A Comprehensive Nontarget Analysis for the Molecular Reconstruction of Organic Aerosol Composition from Glacier Ice Cores

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Abstract. Ice cores are climate archives suitable for the reconstruction of past atmospheric
 composition changes. Ice core analysis provides valuable insight into the chemical nature of
 aerosols and enables constraining emission inventories of primary emissions and of gas-phase
 precursors. Changes in the emissions of volatile organic compounds (VOCs) can affect formation
 rates and mechanisms as well as chemical composition of aerosols during the pre-industrial era, a

key information for understanding aerosol climate effects. Here, we present an analytical method for the reconstruction of organic aerosol composition preserved in glacier ice cores. A solid-phase-extraction method, optimized toward oxidation products of biogenic VOCs, provides an enrichment factor of ~200 and quantitative recovery for compounds of interest. We applied the pre-concentration method on ice core samples from the high-alpine Fiescherhorn glacier (Swiss Alps), and used high-performance liquid chromatography coupled to high-resolution mass spectrometry as a sensitive detection method. We describe a nontarget analysis that screens for organic molecules in the ice core samples. We evaluate the atmospheric origin of the detected compounds in the ice by molecular-resolved comparison with airborne particulate matter samples from the nearby high-alpine research station Jungfraujoch. The presented method is able to shed light upon the history of the evolution of organic aerosol composition in the anthropocene- a research field in paleoclimatology with a considerable potential.

1. Introduction. The effects of atmospheric aerosol particles on the Earth's radiative balance are a major source of uncertainty in global climate models. The number concentration of particles that act as cloud condensation nuclei (CCN) affects the albedo and lifetime of clouds, making polluted clouds more reflective and long-lived (1). Since the beginning of the industrialization, increasing aerosol pollution has led to negative radiative forcing, and hence masked around one-third of the continental warming due to greenhouse gases (2). However, the number of natural particles present in the atmosphere before anthropogenic pollution is largely unknown and is currently the main source of uncertainty in the determination of the magnitude of aerosol-related negative forcing (3, 4).

Our understanding of processes that affect pre-industrial CCN number concentration has substantially improved in recent years. We know now that oxidation of biogenic VOCs (especially

monoterpenes) yields a complex mixture of highly oxygenated organic molecules, which can form new particles on their own (5, 6). In terms of aerosol mass, secondary organic aerosol (SOA) is the major class responsible for particle growth into CCN active sizes over vegetation-covered continents (7–9). Based on this understanding, models can now estimate a natural baseline number concentration of aerosols and CCN: Gordon et al. showed that removing biogenic SOA in a global aerosol model results in a ~41% and ~26% lower CCN number in the pre-industrial (PI) and a present-day (PD) atmosphere, respectively (10). This demonstrates that a quantitative understanding of biogenic emissions is highly relevant for accurately predicting aerosol number concentrations, especially in the pre-industrial atmosphere. However, how the perturbation of natural atmospheric processes by anthropogenic emissions changes the amounts and the nature of condensable organics remains unknown. Global aerosol models usually do not account for the interference of anthropogenic pollutants with the oxidation of biogenic VOCs, resulting in an anthropogenic enhancement of SOA (11, 12). Furthermore, it is commonly recognized that CO₂, temperature and land cover changes have an effect on biogenic emissions (13, 14), but validation and quantification of these processes through the analysis of ice cores that cover the PI-PD-transition is still at a very early stage.

Apart from trace gas reconstructions, the focus in ice core analysis during the past decades has been on quantifying major ions and trace metals (15, 16), as well as primary particles (e.g., fly ash, charcoal, and pollen) (17, 18). Analysis of water-soluble organic carbon and total organic carbon (review by Legrand et al. (19)), and molecular-resolved measurements of organic aerosol tracers and persistent organic pollutants receive now increasing attention (review by Giorio et al. (20)). Selected biogenic SOA (BSOA) tracers in ice cores are usually present in the upper-ppt-lower-ppb range, which requires sample pre-concentration before the actual measurement (21, 22). Only a

limited number of studies quantified selected BSOA tracers in glacier ice cores (23–28), as only a few authentic BSOA standards exist (29). Besides these targeted analysis methods, the large number of unknown compounds in ice cores (30) requires a new approach that uncovers relevant changes of the secondary organic aerosol concentration and composition during the PI-PD-transition. Therefore, we present a nontargeted screening, which provides a deeper insight into relative concentration changes of a multitude of biogenic and anthropogenic SOA compounds in glacier ice cores.

2. Methods. *2.1. Ice core - sample preparation.* The ice core was collected at the Fiescherhorn glacier (46°33'N, 08°04'E) at an altitude of ~3900 m a.s.l. in the year 2002. The ice core has a total length of 150.5 m reaching bedrock and covers the time period back to the year ~1650. The depth-age relationship was inferred from annual layer counting as described by Jenk et al. (31). The temperature profile of the ice core indicates that the Fiescherhorn glacier is a cold glacier with an ice temperature between –6 to –2°C. Until analysis, the ice core was stored in sections of ~70 cm length in polyethylene (PE) tubes in polystyrene/cardboard boxes at -20°C.

The ice core (8 cm in diameter) and blank ice (prepared from frozen ultra-pure water, Sartorius, Arium pro) were cut by a stainless steel band saw in a cold-room at –20°C. The outer parts of a quarter of the ice core were cut off to prevent organic contamination from the ice surface. This resulted in a 2.5 x 2.5 cm quadratic cross-section available for analysis. Sticks of ~15 x 2.5 x 2.5 cm were combined into one jar (polyethylene terephthalate jar with a polypropylene lid) until a total sample weight of ~350 g was reached. This relatively large amount was necessary since we prepared samples in parallel for this work as well as for determining the concentration of dissolved organic carbon (DOC) and its ¹⁴C content (33). We found that adhesion of ice sawdust to the prepared ice sticks can be a source of organic contamination. Thus, a further

clean-up step was to rinse the ice core sticks three times with ultrapure water under an inert helium atmosphere in a glass vessel. The remaining ice was melted in the glass vessel, and 60 mL of the samples were refrozen into glass vials until solid phase extraction (SPE).

2.2. Ice core - solid phase extraction. Prior to the SPE, samples were slowly melted in the glass vials at room temperature and spiked with internal standards. Internal standards were hydroxyl carboxylic acids (see SI) in which the hydroxyl group was acetylated using acetyl chloride- $1-^{13}\text{C}$. We adjusted the amount of added internal standard such that it appears in the same intensity range as the analyte's signals, and kept the added amount constant for all analyzed samples. In order to de-protonate organic acids in solution, we adjusted to pH 8-9 using $\sim 10\ \mu\text{L}$ aqueous ammonia (25% v/v). The utilized strong anion-exchange SPE column (Oasis MAX 1cc, 10 mg bed-weight, $30\ \mu\text{m}$ particles, Waters, U.S.A.) provided a sorbent material for anionic analytes. The SPE cartridge was conditioned before sample loading with $\sim 1\ \text{mL}$ of methanol and 5-10 mL of ultrapure water. Then, the samples were loaded at a flow rate of $1\ \text{mL}/\text{min}$ onto the cartridge using transfer tubes, and, without a washing step, eluted into a $2\ \text{mL}$ vial using first a solution of $250\ \mu\text{L}$ 5% formic acid and 0.5% hydrochloric acid in methanol, followed by twice a $250\ \mu\text{L}$ solution of 5% formic acid in methanol. By adding hydrochloric acid, we improved the elution strength of the solvent mix. The obtained eluates ($\sim 750\ \mu\text{L}$) were concentrated at $30\ ^\circ\text{C}$ under a gentle stream of nitrogen (Reacti-Vap Evaporator, Thermo Fisher Scientific, U.S.A.) to a volume of approximately $10\ \mu\text{L}$. The remaining samples were redissolved in $0.3\ \text{mL}$ of methanol/water (5% v/v), to which $5\ \mu\text{L}$ of ^{13}C -vanillin ($\sim 90\ \mu\text{M}$) was added as an internal standard for monitoring the instrumental performance. The samples were immediately transferred to a thermostated ($10\text{-}12^\circ\text{C}$) auto-sampler and measured by ultra-high performance liquid chromatography coupled to high-resolution mass spectrometry (UHPLC/HRMS).

2.3. *Particulate matter samples and recovery of the SPE method.* We obtained a set of selected aerosol filter samples (PM₁₀) from the Swiss National Air Pollution Monitoring Network (NABEL), and from α -pinene oxidation experiments in a smog chamber. For this work we analyzed ambient filters from the locations Zürich Kaserne (47°22'39"N, 08°31'49"E, 23 July 2013), Magadino-Cadenazzo (46°09'36"N, 08°56'01"E, 03 January 2014), and from the high-alpine research station Jungfraujoch (JFJ) (46°32'51"N, 07°59'08"E, ~3600 m a.s.l., 22 June 2017). Zürich Kaserne is an urban site north of the Alps, and Magadino-Cadenazzo a rural site in a mountain valley south of the Alps. Especially during the winter season, the Magadino-Cadenazzo site is heavily impacted by domestic wood combustion. As the Jungfraujoch research station lies within 6 km distance from the Fiescherhorn ice core drilling site, we presumed that aerosol composition from this site resembles most closely the organic composition in the ice core.

We used a Jungfraujoch-sample from 22 June 2017 (a day with high SOA loadings, likely affected by transported biomass burning plumes from Portugal) for analyzing high-alpine SOA composition and determining the recovery of our SPE method. PM₁₀ samples at Jungfraujoch were collected for 24 hours (changes at midnight) onto pre-baked quartz fiber filters (Pallflex XP56 Tissuquartz 2500QAT-UP, Pall Life Science, U.S.A.) using a high-volume sampler (DHA-80, Digitel, Switzerland) at a flow rate of 30 m³/h. We extracted six filter punches (11 mm diameter) from each of the samples in a glass vial with 1.4 mL of methanol, 0.1 mL of ultrapure water and 10 μ L of the internal standards. After 15 minutes of sonication, we transferred the solution into a 2 mL vial and evaporated at 30 °C under a gentle nitrogen stream to a volume of ~10 μ L. Subsequently, 1.5 mL of 5% methanol in water (v/v) was added to the concentrated extract. Thereafter, the extract was split into three aliquots of 0.5 mL. We added 0.5 mL ultra-pure water to each aliquot with which we determined the recovery of the SPE method. Therefore,

0.5 mL of each aliquot was filtered through a 0.22 μm PTFE syringe filter and analyzed by UHPLC/HRMS as the reference sample. The other three 0.5 mL aliquots were each diluted with ultra-pure water to 60 mL as surrogate ice core samples. These samples were then enriched (in triplicate) using the SPE method as described above (see Scheme S1). Comparison of the signal intensity of selected molecules between the reference samples and the concentrated surrogate ice core samples allows us to determine the recovery for all the relevant (known and unknown) aerosol compounds that we can detect on the Jungfraujoch filter.

2.4. UHPLC/HRMS method. We performed organic tracer analysis using chromatographic separation and mass spectrometric detection with a high-resolution hybrid quadrupole-Orbitrap mass spectrometer (Q Exactive Focus, Thermo Fisher Scientific, U.S.A.) equipped with a UHPLC system (Ultimate 3000, Thermo Fisher Scientific, U.S.A.). The analytical column (Accucore RP-MS 150 x 2.1 mm, 2.6 μm particle size, Thermo Fisher Scientific, U.S.A., with the corresponding pre-column) was operated in gradient mode and maintained at 50 °C. Eluents were ultrapure water with 1% acetonitrile, 1% methanol, and 0.2% formic acid (v/v/v, eluent A) and methanol (eluent B). The gradient started with 1% eluent B (0-2 min), linearly increasing to 99% B (2-12 min), and staying at 99% B (12-16 min) at 400 $\mu\text{L}/\text{min}$ flow rate. The injection volume was 20 μL , and the total run time was set to 16 min. Mass spectrometric detection was achieved using a heated electrospray ionization (HESI) source in negative ion mode, and a scan range of mass to charge ratios (m/z) from 70 – 1000 with a resolution of $\sim 70\text{k}$ at m/z 200. The ion source settings were: 50 psi sheath gas (nitrogen), 13 psi aux gas (nitrogen), 425 °C gas temperature, and 3.4 kV capillary voltage. The HESI source generated deprotonated molecular ions ($[\text{M}-\text{H}]^-$). The MS-data were recorded in centroid mode using a data-dependent MS/MS (dd-MS²) method. The sodium-dimer of formic acid $[(\text{CHO}_2)_2\text{Na}]^-$ at m/z 112.9856 was used as lock mass for internal

mass calibration. All ice core samples were measured in instrumental triplicate, while we performed procedural triplicates for the SPE-recovery experiments (see section 2.3).

2.5. Nontarget analysis. The obtained data files of the Jungfraujoch aerosol sample and the ice core sample (dated to the year 1984) were processed together in one experiment file using the open-source software *mzmine2* (version 2.37) (34) and the automated data analysis pipeline (ADAP) for chromatogram deconvolution (35). Only the full scans of the raw-files were used for the nontarget analysis (NTA). In an iterative process, we optimized a workflow (see SI) and extracted exact mass, retention time and peak area of the compounds in the samples. The software uses the measured exact mass, isotopic signature and constrained elemental ratios to determine the sum formula of unknown compounds (36). Due to their un-natural isotopic signature, we identified the internal standards manually. We validated the automated peak integration by *mzmine2* by comparison with manual integration using *XCalibur* (Thermo Fisher Scientific) and found excellent agreement ($R^2=0.99$). For the graphical illustration of the NTA results, we plot only compounds that are significantly different from the ice blank (triplicate measurement of the same sample, two-sample *t*-test, $p \leq .005$), which exhibit signal/blank > 9, have a peak area of the molecular ion $[M-H]^- > 1.0 \times 10^5$, and retention time > 0.8 min. The area is background corrected by subtracting 1*mean signal area detected in the ice-blanks from ultrapure water. Finally, by classification into the molecular formula groups (CHO, CHNO, CHOS, CHNOS) we are able to visualize the molecular fingerprints of ice-core and PM samples.

In order to evaluate the *mzmine2* workflow and to verify the assignment of molecular formulas to the measured ion signals, we analyzed the same raw-files with another NTA software (Compound Discoverer version 3.0 (CD), Thermo Fisher Scientific, workflow Figure S2) and found qualitatively as well as quantitatively good agreement (see Figure S3). In the CD workflow

all standard parameter were used except: *i*) lower RT limit set to 0.8 min in Select Spectra node; *ii*) Min. Peak Intensity to 10^5 in Detect Compounds, and *iii*) Mass Tolerance to 4 ppm in Detect Compounds, Group Compounds, Fill Gaps, and Predict Compositions.

3. Results and Discussion. Sample pre-concentration of organics in ice cores is a pre-requisite for successful analysis of organic molecules in ice. There are alternative ways to SPE for sample pre-concentration, such as stir bar sorptive extraction or rotary evaporation (21, 22). A wide variety of different SPE materials (e.g., C₁₈, ion exchange, hydrophilic-lipophilic balanced polymers) allows tailoring SPE procedures toward specific target analytes. However, it is a challenge to develop multi-compound SPE procedures, which give satisfactory recovery for a large number of different compounds.

3.1. SPE-recovery of a PM₁₀ filter extract obtained by nontarget analysis. The development of a comprehensive SPE method for atmospheric SOA molecules is usually restricted to a small number of available authentic standards. To overcome this limitation, we used chemically complex extracts of PM₁₀, collected in summer at the high-alpine research station Jungfraujoch, to develop and validate the SPE procedure for atmospherically relevant compounds. When we tested the SPE-recovery of a Jungfraujoch PM₁₀ filter extract from winter, we found much fewer compounds in terms of number and concentration. This can be explained by less atmospheric convection and mixing during the winter season. Measurements of the 22 June 2017 reference filter sample (filter extraction followed by LC/MS analysis) and the SPE filter sample (filter extraction, dilution of the extract to 60 mL, enrichment by SPE, LC/MS analysis) enabled us to determine the recovery of all measured compounds that are detected by nontargeted screening (**Figure 1 A**). We find that the internal standards show a mean recovery of 81% with a relative standard deviation (RSD) of 8 % (**Figure 1 B**), spanning from 61% ($\pm$ 8%) for C₉[13]CH₁₀O₅ (the acetate ester of vanillic acid) to

203 94% ($\pm 10\%$) for $C_9[13]CH_{18}O_4$ (the acetate ester of hydroxy octanoic acid). The area-weighted
204 mean recovery for all carbon-, hydrogen- and oxygen-containing (CHO) compounds was $89\% \pm$
205 20% , contributing $\sim 74\%$ of the total identified signal (area-wise). The SOA markers pinic acid and
206 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) (37, 38) show quantitative recovery with
207 procedural relative standard deviation (RSD) smaller than 10% (see **Table 1**). We find low
208 recovery for small organic sulfates which show high signal intensity in the reference sample (large
209 red circles in **Figure 1**). For example, CH_4O_3S (likely methanesulfonic acid) shows no enrichment,
210 and the compounds $C_5H_8SO_7$ and $C_5H_{12}SO_7$ (likely isoprene-derived organic sulfates (39, 40))
211 yield a recovery of $20\% \pm 40\%$ and $12\% \pm 32\%$, respectively. Small organic sulfates can strongly
212 bind to the anion exchange material; hence, a weak anion exchange material for their enrichment
213 might be more suitable. Furthermore, the small and polar organic sulfates elute very early from
214 the reversed-phase column, resulting in overlapping isomers, which is why other separation
215 techniques are more appropriate for the analysis of this class of compounds (41). Although we
216 observe low recovery for small organic sulfates, we also detect monoterpene-derived organic
217 sulfates and nitrooxy-organosulfates, which have been described in both laboratory and ambient
218 SOA (42–45). These compounds show quantitative recovery (**Table 1**) after SPE of the high-alpine
219 filter extract.

Table 1. SPE-recoveries of selected SOA tracers, determined from the filter extract dilution experiment.

Compound	Molecular formula	Exact mass [M-H] ⁻	Retention time (min)	Recovery (%) ± RSD
Nitrophenol**	C ₆ H ₅ NO ₃	138.0197	6.8	87 ± 10
Nitrocatechol**	C ₆ H ₅ NO ₄	154.0146	5.4	83 ± 26
Terpenylic acid*	C ₈ H ₁₂ O ₄	171.0663	4.7	101 ± 8
unknown terpenoic acid*	C ₇ H ₁₀ O ₅	173.0455	2.0	101 ± 3
Nitrosalicylic acid**	C ₇ H ₅ NO ₅	182.0095	6.6	114 ± 26
Pinic acid*	C ₉ H ₁₄ O ₄	185.0819	6.2	97 ± 7
unknown terpenoic acid*	C ₈ H ₁₂ O ₅	187.0612	3.3	89 ± 5
MBTCA*	C ₈ H ₁₂ O ₆	203.0561	4.6	102 ± 8
unknown terpenoic acid*	C ₁₀ H ₁₆ O ₆	231.0874	6.3	106 ± 8
MT-organosulfate	C ₁₀ H ₁₈ O ₅ S	249.0802	7.1	127 ± 6
MT-nitrooxy organosulfate	C ₁₀ H ₁₇ NO ₇ S	294.0653	8.0	111 ± 10

*These compounds are observed in the ambient sample from JFJ and in chamber experiments of α -pinene ozonolysis. The monoterpene (MT)-derived organosulfates and nitrooxy-organosulfates show several isomers in the JFJ sample: the ones depicted are the isomers with the highest intensities in the chromatogram. **These compounds are not identified by authentic standards, but likely the reported tracers for biomass burning (46–49).

Nitrophenol, a tracer for biomass burning, was not detected on the filter sample from Jungfraujoch, but we conducted the same recovery determination experiment based on the extract of the Magadino-Cadenazzo filter, which contains large amounts of PM from domestic wood burning. In this experiment, nitrophenol yields almost quantitative recovery (87% ± 10%). Furthermore, we detect the biomass burning markers nitrocatechol and nitrosalicylic acid on the Jungfraujoch filter with recoveries >80%, but with higher relative standard deviation. Compounds with quantitative SPE-recovery are enriched by a factor of 200, enabling the analysis of

compounds that otherwise are not detectable in the original ice sample. Overall, the developed SPE method is suitable for a large variety of aerosol-related organic molecules that are present at unknown concentrations in high-alpine ice cores.

Figure 1. Evaluation of the SPE recovery using a PM10 filter extract from JFJ on 22 June 2017. (A) Integrated peak areas of compounds from the pure filter extract (reference) and after SPE following the dilution. Colors represent different composition classes. Internal standards (ISTD) appear as pentagrams. Diagonal lines indicate the recovery; the lowermost line illustrates where the signal intensity would be without SPE enrichment. (B) SPE recovery on a linear scale versus the relative standard deviation (RSD) of the recovery on a logarithmic scale. Circle size in A and B represents the peak area (linear scale) of the compounds in the reference filter sample.

3.2. Application of the SPE method and nontarget analysis on a Fiescherhorn ice core. We analyzed the Fiescherhorn ice core with the described SPE sample preparation method. The NTA of the ice core provides relative peak area and molecular formulas for more than 500 compounds with the used intensity threshold and filter criteria. The classification of the molecular formulas into composition groups is the same as for the JFJ filter. We correlated the sum of the peak areas

of all compounds for the 81 measured ice core samples with the DOC concentration. The comparison of the ion signal sum of all compounds (CHO + CHON + CHOS + CHNOS) and of the sum of the CHO compounds versus DOC resulted in a Pearson R of 0.84 and 0.86, respectively (see Figure S4). We interpret this behavior as an indication for the linearity of the SPE effectiveness over the observed concentration range.

We illustrate the complex chemical composition pattern of a particular ice core sample (dated to the year 1984) by three visualization methods: (A) m/z vs. retention time (RT), (B) Van Krevelen diagram (O/C vs. H/C) and (C) Kroll diagram (inverse scale of the carbon number vs. average carbon oxidation state) (**Figure 2 A-C**). The area of the circles represents the measured ion intensity, which we do not convert into concentration, due to the generally large and non-predictable variation in ESI calibration factors, even for chemically similar surrogate molecules. Furthermore, the area is not corrected for the recovery of the different compounds, since we could not determine the recoveries of all appearing compounds, and the low recovery of the small CHOS compounds would lead to large signals masking other compounds. Also, the recovery for small CHOS-compounds is largely uncertain, thus we emphasize that signal intensities of different compounds cannot simply be compared among each other.

The m/z -RT plot (**Figure 2 A**) allows evaluating the fraction of signals to which the nontarget workflow assigned a molecular formula since only in this plot we can depict unassigned ion signals. We find that the developed nontarget workflow leaves very few signals unassigned. The majority of identified organic ion signals are smaller than 300 Da and cover the full range of retention time. The largest subgroup by peak area is the CHO group, followed by the CHOS group, the CHNO, and the CHNOS group. Especially the CHOS group exhibits a broad spectrum in polarity, spanning from polar (short RT) to non-polar compounds (long RT).

The Van Krevelen diagram (**Figure 2 B**) is a method to visualize chemical classes of compounds. In this diagram, we find that the large signals of nitrogen containing compounds fall into the region with $H/C < 1$, which suggests an aromatic character. The nitrogen-containing (CHNO) compounds were identified as nitrophenol ($C_6H_5NO_3$), dinitrophenol ($C_6H_4N_2O_5$) and methyl-dinitrophenol ($C_7H_6N_2O_5$) database-assisted by CD and mzcloud.org (HighChem Ltd., Slovakia). Methyl-nitrophenol ($C_7H_7NO_3$) is not included in mzcloud, hence this compound is only tentatively identified. As reported by Mohr et al. (48), nitrophenol, methyl-nitrophenol and dinitrophenol are attributed to biomass burning emissions. However, we cannot detect the dinitrophenols in equal intensity in the Magadino valley filter sample close to the domestic biomass burning emissions, which might be an indication for further nitration of nitrophenols during atmospheric transport. Another explanation might be a different source than biomass burning, as dinitro-*ortho*-cresol ($C_7H_6N_2O_5$) has been used as an insecticide and herbicide in Europe until the ban in the year 1991 (European Union legislation 99/164/EC). Hence, the origin of the dinitro-compounds remains elusive, and investigation on aging studies of biomass burning emissions and unambiguous compound identification using authentic standards need to be further explored.

The majority of CHO compounds in the Van Krevelen diagram appear into the region of $1.2 < H/C < 1.9$ and $0.3 < O/C < 1$. This space is representative of oxidation products of monoterpenes (50). The CHOS compounds with $H/C \geq 2$ represent an aliphatic series of organic sulfates or sulfonates, as we observe an HSO_4^- -fragment in MS/MS experiments (Figure S5). We find the homolog series of $C_nH_{2n+2}SO_4$ and $C_nH_{2n+2}SO_5$ ($n=2-10$) with slopes in the Van Krevelen diagram of 0.5 and 0.4, respectively (H/C -intercept at 2). The homolog series of $C_nH_{2n}SO_{4-6}$ ($n=4-8$) appears in the Van Krevelen diagram on a horizontal line at $H/C=2$. Aliphatic organosulfates

have been described as products from diesel emissions and atmospheric processing in the presence of SO₂ (51). However, also isoprene derived organosulfates with four and five carbon atoms fall in this aliphatic series, and hence these compounds can only tentatively be attributed to diesel emissions.

The Kroll diagram (**Figure 2 C**) depicts the average carbon oxidation state ($\overline{OS}_C$) versus the number of carbon atoms. Here, we calculate the average carbon oxidation state as $2 \cdot O/C - H/C$ (52), without correction for oxygen attached to non-carbon atoms, since we cannot confirm for each sulfur-containing ion signal that it is an organic sulfate. Hence, organic sulfates (and nitrates) are biased in the diagram toward higher $\overline{OS}_C$ -values. However, the visualized molecular distribution of the carbon numbers provides insight into the relative contributions of biogenic precursor VOCs. We observe the largest abundance of organic compounds of the CHO class for compounds between 6 and 10 carbon atoms. In this range, one can expect oxidation products of monoterpenes (C₁₀H₁₆). However, we cannot rule out a contribution of anthropogenic SOA products in this range of carbon atoms. For example, mesitylene (C₉H₁₂) can serve as a precursor for oxidation products, e.g. C₉H₁₄O₆ (53), of which isomers are formed in the oxidation of α -pinene. Hence, future research needs to go into the direction of molecular resolved analysis of SOA oxidation products, in which product isomers are chromatographically separated before mass spectrometric detection, and oxidation of different VOC precursor gases is studied individually.

Figure 2. Molecular fingerprints of an ice core sample from the Fiescherhorn glacier, dated to the year 1984. (A) Mass-to-charge ratio (m/z) vs. retention time. (B) Van Krevelen diagram. (C) Kroll diagram, where $\overline{OS}_C$ is the average carbon oxidation state. Circle area depicts the signal intensity (linear scale) of the molecular ions.

Finally, after nontarget analysis we do not observe oxidation products of larger VOC precursors, such as sesquiterpenes ($C_{15}H_{24}$) nor do we detect dimers of monoterpene oxidation. However, we do see significant differences between blank ice and the ice core sample in the chromatograms of suspect-target masses of higher molecular weight oxidation products. For example, the extracted ion chromatograms (EIC) of 299.1136, 299.1501, and 357.1558 (± 4 ppm) all show broad hedgehog-like features, that do not appear in the blank samples (Figure S6). On the nominal mass 299, the molecular formulae $C_{14}H_{20}O_7$ and $C_{15}H_{24}O_6$ have been described (54), which are likely oxidation products of sesquiterpenes. On the mass 357.1558, the α -pinene-derived dimer $C_{17}H_{26}O_8$ has been described (55–57), which is formed in α -pinene ozonolysis under humid conditions (58) and plays (together with other dimers) an important role in new particle formation (59). Due to the broad peak shape and low signal intensity of these EICs in the ice core sample, here the NTA did not extract any signal. Since these organic compounds can be seen as marker compounds for nucleation of aerosol particles from gas-phase vapors, further improvement on sample enrichment and chromatographic separation is needed.

3.3. Validation of the atmospheric origin of the organic compounds in ice. We evaluate the atmospheric origin of the individual organic compounds, which are detected in the ice core, based on molecular-resolved comparison with the high-alpine atmospheric PM filter sample. The three parameters accurate mass, retention time and MS/MS fragmentation pattern allow unambiguous verification that a certain ion signal from the aerosol sample can be assigned to the same molecule detected in the ice core. In this way, we are able to assess the atmospheric origin of organic compounds in the ice core sample. **Figure 3 (A-E)** shows chromatograms of the exact mass trace 185.0819 (± 4 ppm) of five different samples (laboratory SOA, ambient SOA, and ice core samples). In the PM10 filter sample from Jungfraujoch (**Figure 3 B**), we identified by NTA seven

isomers of $C_9H_{14}O_4$ (colored peaks in the chromatogram). The isomer at ~6.2 minutes retention time is pinic acid, which appears in all five samples. This identification is based on retention-time matching with chamber SOA from α -pinene oxidation (**Figure 3 A**). To further verify this assignment, we compare the MS/MS fragmentation pattern of m/z 185 at 6.2 min in the chamber experiment with the preindustrial ice core sample (**Figure 3 E**) and find the same fragmentation signals with almost identical intensities (**Figure 3 F**). Although carboxylic acids usually show the loss of CO_2 in MS/MS fragmentation, we obtain characteristic fragmentation spectra for different $C_9H_{14}O_4$ isomers (**Figure 3 F-I**). E.g., the elimination of $[CO_2 \cdot H_2O]$ (fragment $C_8H_{11}O$) has been observed for the m/z 185 products of Δ^3 -carene (**Figure 3 G**), and the characteristic appearance of the fragment $C_5H_7O_3$ at m/z 115.0401 (elimination of C_4H_6O) (**Figure 3 H**) has been described for ketolimononic acid- an oxidation product of limonene (60, 61).

Overall, we demonstrate with the example of the exact mass trace at m/z 185.0819 that the compound matching between atmospheric PM samples and ice core samples, based on the comparison of retention time and MS/MS pattern, is a useful tool to identify and attribute oxidation products to their precursor VOCs. However, for unambiguous attribution of the unknown signals to their precursor VOC, we need further laboratory studies in which oxidation products of single VOCs are investigated. This can then serve as a basis for the establishment of an aerosolomics database (precursor - oxidation-conditions - products) that contains information on the exact mass, retention time characteristics and MS/MS fragmentation spectra of single product molecules.

Figure 3. Chromatograms of the exact mass 185.0819 ($\pm$ 4 ppm), recorded by UHPLC/(-)HESI-HRMS. The retention time axis is zoomed from 3.5 to 8.8 minutes (no ion signals present outside this range). (A) A reference chamber experiment of α -pinene oxidation. (B) JFJ, PM10 (22 June 2017): the reference sample for high-alpine aerosol composition. (C) Zurich Kaserne PM10 (23 July 2013). (D) and (E) Fiescherhorn ice core sample after SPE of the time periods 1936-1937.5 and 1682-1692, respectively. (F)-(I) show MS/MS spectra of different m/z 185 isomers, which are labeled with distinct symbols in the chromatograms (A)-(E). The upward fragmentation spectra are from aerosol samples, while the downward fragmentation spectra refer to the ice core samples.

Now, we extend the compound-matching approach to all compounds, which are identified by the NTA, presented in the two-dimensional space of m/z vs. retention time. Figure 4 contrasts the

composition of the Fiescherhorn ice core sample from the year 1984 against the JFJ PM10 composition from 22 June 2017. The area of the circles in **Figure 4 A and C** depict the peak intensities in the ice core sample, as in **Figure 2 A**. The compounds that are in common with the JFJ filter are shown in **Figure 4 A**, while in **4 C** we display only compounds that are uniquely detected in the ice core. We observe the majority (area-wise) of CHO-containing compounds to be present in both, aerosol and ice core samples. Most clearly, the homolog series of aliphatic organosulfates, detected in the ice sample from 1984, is not present in the JFJ PM10 sample from 2017. Flue-gas desulfurization was introduced in European coal-fired power plants in the 1980s, and later on, filter-equipped diesel cars were progressively introduced. Between 1984 and 2017, SO₂ concentrations in Switzerland have decreased approximately by a factor of 20 (62). Therefore, it is likely that the sulfur-containing organic compounds were present in the atmosphere in 1984, but are not detected in significant amounts in the present-day atmospheric aerosol. However, we do observe organic sulfates in the ice core and aerosol sample, appearing at very short retention times. Small organic sulfates C₅H_{8,10,12}O₇S (*m/z* 211, 213, 215) are detected in the ice core sample after SPE, although we showed that these compounds have a low recovery. Since the areas in **Figure 4 A and C** are not corrected for the recovery of each individual compound, the early-eluting organic sulfates were likely present at much larger concentrations in the year 1984 in relation to the organic compounds with quantitative SPE recovery. The nitrophenols present in the ice sample were not detected in the PM10 filter sample from Jungfraujoch, but it is unlikely that the nitrophenols detected in the ice have another origin than atmospheric deposition. We suggest further long-term analysis of high-alpine PM10, in order to identify atmospheric transport processes, which can explain the detection of nitrophenols on high-alpine cold glaciers. It is

important to note that the majority of compounds in the filter sample (**Figure 4 B**) are also detected in the Fiescherhorn ice core and only a few compounds appear uniquely on the filter (**Figure 4 D**).

Figure 4. Comparison between ice core and atmospheric PM samples by retention time matching. (A) Area of compounds in the Fiescherhorn ice core sample (year 1984) that are in common with the Jungfraujoch filter sample (22 June 2017) (B) Area of compounds detected in the Jungfraujoch filter sample (22 June 2017) that are in common with the Fiescherhorn ice core sample (year 1984). (C) Unique compounds in the Fiescherhorn ice core sample. (D) Unique compounds in the JFJ filter sample (see Figure S7 and S8 for the Van Krevelen- and Kroll-diagram, respectively).

Thus, we see this as an indication that the majority of atmospheric organic tracers are preserved in cold glaciers, which do not experience summer melt events.

4. Limitations and Implications. We note that with the used technique, we rather detect stable products of oxidation (e.g., organic acids) and not highly oxygenated organic molecules with high reactivity (e.g. peroxides, peroxy acids) that are formed intermediately in the process of VOC oxidation. However, future experiments are needed in order to study photochemical transformation processes that might alter the deposited SOA on glacier surfaces, or which compounds originate from gas-phase adsorption. Here, we estimated the volatility of the observed compounds from their molecular formulae (63, 64), and find C*-values that suggest their predominant occurrence in the particle phase (Fig. S9). We like to emphasize that the presented SPE method is not designed to retain small (intermediate) volatiles, which occur in high-alpine ice due to gas-phase adsorption (19). As a rule of thumb, the described SPE method exhibits good recovery (>80%) and reproducibility (RSD < 20%) for abundant compounds that are retained by the reversed-phase column by >1.5 minutes (Figure S10 and Figure S11). Overall, the presented approach of molecular resolved analysis validates the use of ice cores from cold glaciers to reconstruct organic aerosol composition from the past atmosphere and opens up the possibility to investigate time series of individual compounds over the pre-industrial to present-day transition. Such time series have the potential to (1) constrain emission inventories of biogenic and anthropogenic VOCs, (2) helping to understand atmospheric VOC transformation and secondary aerosol formation, and (3) eventually can be used to derive the evolution of the atmospheric oxidation capacity in the anthropocene.

424 ASSOCIATED CONTENT

425 **Supporting Information.** Synthesis of internal standards, chemicals and reagents, workflow of
426 mzmine2 and compound discoverer, comparison between mzmine and compound discoverer,
427 comparison of sum ion intensity (from UHPLC/HRMS) with DOC in all ice samples, MS/MS
428 fragmentation spectra of aliphatic organic sulfates, EICs of suspected-target compounds
429 (sesquiterpene oxidation products and the MW-358 α -pinene dimer oxidation product) , Van
430 Krevelen and Kroll diagram space of Figure 4, estimated C* of CHO compounds, a sensitivity
431 analysis of the recovery and the RSD of the recovery, and the laboratory workflow of the filter-
432 dilution-SPE-recovery experiment.

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Author Contributions

A.L.V. and A.L. wrote the manuscript. A.L.V., U.B., I.E.-H., M.S., and S.B. conceptualized and designed the study. A.L.V., L.F., A.L. and A.V. prepared ice core samples. A.L.V., K.R.D., K.A., T.K. and S.B. extracted filter samples and performed LC/MS analysis. V.P. prepared chamber experiments and performed filter sampling. A.L.V., A.L., L.F., F.B. and S.B. developed the NTA workflow and analyzed the data. All authors have contributed to the scientific discussion. All authors have given approval to the final version of the manuscript.

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Notes

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ABBREVIATIONS

CCN: Cloud condensation nuclei
EIC: Extracted ion chromatogram
FH: Fiescherhorn

467 HESI: Heated electrospray ionization
 468 HRMS: High-resolution mass spectrometry
 469 JFJ: Jungfraujoeh
 470 PM: Particulate matter
 471 PI: Pre-industrial
 472 PD: Present-day
 473 RSD: Relative standard deviation
 474 SOA: Secondary organic aerosol
 475 SPE: Solid phase extraction
 476 UHPLC: Ultra-high performance liquid chromatography
 477 VOC: Volatile organic compounds

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