Melt-Induced Fractionation of Major Ions and Trace Elements in an Alpine Snowpack

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Abstract Understanding the impact of melting on the preservation of atmospheric compounds in high-Alpine snow and glacier ice is crucial for future reconstruction of past atmospheric conditions. However, detailed studies investigating melt-related changes of such proxy information are rare. Here we present a series of five snow pit profiles of 6 major ions and 34 trace elements at Weisfluhjoch, Switzerland, collected between January and June 2017. Atmospheric composition was preserved during the cold season, while melting toward the summer resulted in preferential loss of certain species from the snowpack or enrichment at the base of the snowpack. Increasing mobilization of major ions with meltwater (NH₄⁺ < Cl⁻ < Na⁺ < NO₃⁻ < Ca²⁺ < SO₄²⁻) can be related to their stronger enrichment at ice crystal surfaces during snow metamorphism. Results for trace elements show that less abundant elements such as Ce, Eu, La, Mo, Nd, Pb, Pr, Sb, Sc, Sm, U, and W were best preserved and may still serve as tracers to reconstruct past natural and anthropogenic atmospheric emissions from melt-affected snow pit and ice core records. The obtained elution behavior matches the findings from another high-Alpine site (upper Grenzgletscher) for major ions and the large majority of investigated trace elements. Both studies indicate that water solubility and location at the microscopic scale are likely to determine the relocation behavior with meltwater and also suggest that the observed species-dependent preservation from melting snow and ice is representative for the Alpine region, reflecting Central European atmospheric aerosol composition.

1. Introduction

Major ions (MIs) and trace elements (TEs) serve as important proxies for reconstructing past environmental conditions from high-Alpine snow pits (e.g., Gabrieli et al., 2011; Greilinger et al., 2016; Hilbrunner et al., 2005; Kuhn et al., 1998; Kutuzov et al., 2013; Nickus et al., 1997) and ice cores (e.g., Döscher et al., 1996; Eichler et al., 2000; Preunkert et al., 2000; Schwikowski et al., 1999, 2004). For instance, concentration records of ammonium, mainly released from livestock breeding and agriculture (Döscher et al., 1996; Schwikowski et al., 1999); nitrate, primarily emitted by traffic (Döscher et al., 1995; Preunkert et al., 2003; Wagenbach et al., 1988); sulfate, typically from fossil fuel burning (Döscher et al., 1995; Preunkert et al., 2001; Schwikowski et al., 1999); and lead, a heavy metal mainly emitted by mining activities, metal production, coal combustion, or the use of leaded gasoline (Schwikowski et al., 2004), revealed the strong impact of Western European industry and society on the atmosphere over the last decades. Concentration records of Ca, Mg, or the rare-earth elements can be used to reconstruct historic variations of mineral dust emissions to the atmosphere (Gabrieli et al., 2011; Gabrielli et al., 2008). However, postdepositional melting induced by climate warming can significantly alter concentration records of atmospheric trace species from high-altitude glaciers and snowpack as shown for MIs, organic pollutants, or water stable isotopes (WSIs; Eichler et al., 2001; Herreros et al., 2009; Kang et al., 2008; Müller-Tautges et al., 2016; Pavlova et al., 2015; Sinclair & MacDonell, 2016; You et al., 2015). As glaciers, which have served as environmental archives to assess the natural and anthropogenic impact on the atmosphere, are progressively in danger of being affected by melting (Zhang et al., 2015), there is an increasing need to understand the impact of melting on the preservation of various environmental proxies in these archives.
Virkkunen et al., 2007; Wang et al., 2018; Zong-Xing et al., 2015). Preferential elution of certain ions relative to others has been observed, being strongly dependent on the respective geographical location of the snowpack. These studies further indicate that $SO_4^{2-}$ is generally significantly depleted with melting, while $NH_4^+$ appears to be preserved despite meltwater percolation.

In the majority of these studies available in the literature, either melting had strongly affected the MI records making the initial conditions before melting unknown or a direct comparison of concentration records before and after melting to quantify the degree of depletion has not been performed. In contrast to MIs, the effect of melting on the fate of TEs in snow has still not been well characterized. To the best of our knowledge, only a few studies have addressed the influence of melting on TE concentration records in snow pits. Wong et al. (2013) artificially infiltrated meltwater into Greenland snow pits to investigate melt effects on 12 different TE records. They observed that mineral dust particle-bound TEs remained immobile during meltwater percolation resulting in the preservation of their seasonal chemical signal. On the contrary, Zhongjin et al. (2007) reported from the analyses of snow-firm pits taken in the Central Asian Tien Shan Mountains that meltwater percolation during the summer may have eluted the five investigated TEs (Al, Cd, Fe, Pb, and Zn) from the snow-firm pack. The TE records from the analysis of a meltwater-affected firm part of an Alpine ice core indicated that meltwater percolation led to preferential loss of certain TEs (Avak et al., 2018). Water-insoluble TEs and low-abundant water-soluble TEs remained largely immobile with meltwater. Since this study proposed a geographical site specificity for the preferential elution of TEs (Avak et al., 2018), it remains unclear how representative these findings are for the Alpine region.

The high-Alpine snow field site at Weissfluhjoch (WFJ), Switzerland, is well suited for snowpack studies. Numerous studies have been conducted at this site focusing on snow characterization, snow mechanics, snow metamorphism, and the development of measurement methods since 1936 (Marty & Meister, 2012). So far, studies investigating the chemical impurities in the snowpack at WFJ focused on $SO_4^{2-}$, $NO_3^-$, Cl, $K^+$, $Na^+$, $NH_4^+$, $Ca^{2+}$, and $Mg^{2+}$. Baltensperger et al. (1993) compared consecutive measurements of surface snow sampled from January to March 1988 to that from a snow pit taken at the end of March at WFJ. The snow pit samples were found to be representative of precipitation deposition during the winter. Snow pit sampling, sample handling procedures, and chemical analysis of MIs were further refined by Schwikowski et al. (1997). In addition, the seasonal variability in deposition and the different emission sources of impurities were reflected in the vertical distribution of MIs in the snowpack (Schwikowski et al., 1997).

Here we present the first study monitoring the postdepositional fate of an extensive set of environmentally relevant atmospheric impurities in the high-Alpine snowpack at WFJ. We monitored 6 MIs and 34 TEs during an entire winter/spring season and investigated their behavior during melting of the snowpack in early summer. Five snow pits sampled from January to June 2017 allowed us to capture both the initial, undisturbed records of atmospheric compounds in the snowpack and the records after melting had occurred during the warmer season. Impurity profiles reflecting dry conditions (without significant melting) were compared with profiles reflecting wet conditions to systematically investigate the impact of melting on the preservation of atmospheric tracers in high-Alpine snow.

2. Materials and Methods

2.1. Study Site and Meteorological Setting

Five snow pit samplings were conducted at the high-Alpine snow field site WFJ of the WSL-Institute for Snow and Avalanche Research, Eastern Switzerland (2,536 m above sea level, 46°49′47″N 9°48′33″E) at regular time intervals in the winter, spring, and early summer seasons in 2017. Sampling dates were 25 January, 22 February, 21 March, 17 April, and 1 June. Earlier snow sampling studies suggest uniform spatial snow deposition and insignificant perturbations of the snow stratigraphy due to strong winds at this site (Baltensperger et al., 1993; Schwikowski et al., 1997). Samples were obtained from the snow pits either 1 day before or after the weekly density measurements with 3-cm resolution, which were part of an extensive snowpack monitoring program of the WSL-Institute for Snow and Avalanche Research during the winter season 2016/2017 (Calonne et al., 2016). The snow heights during the sampling were 87 cm (25 January), 126 cm (22 February), 185 cm (21 March), 166 cm (17 April), and 83 cm (1 June; Figure 1). Snow surface (via an infrared radiometer) and 2-m air temperatures (by an automated weather station) indicated that
dry conditions without significant melting prevailed for the first three sampling dates on 25 January, 22 February, and 21 March (Figure 1). Only 6 days with a mean 2-m air temperature above 0 °C occurred during the period 1 January until 21 March (1.3 ± 0.8 °C on average). Partial melting was identifiable in the snow pit on the fourth sampling date on 17 April due to 13 days between 21 March and 17 April with mean 2-m air temperatures above 0 °C (1.8 ± 1.3 °C on average). The snowpack was entirely wet on the fifth sampling date on 1 June due to another 25 days between 17 April and 1 June with mean 2-m air temperatures above 0 °C (4.8 ± 3.4 °C on average).

2.2. Snow Pit Sampling

As snow is particularly sensitive to trace levels of contamination due to its low impurity content, precautions were taken during sampling. Sterile clean room overalls (Tyvek® IsoClean®, DuPont, Wilmington, DE, USA), particulate respirator face masks (3M, Maplewood, MN, USA), and ultraclean plastic gloves (Semadeni, Ostermundingen, Switzerland) were worn during the sampling. All tools were carefully rinsed with ultrapure water (18 MΩ cm quality, arium® pro, Sartorius, Göttingen, Germany) prior to use. Snow pits were sampled with a vertical resolution of 6 cm down to the bottom of the snowpack by pushing a custom-built rectangular (15 × 24 cm) sampler made from polycarbonate into the pit wall. To allow for sufficient sample volume, the snow was filled into 50-ml polypropylene vials (Sarstedt, Nürnberg, Germany) by pushing them twice with the opening facing downward into the snow. Separate vials were used for MI, WSI, and TE analyses. Polypropylene vials were precleaned five times with ultrapure water for MI and WSI samples. For TE samples, the tubes were precleaned five times with ultrapure water (18 MΩ cm quality, Milli-Q® Element, Merck Millipore, Burlington, MA, USA) plus once with 0.2 M HNO₃ prepared from ultrapure HNO₃ (Optima™, Fisher Chemical, Loughborough, UK). Samples for TE analysis were taken from the snow at the front part of the sampler to prevent possible cross contamination of the vials used for MI sampling with HNO₃.

2.3. Major ion, water stable isotope, and trace element analysis

A total of 324 samples for MI, WSI, and TE analyses was kept frozen at −20 °C until analysis at the Paul Scherrer Institute (Villigen, Switzerland).

MIs (Na⁺, NH₄⁺, Ca²⁺, Cl⁻, NO₃⁻, and SO₄²⁻) present in the snow pit samples were analyzed after melting at room temperature using ion chromatography (IC; 850 Professional IC equipped with a 872 Extension Module Liquid Handling and a 858 Professional Sample Processor auto sampler, Metrohm, Herisau, Switzerland). Cations were separated using a Metrosep C4 column (Metrohm) and 2.8 mM HNO₃ as eluent at a flow rate of 1 ml/min. Anions were separated using a Metrosep A Supp 10 column (Metrohm) and were eluted stepwise using first, a 1.5 mM Na₂CO₃/0.3 mM NaHCO₃ (1:1 mixture) eluent, and then an 8 mM Na₂CO₃/1.7 mM NaHCO₃ (1:1 mixture) eluent at a flow rate of 0.9 ml/min. Possible instrumental drifts were monitored by measuring an in-house standard after every twentieth sample. The precision of the method was ~5%.

WSI samples were melted at room temperature, and 1 ml aliquots were analyzed for δD and δ¹⁸O using a wavelength-scanned cavity ring down spectrometer (WS-CRDS, L2130-i Analyzer, Picarro, Santa Clara, CA, USA). Samples were injected into the vaporizer (A0211, Picarro, Santa Clara, CA, USA) using a PAL HTC-xt autosampler (LEAP Technologies, Carrboro, NC, USA). Three in-house standards were measured after every tenth sample for calibration and to monitor instrumental drifts. The measurement uncertainty was <0.1‰ for δ¹⁸O and <0.5‰ for δD.

Snow pit samples were melted at room temperature, acidified with concentrated ultrapure HNO₃ to 0.2 M (1% v/v), and analyzed 3–4 hr after acidification following the same procedure as described in Avak et al. (2018) using discrete inductively coupled plasma sector field mass spectrometry (Element 2, Thermo Fisher Scientific, Bremen, Germany). Low (LR, R = 300) or medium resolution (MR, R = 4,000) data were
acquired for Ag (LR), Al (MR), Ba (LR), Bi (LR), Ca (MR), Cd (LR), Ce (LR), Co (MR), Cs (LR), Cu (LR and MR), Eu (LR), Fe (MR), La (LR), Li (LR and MR), Mg (MR), Mn (MR), Mo (LR), Na (MR), Nd (LR), Ni (LR and MR), Pb (LR), Pr (LR), Rb (LR), Sb (LR), Sm (LR), Sr (LR), Ti (LR), Th (LR), U (LR), V (MR), W (LR), Yb (LR), Zn (LR and MR), and Zr (LR). If both LR and MR resolution data were available, MR data were used for further data evaluation. Quantification of intensity values was performed by internal and external calibrations using a Rh-standard and seven liquid standards covering the typical concentration range of TEs in natural snow and ice samples, respectively. Linear regressions of the calibration curves consistently revealed correlation coefficients >0.999.

2.4. Data Evaluation

IC raw data were processed using the MagIC Net 3.2 software (Metrohm, Herisau, Switzerland). Sample concentrations were not blank-corrected as the concentrations of the blank, determined by analyzing ultrapure water, were below the detection limit (DL). Sample concentrations below the DL were substituted with half the value of the DL. On average, 10% of the measurement values were below the DL. Inductively coupled plasma mass spectrometry raw data were evaluated following the method described by Knüsel et al. (2003). Concentrations were blank-corrected by subtracting a measurement blank consisting of four measurements of ultrapure 0.2 M HNO₃. The instrumental DL was defined as 3σ of the measurement blank, and concentrations below the DL were substituted with half of the value of the DL. ¹⁰⁹Ag was excluded from the data set for further evaluation and discussion as concentrations of all samples were below the DL.

Total depths of the snow profiles were converted to water equivalents (w. eq.) by multiplying with the respective density. As 17 April had the largest snow depth, the profiles of 25 January, 22 February, 21 March, and 1 June were aligned relative to the profile of 17 April, with 0-cm w. eq. being the surface on this day and assuming the same bottom depth for all profiles. All five profiles cover the depth interval 45- to 65-cm w.eq. The profiles of 22 February, 21 March, 17 April, and 1 June cover 36- to 65-cm w.eq., the profiles of 22 February, 21 March, and 17 April cover 30- to 65-cm w.eq., and the profiles of 21 March and 17 April cover 5- to 65-cm w.eq. The sample at the base of each snow pit was omitted from all chemical profiles to exclude a possible influence of the soil at WFJ.

3. Results and Discussion

3.1. Major ions

3.1.1. Comparison of the Five MI Concentration Profiles

The chemical profiles of selected MIs (NH₄⁺, Cl⁻, and Ca²⁺) and the δ¹⁸O records in the five snow pits are shown in Figure 2. The general MI patterns of the four profiles, reflecting the winter and spring periods (January–April), show a strong correspondence in the respective overlapping parts. Apart from possible changes caused by melting (17 April), slight concentration differences in the profiles can be attributed to the spatial variability of impurities within the snowpack as the locations of the individual snow pit samplings were several meters (up to 20 m) apart. The resemblance between the four winter and spring snow pits is also visible for the corresponding δ¹⁸O profiles which support the depth assignment of the different snow pits.

The chemical profiles of NH₄⁺, Cl⁻, and Ca²⁺ are exemplary for the different emission sources and transport characteristics of MIs in Alpine snow and ice. The depths 0- to 30-cm w.eq. (21 March and 17 April) indicate...
Concentration Ratio, Classification, Mean Concentration of the Dry Snow Pits (25 January, 22 February, and 21 March), and Detection Limits of Major Ions and Trace Elements Investigated in This Study

<table>
<thead>
<tr>
<th>Concentration ratio/classification</th>
<th>Mean concentration (ng/L)</th>
<th>Detection limit (ng/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.62 ± 0.45</td>
<td>17,000 ± 2,840</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0.77 ± 0.27</td>
<td>26,300 ± 4,580</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.37 ± 0.18</td>
<td>71,500 ± 11,400</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.64 ± 0.43</td>
<td>34,000 ± 4,980</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.37 ± 0.11</td>
<td>249,000 ± 21,200</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.36 ± 0.10</td>
<td>57,300 ± 5,330</td>
</tr>
<tr>
<td>Al</td>
<td>i.b.s.</td>
<td>4,870 ± 792</td>
</tr>
<tr>
<td>Ba</td>
<td>0.39 ± 0.26/group 2</td>
<td>262 ± 67</td>
</tr>
<tr>
<td>Bi</td>
<td>0.50 ± 0.28/group 2</td>
<td>4.5 ± 0.91</td>
</tr>
<tr>
<td>Ca</td>
<td>0.46 ± 0.24/group 2</td>
<td>110,000 ± 21,400</td>
</tr>
<tr>
<td>Cd</td>
<td>0.55 ± 0.23/group 2</td>
<td>1.9 ± 0.26</td>
</tr>
<tr>
<td>Ce</td>
<td>1.5 ± 1.1/group 1</td>
<td>14 ± 2.9</td>
</tr>
<tr>
<td>Co</td>
<td>i.b.s.</td>
<td>24 ± 4.5</td>
</tr>
<tr>
<td>Cr</td>
<td>i.b.s.</td>
<td>21 ± 0.33</td>
</tr>
<tr>
<td>Cu</td>
<td>i.b.s.</td>
<td>48 ± 5.6</td>
</tr>
<tr>
<td>Eu</td>
<td>1.1 ± 0.79/group 1</td>
<td>0.51 ± 0.10</td>
</tr>
<tr>
<td>Fe</td>
<td>i.b.s.</td>
<td>5,990 ± 1,180</td>
</tr>
<tr>
<td>La</td>
<td>1.5 ± 1.1/group 1</td>
<td>6.1 ± 1.2</td>
</tr>
<tr>
<td>Li</td>
<td>i.b.s.</td>
<td>6.1 ± 0.90</td>
</tr>
<tr>
<td>Mg</td>
<td>i.b.s.</td>
<td>37,000 ± 6,600</td>
</tr>
<tr>
<td>Mn</td>
<td>i.b.s.</td>
<td>612 ± 110</td>
</tr>
<tr>
<td>Mo</td>
<td>1.1 ± 0.59/group 1</td>
<td>3.1 ± 0.46</td>
</tr>
<tr>
<td>Na</td>
<td>0.50 ± 0.32/group 2</td>
<td>15,900 ± 2,620</td>
</tr>
<tr>
<td>Nd</td>
<td>1.2 ± 0.92/group 1</td>
<td>7.7 ± 1.7</td>
</tr>
<tr>
<td>Ni</td>
<td>i.b.s.</td>
<td>10 ± 22</td>
</tr>
<tr>
<td>Pb</td>
<td>0.84 ± 0.36/group 1</td>
<td>180 ± 15</td>
</tr>
<tr>
<td>Pr</td>
<td>1.1 ± 0.84/group 1</td>
<td>1.8 ± 0.38</td>
</tr>
<tr>
<td>Rb</td>
<td>i.b.s.</td>
<td>15 ± 2.1</td>
</tr>
<tr>
<td>Sb</td>
<td>0.88 ± 0.36/group 1</td>
<td>9.1 ± 1.2</td>
</tr>
<tr>
<td>Sc</td>
<td>1.5 ± 1.4/group 1</td>
<td>1.8 ± 0.41</td>
</tr>
<tr>
<td>Sm</td>
<td>1.2 ± 0.88/group 2</td>
<td>2.0 ± 0.46</td>
</tr>
<tr>
<td>Sr</td>
<td>0.37 ± 0.21/group 2</td>
<td>270 ± 55</td>
</tr>
<tr>
<td>Th</td>
<td>0.45 ± 0.30/group 2</td>
<td>1.4 ± 0.25</td>
</tr>
<tr>
<td>Tl</td>
<td>i.b.s.</td>
<td>0.39 ± 0.04</td>
</tr>
<tr>
<td>U</td>
<td>1.5 ± 0.99/group 1</td>
<td>2.3 ± 0.64</td>
</tr>
<tr>
<td>V</td>
<td>i.b.s.</td>
<td>19 ± 2.5</td>
</tr>
<tr>
<td>W</td>
<td>1.2 ± 0.69/group 1</td>
<td>0.54 ± 0.07</td>
</tr>
<tr>
<td>Yb</td>
<td>i.b.s.</td>
<td>0.63 ± 0.13</td>
</tr>
<tr>
<td>Zn</td>
<td>0.47 ± 0.36/group 2</td>
<td>2,780 ± 463</td>
</tr>
<tr>
<td>Zr</td>
<td>0.13 ± 0.08/group 2</td>
<td>5.4 ± 0.75</td>
</tr>
</tbody>
</table>

*Trace elements were classified depending on whether the profile of the snow pit of 1 June showed a strong enrichment from the soil at Weisstuljahoc below 55-cm water equivalent (influenced by soil [i.b.s.]), an unbiased profile pattern compared to the dry condition profiles (group 1), or a heavily depleted concentration profile (group 2).*

After several weeks with temperatures above 0°C, the snowpack was very wet from meltwater (and rainwater) at the beginning of the summer (1 June; Figure 1). The uppermost (surface) sample of the snow pit from 1 June (red dotted line in Figure 2) is most likely influenced by residual snow impurities after surface melting and wet or dry deposition between 17 April and 1 June (Figure 1) and was thus not taken into consideration. The δ¹⁸O profile of 1 June reveals a strong smoothing compared to the previous profiles, indicative of strong melting (Thompson et al., 1993). However, a signature between 45- and 65-cm w.eq. resembling that from the previous profiles is still visible. This indicates that at this depth, meltwater percolation was concentrated to the porous space in the snowpack and primarily percolated along ice surfaces, keeping the ice matrix in principle preserved. The MI profiles of 1 June compared to those of the first three sampling dates are almost unaltered (NH₄⁺), slightly depleted (Na⁺ and Cl⁻), or strongly depleted (Ca²⁺, NO₃⁻, and SO₄²⁻), most likely due to different elution behavior of the investigated ions with meltwater (Eichler et al., 2001).

### 3.1.2. Preferential Elution of MI: Elution Sequence and Discussion

To quantify and compare the apparent preferential elution of MI, a concentration ratio c<sub>wt</sub>/c<sub>dry</sub> for the overlapping depth (45- to 65-cm w.eq.) was calculated for each MI (Table 1). c<sub>wt</sub> corresponds to the integrated MI concentration for the wet profile of 1 June, whereas c<sub>dry</sub> represents the mean of the integrated concentration profiles during dry (no significant melting) periods (25 January, 22 February, and 21 March). The profiles on 17 April were not included as the snowpack was neither completely dry nor very wet. Corresponding to the concentration ratio, an elution sequence was established: NH₄⁺ < Cl⁻ < Na⁺ < NO₃⁻ < Ca²⁺ < SO₄²⁻, where NH₄⁺ is the least mobile ion and SO₄²⁻ the most mobile ion. Similar elution sequences were reported by Eichler et al. (2001; from another melt-affected Alpine site), Z. Li et al. (2006), Ginot et al. (2010), and recently by Zong-Xing et al. (2015), who all observed a particularly pronounced leaching of SO₄²⁻ and Ca²⁺, while NH₄⁺ and Cl⁻ were retained in melting firn and snowpack.
Elution sequences of MIs were also determined through laboratory studies (Cragin et al., 1996; Tranter et al., 1992; Tsouris et al., 1985). We recently performed an elution experiment where, for the first time, homo-geneous impurity-doped artificial snow was exposed to well-defined snow metamorphism conditions prior to leaching with 0 °C ultrapure water. This experiment was conducted to determine enrichment differences of MIs between ice crystal interiors and surfaces after metamorphism (Trachsel et al., 2017). Snow undergoes drastic structural transformation cycles during metamorphism (Pinzer et al., 2012), which may result in significant impurity redistribution. Our elution sequence at the WFJ agrees well with the findings of the laboratory-based elution experiment (Figure 3). MIs having a higher solubility in ice such as NH$_4^+$ and Cl$^-$ (Feibelman, 2007; Hobbs, 1974) showed less mobility most likely due to incorporation into the crystal interior during snow metamorphism. They can be incorporated either by substituting water molecules located on lattice sites of the ice crystal (Zaromb & Brill, 1956) or by occupying interstitial spaces of the crystal structure (Petrenko & Whitworth, 2002).

On the other hand, Ca$^{2+}$ and SO$_4^{2-}$ were enriched on ice crystal surfaces with progressing snow metamorphism (Figure 3); explaining their availability for mobilization with meltwater. This is supported by previous location studies of salts in ice. Mulvaney et al. (1988) used a combination of scanning electron microscopy and energy-dispersive X-ray microanalysis to show that H$_2$SO$_4$ concentrations at triple junctions are several orders of magnitude higher compared to grain interiors in polar ice from Antarctica. Similar observations for H$_2$SO$_4$ and HNO$_3$ using Raman spectroscopy were reported by Fukazawa et al. (1998). Accumulation of MgSO$_4$ at grain boundaries in ice from the Greenland Ice Sheet Project (GISP) ice core 2 was revealed by low-vacuum scanning electron microscopy-energy-dispersive X-ray (Baker et al., 2003). The varying elution behavior of MIs observed in the snow pit of 1 June with NO$_3^-$, Ca$^{2+}$, and SO$_4^{2-}$ being most heavily depleted can therefore be explained by their microscopic locations on ice surfaces, exposing them to relocation during melting.

Our findings show that the atmospheric composition of MIs is well preserved in the snowpack at WFJ during the cold season. Melting during the warm season leads to preferential leaching of MIs depending on their microscopic location either on the ice surface or in the ice interior. The loss of MIs is particularly significant for Ca$^{2+}$ and SO$_4^{2-}$. In contrast, the strong persistence of NH$_4^+$ emphasizes that NH$_4^+$ can still serve as environmental tracer for the interpretation of snow pit and ice core records affected by melting.

### 3.2. Trace Elements

#### 3.2.1. TE Concentration Profiles

Concentrations of Co, Fe, Ce, Sb, Ca, and Sr in the snow pits on 25 January, 22 February, 21 March, 17 April, and 1 June are exemplarily shown in Figure 4. The general pattern of the profiles of the first four snow pits (January to April) agrees well in the overlapping depths. As for the MI profiles, misalignment in peaks can be attributed to small-scale spatial variability of impurities in the snowpack. The reproducibility of chemical profiles with ultratrace level concentrations (e.g., Ce and Sb) from different sampling campaigns demonstrates that significant contamination during the snow pit sampling did not occur. Inductively coupled plasma mass spectrometry measurements of Ca and Na concentration profiles are in good agreement with the records of Ca$^{2+}$ and Na$^+$ concentrations obtained by IC (Figures 2 and 4). The uppermost (surface) sample of the snow pit from 1 June revealed highly elevated concentrations for many TEs (red dotted line in Figure 4). This is most likely due to residual snow impurities after surface melting and TEs that reached the snowpack by wet or dry deposition between 17 April and 1 June (Figure 1). For this reason, the uppermost sample of the snow pit from 1 June was not taken into consideration for the following discussion.

The 34 TEs can be either of geogenic origin or emitted by anthropogenic sources. At high-Alpine sites, Al, Ba, Bi, Ca, Cs, Fe, Li, Mg, Mn, Na, Rb, Sr, Th, Ti, U, W, Zr, and the rare-earth elements (Ce, Eu, La, Nd, Pr, Sc,
Sm, and Yb) are mainly deposited with mineral dust (Gabrieli et al., 2011; Gabrieli et al., 2008), whereas Ag, Cd, Co, Cu, Mo, Ni, Pb, Sb, V, and Zn in Alpine snow and ice are characteristic of anthropogenic atmospheric pollution (Barbante et al., 2004; Gabrieli et al., 2011; Gabrielli et al., 2008; Schwikowski et al., 2004; van de Velde et al., 1999, 2000). The chemical profiles of Ca, Ce, Fe, and Sr (Figure 4) are representative of TEs originating from mineral dust particles and reveal an enrichment in the depths reflecting winter precipitation (30- to 65-cm w.eq.), where dry conditions prevailed (25 January, 22 February, and 21 March). These TEs show a major peak between 50- and 60-cm w.eq. due to a Saharan dust event beginning of January 2017 (see section 3.1.1). As explained above for NH₄⁺, TEs indicative of anthropogenic influence such as Sb (Figure 4) are enriched in depths reflecting spring precipitation deposited after 22 February (0- to 30-cm w.eq.). This is due to the typical seasonality of convective air mass transport from the planetary boundary layer to high-Alpine sites occurring in spring and summer (Baltensperger et al., 1997).

Based on the concentration profiles on 1 June, the 34 investigated TEs were divided into three groups (Table 1). Group 1 (Ce, Eu, La, Mo, Nd, Pb, Pr, Sb, Sc, Sm, U, and W) is characterized by an almost unchanged profile pattern between 45- and 65-cm w.eq. compared to the dry condition profiles (e.g., Ce and Sb, Figure 4). This indicates that group 1 TEs were not affected by melting. Group 2 TEs (Ba, Bi, Ca, Cd, Na, Sr, Th, Zn, and Zr) were strongly depleted on 1 June compared to winter and springtime records (as shown for Ca and Sr in Figure 4).

Group 3 TEs (Al, Co, Cs, Cu, Fe, Li, Mg, Mn, Ni, Rb, Ti, V, and Yb) exhibit a strong enrichment below 55-cm w.eq. close to the soil (see, e.g., Co and Fe, Figure 4). The bottom of the snowpack on 1 June was very wet, probably enriched with impurities not of atmospheric origin, but present in the soil at WFJ. We therefore attribute the strong increase in concentration below 55-cm w.eq. to the contact with soil and denote this group as “influenced by soil.” Group 3 TEs were therefore not included in further evaluation.

### 3.2.2 Different Preservation of TEs Under Melt Conditions

A quantitative classification of TE fractionation during melting of the snowpack (groups 1 and 2) was performed by calculating a concentration ratio $c_{wet}/c_{dry}$ for each TE in the overlapping depths (see above, Table 1). The highest concentration ratio was obtained for La, indicative of its well preserved concentration record on 1 June, whereas the concentration profile of Zr is most severely affected by melting, having the lowest concentration ratio. Concentration ratios of TEs classified as group 1 are close to 1 and range between 1.5 ± 1.1 (La) and 0.84 ± 0.36 (Pb). Concentration ratios of group 2 TEs are significantly below 1 and range between 0.55 ± 0.23 (Cd) and 0.13 ± 0.08 (Zr). Arranging the concentration ratios according to size and plotting this rank against the ratio indicates that each TE belonging to groups 1 and 2 was differently preserved in the snowpack during melting (Figure 5).

The preservation of group 1 TEs with observed concentration ratios >0.7 (Ce, Eu, La, Mo, Nd, Pb, Pr, Sb, Sc, Sm, U, and W) is in excellent agreement with findings from another Alpine site (Avak et al., 2018, Figure 5). At this ∼180-km distant site, meltwater percolation led to postdepositional disturbance of a 16-m firn section of a high-Alpine ice core from the upper Grenzgletscher (Monte Rosa massif, southern Swiss Alps, 4,200 m above sea level, 45°55′28″N 7°52′3″E). Preferential elution of TEs led to significant concentration depletion in the records of Ba, Ca, Cd, Co, Mg, Mn, Na, Ni, Sr, and Zn, whereas...
the seasonality in the Al, Bi, Ce, Cs, Cu, Eu, Fe, La, Li, Mo, Nd, Pb, Pr, Rb, Sb, Sc, Sm, Ti, Th, U, V, W, Yb, and Zr records was well preserved (Avak et al., 2018). The different behavior of TEs during meltwater percolation was related to their varying water solubility and location at the microscopic scale. TEs mainly present in water-insoluble mineral dust particles at the upper Grenzgletscher site (Al, Fe, Zr, and the rare-earth elements) were enriched on firm grain surfaces and mostly preserved, since their insolubility in water resulted in immobility with meltwater. TEs likely present in water-soluble compounds (Ba, Bi, Ca, Cd, Co, Cs, Cu, Li, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sr, Ti, Th, U, V, W, and Zn; Avak et al., 2018; Birmili et al., 2006; Greaves et al., 1994; Hsu et al., 2010; T. Li et al., 2015) revealed variable mobility with meltwater presumably due to the different microscopic location of the ions in the ice structure. For those rather water-soluble TEs, the concentration at the upper Grenzgletscher site was found to be primarily decisive determining either incorporation into the ice interior during snow metamorphism or segregation to ice surfaces because of exceeded solubility limits in ice.

In correspondence with the upper Grenzgletscher study and the work reported by Wong et al. (2013), also at WFJ, records of investigated TEs present as water-insoluble mineral dust particles (rare-earth elements: Ce, Eu, La, Nd, Pr, Sc, and Sm) are well preserved most probably due to their immobility with meltwater. Contrariwise, Zhongqin et al. (2007) observed a depletion of mineral dust-bond elements, such as Fe and Al at Urumqi glacier 1 (eastern Tien Shan) in summer and relate this to meltwater relocation. However, it cannot be excluded that the low concentrations in summer observed for all investigated elements are due to dilution effects during the wet season.

There is also strong agreement in the behavior of rather water-soluble TEs between upper Grenzgletscher and WFJ, showing a dependence on the concentration level. While TEs present in ultratrace amounts tend to be preserved, more abundant TEs were preferentially eluted (Figure 5). The only three TEs revealing a different behavior between the two sites are Bi, Th, and Zr, which still show a preservation of the seasonality at upper Grenzgletscher, but significant depletion at WFJ. One explanation could be a higher proportion of the water-soluble fraction of Bi, Th, and Zr deposited during winter at WFJ, favoring higher meltwater mobility. Another possible reason is differing concentrations. However, Th and Zr concentrations are not significantly different between the two sites. Only the higher Bi concentrations at WFJ could explain stronger melt-induced relocation.

These findings in the preservation of TEs corroborate our previous hypothesis (Avak et al., 2018) that for ice cores and snow pits from Alpine areas, representing central European atmospheric aerosol composition, and affected by partial melting, Ce, Eu, La, Mo, Nd, Pb, Pr, Sb, Sc, Sm, U, and W may still be used as robust environmental proxies. However, chemical profiles of Ba, Ca, Cd, Na, Zn, and Sr are prone to be depleted by melting. Records of Bi, Th, and Zr behaved differently at the two Alpine sites. The potential of TEs classified as influenced by soil here and previously found to be preserved (Al, Cs, Cu, Fe, Li, Rb, Ti, V, and Yb) or depleted (Co, Mg, Mn, and Ni) in firm (Avak et al., 2018) could not be further investigated at the WFJ site because of the influence of the soil in the presence of meltwater.

**4. Conclusions**

Melt processes induced by climate warming can significantly alter concentration records of atmospheric pollutants deposited in high-altitude glacier ice and snowpacks. Understanding the postdepositional behavior of atmospheric trace species is essential for reconstructing past environmental conditions from these natural archives. The analysis of five snow pits sampled during the winter/spring season of 2017 at the high-Alpine site WJF, Switzerland, is presented here. Comparison of impurity profiles representing dry and wet snow conditions allowed to systematically investigate the impact of melting on the preservation...
of atmospheric tracers in high-Alpine snow. While the atmospheric composition was found to be well- preserved during the winter, melting in the spring and early summer caused a preferential loss of certain MIs and TEs. We propose that the elution behavior of MIs is depending on their microscopic location, which is most likely defined by redistribution processes occurring during snow metamorphism. Among the six investigated MIs (Ca²⁺, Cl⁻, Na⁺, NH₄⁺, NO₃⁻, and SO₄²⁻), NH₄⁺ was retained the strongest, probably due to its preferred location in the ice interior. Ca²⁺ and SO₄²⁻ concentrations were significantly depleted; this can be explained by their predominant occurrence on ice crystal surfaces. Variable mobility was also observed for TEs, with Ce, Eu, La, Mo, Nd, Pb, Pr, Sb, Sc, Sm, U, and W being the best-preserved elements. In tendency, high concentrations of TEs were found to favor relocation with meltwater, while low abundant TEs were preferably retained.

The MIs and 18 out of 21 investigated TEs revealed a consistent behavior with meltwater percolation at two Alpine sites, Weissfluhjoch and upper Grenzgletscher, which are 180 km apart. This indicates that the observed species dependent preservation from melting snow and ice is particularly valid for the Alpine region, reflecting central European atmospheric aerosol composition. Based on the observations at the two Alpine sites, we propose that NH₄⁺, TEs deposited as water-insoluble particles, and TEs of water-soluble particles occurring in low concentrations may still be applicable as environmental proxies in snow pits and ice cores affected by melting. Corroborating the existence of meltwater-resistant proxies is particularly relevant as many high-mountain glaciers worldwide, which provide avenues for assessing natural and anthropogenic impact on the atmosphere, are increasingly affected by melting.


