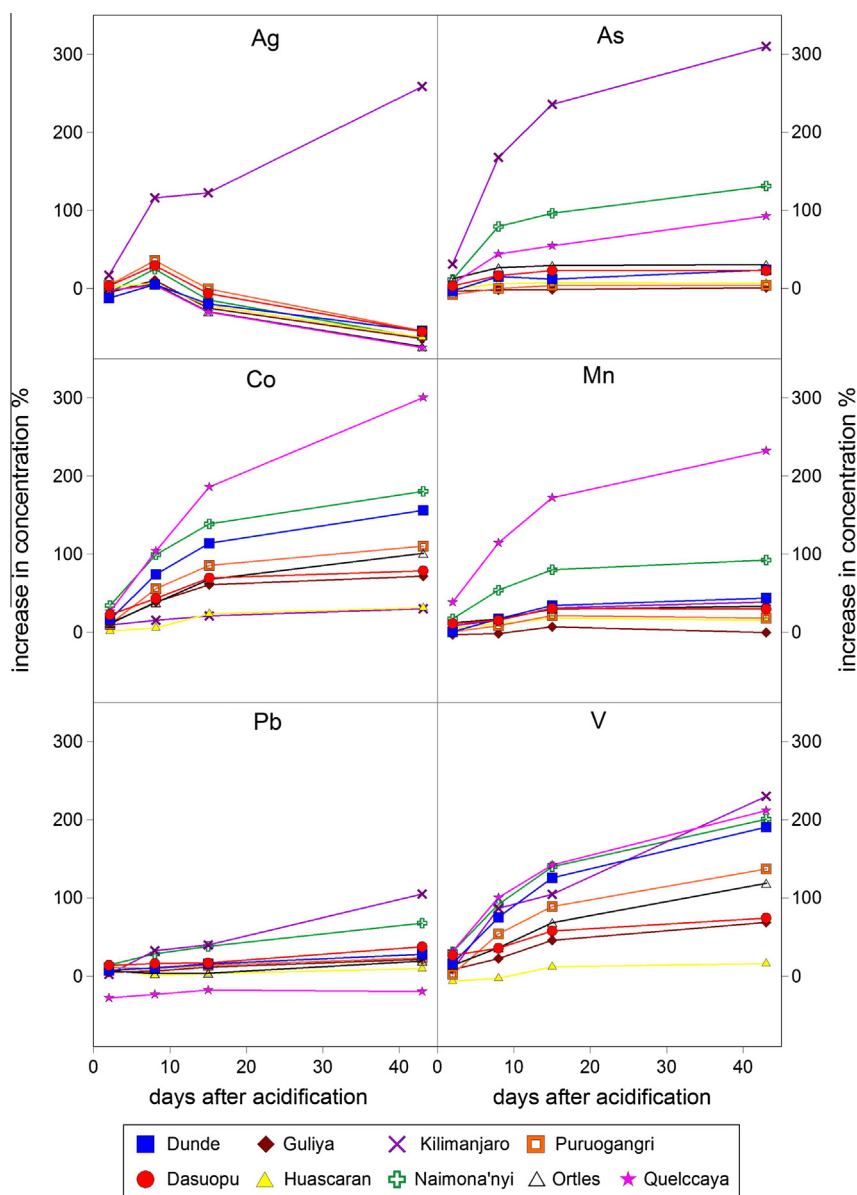

Fig. 4. Relative changes in trace element concentrations over time with respect to the first determination made 24 h after the acidification.

counter (Multisizer 4, Beckman Coulter, Danvers, MA) following the basic procedures described in Thompson (1977).

3. Results and discussion

3.1. Leaching experiment

The results of the leaching experiment are displayed in Figs. 3 and 4 for Ag, As, Co, Mn, Pb and V, which are taken as representative of the entire data set. The trends of the other trace elements (Al, Bi, Cd, Cr, Cu, Fe, Mo, Rb, Sb, Sn, Ti, Tl, U and Zn) are reported in the Supplementary information (Figs. S2 and S3).

During the first week, the analyses showed a mean increase in trace element concentrations ranging between 2% and 10% for As, Bi, Cd, Cu, Mn, Mo, Pb, Sb, U and Zn, while Ag, Rb, Sn and Tl displayed an increase of 15%, and Al, Cr, Co, Fe and V concentrations showed the largest increase (30–50%) (Fig 3). During the second week, concentrations increased at approximately the same rate (5–10% for As, Bi, Cd, Mn, Mo, Pb, Sn, Tl and U; 15% for Cu, Rb, Sb and Zn; 20–30% for Al, Cr, Co, Fe, Ti and V).

However, between weeks 2 and 6 the rise in all the trace element concentrations was slower (1–6% per week), suggesting that

concentration changes were gradually levelling off. At the end of the leaching experiment (1½ months) the total mean increases in concentrations were: 10% for Cd, between 30% and 50% for Pb and U, between 55% and 80% for As, Cu, Mn, Mo, Sn, Tl and Zn, and between 90% and 150% for Al, Bi, Cr, Co, Rb, Sb, Ti and V. Finally the total increase for Fe was ∼200%. However, in some particular cases the increases were much larger. For example, the increase for As in the sample from Kilimanjaro was 300% after 1½ months, pointing to large inter-sample variability of the leaching process. Correlation coefficients between trace element concentrations (day 1) and trace element relative changes during the leaching test show a mean value of −0.20 (SD = 0.31) indicating that relative variations of concentration do not depend on the absolute trace element levels.

We also examined the behaviour of trace element concentrations in ice from the various sites. During the first week all the trace element concentrations in the sections from Dasuopu, Ortles, Guliya and Huascarán increased on average by 5–10%, while Quelccaya, Dunde, Kilimanjaro and Puruogangri sample concentrations increased by 20–30%. The change in the Naimona'nyi sample was the largest (40%). During the second week the samples from all the locations showed a further ∼15% increase in concentrations for all the trace elements, however the increase was reduced to
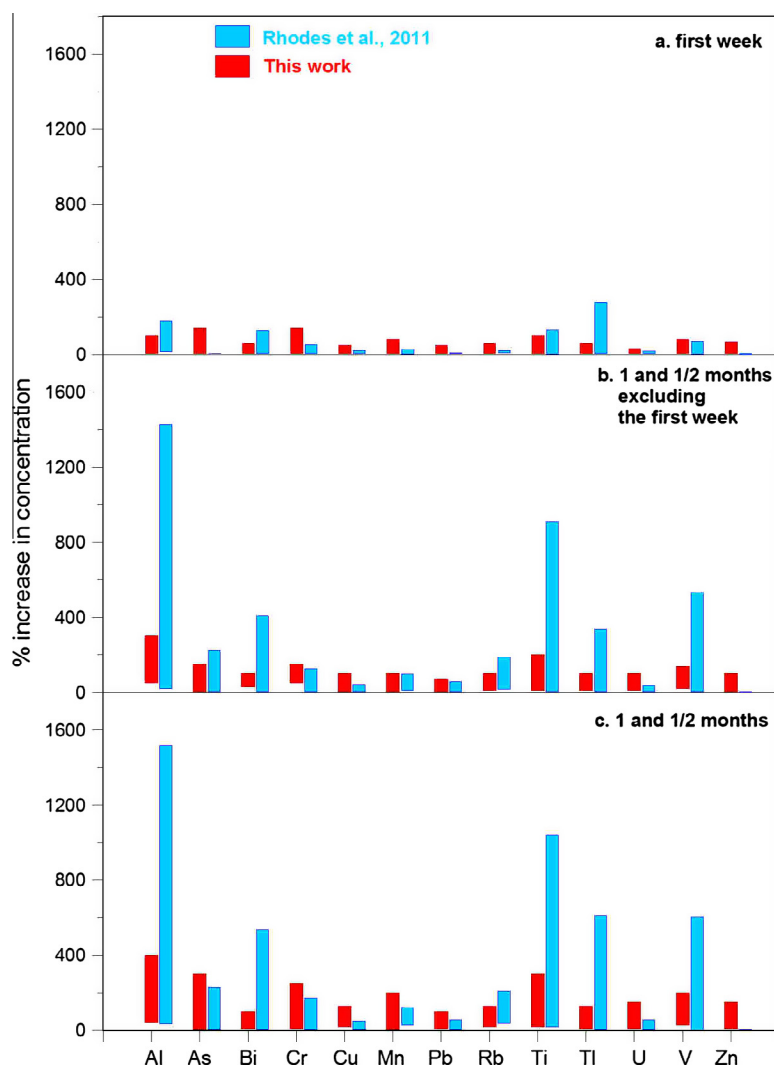
Fig. 5. Comparison between our test (red bars; ice core samples) and the experiment conducted by Rhodes and co-workers (blue bars; synthetic samples) showing the range of relative increases in trace element concentrations (bars represent the minimum to maximum variations among the samples) during different time intervals: the first week (a.); 1½ months period excluding the first week, referenced at day 7 (b.); 1½ months period of the experiment (c). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

approximately 5% during the last four weeks of the leaching test. The exception was the Kilimanjaro sample, the concentration of which rose by about 10% per week.

The micro-particle concentrations in these same samples (Table 1) were on the order of ~50 ng g^{-1} for Quelccaya and Kilimanjaro, and ~2 × 10^2 ng g^{-1} for the Huascarán sample. The samples from Mt. Ortles, Naimona'nyi and Puruogangri displayed mineral particle concentrations between ~6 × 10^2 and ~1 × 10^3 ng g^{-1}, while those from Dasuopu, Dunde and Guliya contained concentrations between ~4 × 10^3 and ~1 × 10^4 ng g^{-1}. The size distribution was similar for all the samples. However the modes varied from 3 to 6 μm for the Dasuopu, Quelccaya, Puruogangri and Kilimanjaro ice to 8–12 μm for those from the Dunde, Guliya, Ortles, Huascarán and Naimona'nyi samples (Table 1).

Correlation coefficients calculated between micro-particle concentration and relative trace elements changes show a mean value of −0.23 (SD = 0.21) while the average correlation coefficient

between dust mode and relative trace element changes are −0.15 (SD = 0.26). Thus, comparisons of the relative change in trace element concentrations over time and the micro-particle-content and size of the corresponding samples indicates that these variables are not correlated.

Differences in the concentration changes among the trace elements could instead be related to their positions in the lattices of the various silicate minerals, which are the main components of fine terrigenous, long-range transported micro-particles entrapped in ice cores (Gaudichet et al., 1988). Clay minerals have planar structures (Grim, 1962) with major elements such as Al and Fe typically occurring in crystalline positions, while other trace elements such Pb are often positioned between the different planes (Adamis et al., 2005). The latter can be leached quickly after acidification and, once they are mostly depleted within the mineral structure, their concentration can increase at a slower rate. In contrast, elements linked mainly to the mineral structure may continually be
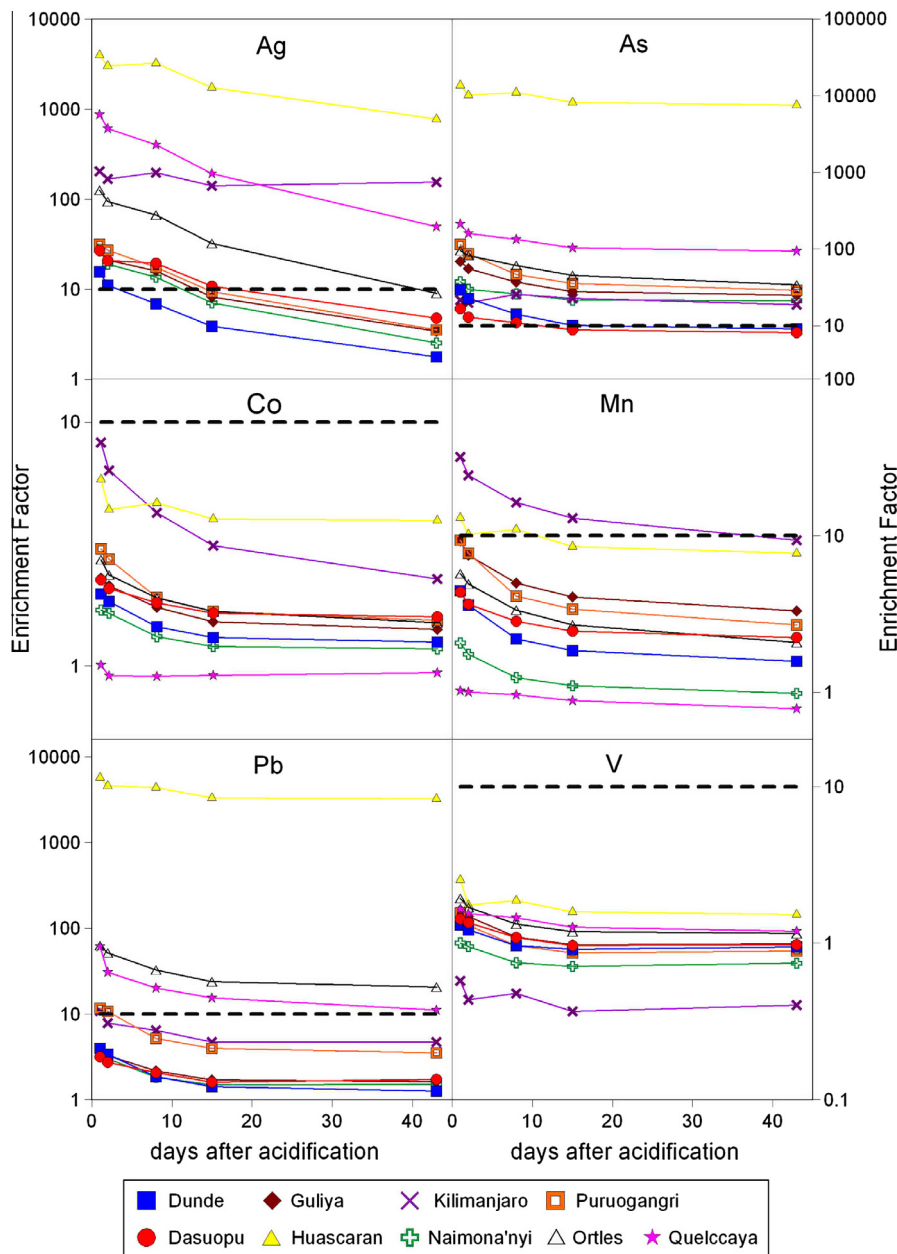

Fig. 6. Changes in the crustal enrichment factor (EFc) over time after acidification; the dashed line indicates the threshold at 10, typically used in the literature to distinguish between the crustal trace element contribution (EFc < 10) from that of different sources (EFc > 10).

leached with a resulting larger relative increase in concentration over time.

Ag concentrations showed unusual behaviour during the analysis of the ice core sections, such that they first increased and then started to decrease one week after the acidification. There was a decrease of 30% by the second week and a further mean decrease of 10% per week during the following four weeks, which was likely due to the Ag complexation with Cl⁻ and the consequent low stability (deposition) of AgCl in the acidified solution. The only exception to this was the sample from Kilimanjaro, which showed an Ag concentration increase during the first two weeks (20% on average), and a further incremental increase of about 10% per week during the last four weeks.

We compared our results with those obtained in the similar test by Rhodes et al., 2011, which used four certified rock standards (involving a few single mineralogies and textures) dissolved in acidified water (Fig. 5). In spite of the fact that Rhode and

co-workers used a lower acidification (HNO$_3$, 1% v/v vs. 2% in our test), their results show a much larger maximum increase for several elements (Al, Bi, Ti, Tl and V) (up to +1500%) than observed during our test on real ice core samples (up to +200%). Our determinations of several other trace elements (As, Cr, Mn, Pb, Rb and U) show maximum relative variations that are less than 100% when compared to those reported by Rhodes et al. (2011). The increase in concentration of Cu and Zn in the ice core samples was larger by a factor of 1.5 than reported by Rhodes et al. (2011).

Concentrations of trace elements that are determined in real acidified ice core samples can change differently over time when compared to levels determined in synthetic samples, especially in the case of Al, Bi, Ti and Tl. This may be related to the larger variety of the mineralogical species contained within every real ice core section, which have undergone several degrees of weathering. Multiple mineralogies of much-weathered crustal particles entrapped in ice cores may be more likely to release into solution
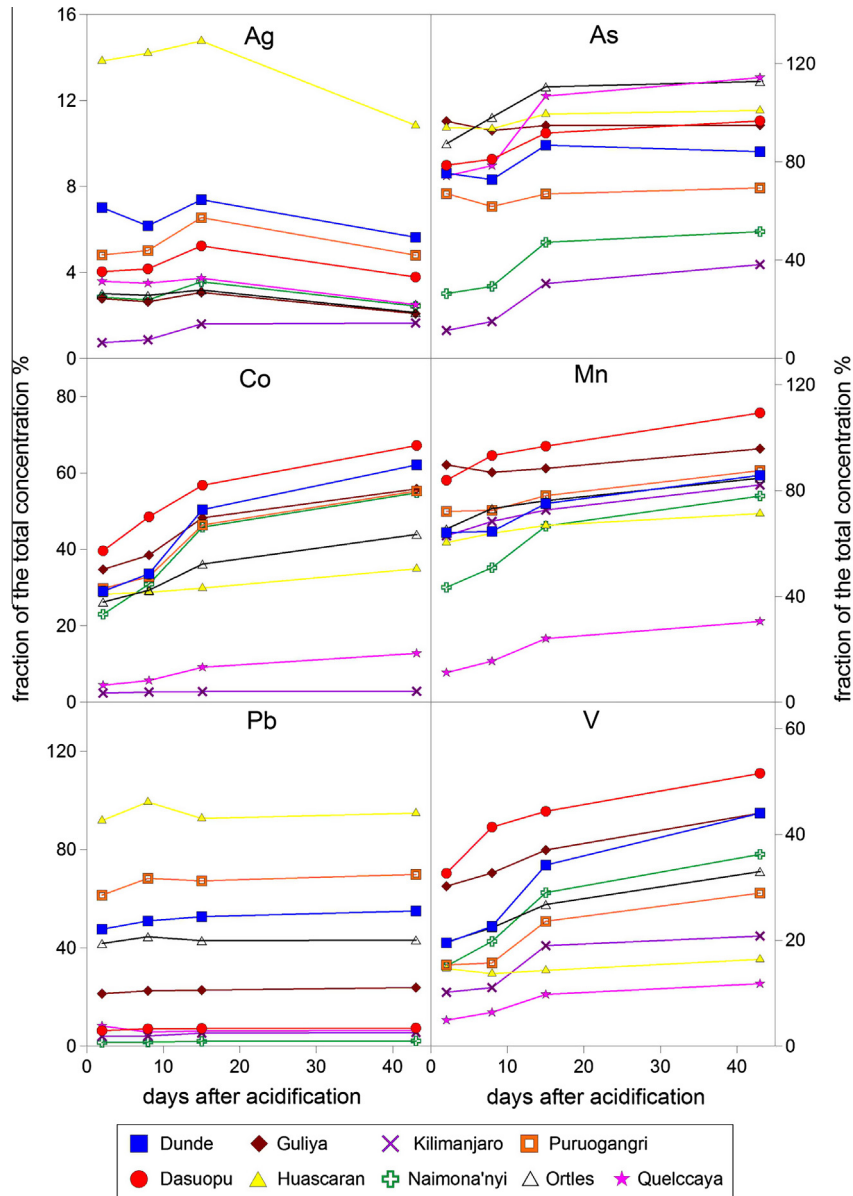

Fig. 7. Trends of the trace element fractions of the total concentrations for six representative elements determined in the nine ice core samples after acidification. A few fractions above 100% are due to analytical uncertainty.

a smaller amount of Al, Bi, Ti and Tl than un-weathered single mono-mineralogical species dispersed in synthetic solutions.

## 3.2. Interpretation of the impact of leaching on trace elements

A widely used approach to evaluate the influence of mineral dust of aeolian origin on trace element concentrations determined in ice cores involves the calculation of the crustal enrichment factor (EFc), defined as:

$$EFc = \frac{\left(\frac{TE_{ice}}{Fe_{ice}}\right)}{\left(\frac{TE_{crust}}{Fe_{crust}}\right)}$$

where TE indicates a specific trace element concentration, and Fe is taken as a typical element assumed to be entirely of crustal origin.

The trace element ratios in the Earth's crust are from Wedepohl (1995). Typically, in order to take into account the natural variability of the dust mineralogy and the analytical uncertainty, trace elements are cautiously considered to be of crustal origin if their EFc falls between 1 and 10 (therefore allowing an EFc variation of one order of magnitude or 1000%) (Gabrielli et al., 2005). In our experiment, we note that the crustal reference (Fe) was also the element that experienced the largest relative variation in concentrations (200%, which is not significantly dissimilar from Al that is also often taken as a crustal reference). This allows us to estimate the maximum possible change of the EFc during the leaching test.

Fig. 6 illustrates the trends of the EFc during the leaching experiment for Ag, As, Co, Mn, Pb and V. The trends of the EFc for the other trace elements (Al, Bi, Cd, Cr, Cu, Mo, Rb, Sb, Sn, Ti, Tl, U and Zn) are reported in the Supplementary information (Fig. S4). During our experiment we noted a progressive influence of the
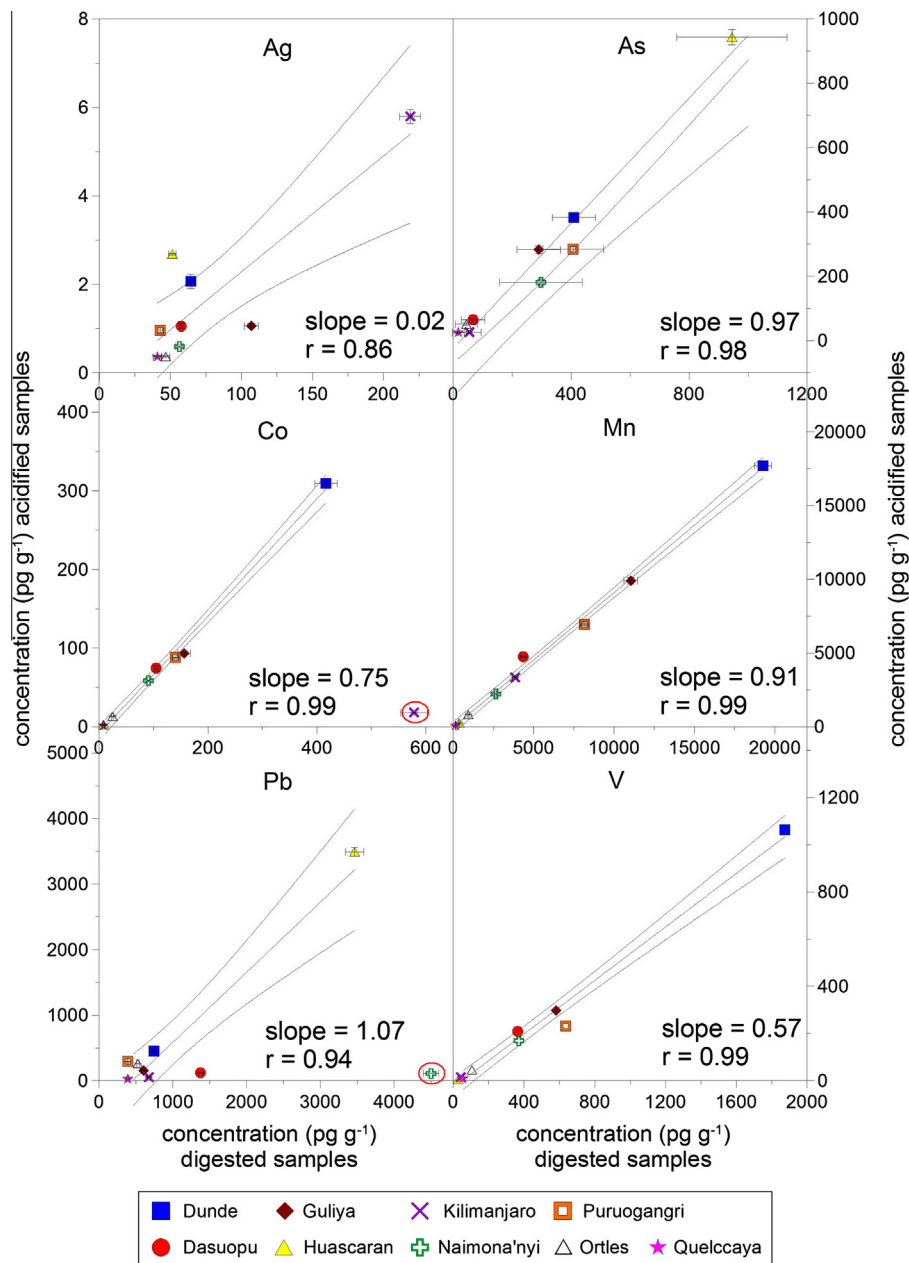
Fig. 8. Scatter plots of the six representative trace element concentrations determined in simply acidified (day 43) and fully digested samples. The error bars indicate the instrumental standard deviation. Slopes and correlation coefficients are also displayed, including a 95% confidence interval of the linear correlation. Two outliers excluded from the analysis for Co and Pb are circled.

trace element leaching on the EFc, such that in general decreases of 25–40% occurred for As, Al, Bi, Cr, Co, Rb, Sb, Sn Ti, V and Zn, while higher percentages (up to 50–70%) were observed for Ag, Cd, Cu, Mn, Mo, Pb, Tl and U. In particular, a mean decrease of the EFc between 10% and 20% per week occurred during the first two weeks after acidification, while a mean decrease between 1% and 5% per week occurred during the last four weeks of the leaching test.

Since the interpretation of the crustal/non-crustal origin of the trace elements in the ice core samples is typically based on variations of the EFc on the order of 1000%, and since Fe allows the maximum EFc changes, we conclude that concentration variations due to progressive and differential leaching are unlikely to affect conclusions based on EFcs. The only exception involves Ag, which is the only element whose EFc trajectory clearly intercepts the EFc threshold of 10 in most cases (Fig. 6) suggesting first a well-defined non-crustal origin (EFc > 10) followed by an inconsistent crustal origin (EFc < 10) during the test period.

3.3. Concentration fractions in the acidified samples

If we assume that nearly 100% of the total trace element concentration can be obtained through the determination by ICP-SFMS after a full acid digestion in closed microwave vessels, the progressively leached and the final total concentration/mass fractions can be monitored and estimated in the acidified samples (Figs. 7 and S5). Our results show a mean final recovery on the order of 80–90% for As and Mn; 50–70% for U, Fe, Ti and Tl; 20–50% for Al, Cd, Co, Cr, Cu, Mo, Pb, Rb, V and Zn; and 15% for Bi. Ag displays a recovery of only 2%. Remarkably, the fraction values do not depend on either the absolute trace elements nor the micro-particle concentrations, and show variability for each trace element (RSD = 50% on average) that in several cases is due to the introduced analytical uncertainty (e.g. some Co, Cr, Cu, Mo, Pb, Sb, Sn and Zn contamination is likely to have occurred for the cleanest samples during the full digestion process) (Fig. S6). Notably, the incomplete determination (less than 100%) of trace element concentrations in simply acidified samples implies a significant underestimation of the corresponding calculated mass fluxes to high altitude glaciers, which are typically determined by combining snow accumulation rate and trace element concentration.

The fractions of Al and Fe determined in this work are similar to those reported previously (Gaspari et al., 2006; Ruth et al., 2008). The low recovery for Ag is most likely related to the precipitation of Ag (as AgCl), while the apparent low recovery of Sb and Sn (less than 5%) can be ascribed to contamination that occurred during the digestion process, which is also suggested by the low correlation coefficient between concentrations in leached and fully digested samples (see below). Here we also note that, with the exception of Ag, the differential recoveries of Fe (our crustal reference) and the various other trace elements are also unlikely to introduce in the EFcs a variation of one order of magnitude that is required to influence the distinction between average terrestrial crustal and non-crustal sources (Section 3.2).

The correlation coefficients (Figs. 8 and S7) between the trace element concentrations determined in the leached and fully digested samples are high for most elements (r between 0.9 and 1 at the 95% confidence level for Ag, Al, As, Cr, Co, Fe, Mn, Pb, Rb, Ti, Tl, V and U), relatively high for Bi, Cd, Cu, Mo and Zn (r between 0.6 and 0.8), and relatively low for Sb and Sn (r between 0.2 and 0.5). We note that in the Co and Pb scatter plots there are outliers linked to the Naimona'nyi sample, possibly due to contamination during the digestion process. When these outliers are not included, the recalculated correlation coefficients of Co and Pb (0.99 and 0.95 respectively) become comparable with those of most of the other trace elements, reflecting an overall good proportionality between

the quantifications of trace elements in the simply acidified and fully digested samples.

Nevertheless, the low recovery and correlation for some other trace elements (e.g. Sb and Sn, due to the very high values obtained after the full acid digestion) indicate that contamination can occur during the digestion procedure. Although it is certainly possible that a cleaner full acid digestion could be performed, it is likely that the direct analysis of simply acidified samples would be however the most clean and reliable method to determine trace elements in ice core samples characterised by ultra low concentrations. A full digestion procedure (including sample preparation) is also time consuming and thus can probably be used only to estimate the fraction of trace elements determined in a few representative samples from a given location. This can be useful to correct the concentrations of the trace elements when they are combined with snow accumulation rates to calculate the corresponding mass fluxes that would otherwise be underestimated.

4. Conclusions

We employed two methodologies (simple acidification at room temperature and full acid digestion at elevated temperature and pressure in a closed vessel microwave digestion system) to evaluate the variability of the leaching and estimated mass fractions of trace elements in ice cores determined by ICP-SFMS.

The leaching test (simple acidification at room temperature) shows a weekly rate of increase in trace element concentrations between 5 and 50% during the first two weeks with a large intersample variability. After two weeks the rate per week increase was smaller, converging towards more stable values for all elements. In general, the relative increases in concentration for all the trace elements appear rather variable among the different ice samples analysed, which is not attributed to the absolute trace elements or dust concentrations but rather to the distinct and complex mineralogies of the micro-particles. The ranges of the relative increases in several trace element concentrations (Al, Bi, Ti, Tl and V) are lower than those reported by Rhodes and co-workers, possibly because the latter test was conducted on acidified powder rock standards which were treated as surrogates for ice core samples. However, other increases are within a factor of 1 (for As, Cr, Mn, Pb, Rb and U) or larger (for Cu and Zn) in ice core samples.

During our leaching test the crustal enrichment factors (EFc) - showed average decreases of 25–70%, which are smaller than the typical 1000% variation allowed (EFc larger or smaller than 10) to discriminate between the crustal and non-crustal origins of trace elements determined in ice cores. We conclude that concentration variations of trace elements due to progressive/distinct leaching in simply acidified samples are unlikely to affect the evaluation of the trace element origins (crustal/non-crustal) based on EFcs. The exception is Ag, possibly due to its progressive precipitation as AgCl.

Notably, the mass fractions of the various trace elements obtained at the end of the leaching test vary between 20% and 90% of the estimated total value. This implies a general systematic underestimation of the corresponding mass fluxes, which are calculated by combining trace element concentrations and snow accumulation rates. Depending on the specific trace element determined, we recommend that: (i) a suitable time lag between acidification and analyses (e.g. 1 day for Ag and 30 days for the other trace elements) should be used, and (ii) the fraction of the estimated total mass concentrations should always be empirically determined for any given drilling site.

Our test sets the basis for a standard methodology for the evaluation of trace elements in ice core samples and calls for further

assessments of the impacts of sample preparation on the determination of trace element concentrations. In the future, further tests should be performed by including a significant number of samples from each study site in order to check any particular trace element behaviour possibly related to the specific mineralogies and site-specific lithologies of the mineral dust. We also suggest that this test be extended to fresh water matrices characterised by significant micro-particle concentrations.

Acknowledgments

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2014.05.019.

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