Answer to Anonymous Referee #2

We would like at first thank the reviewer for his comments. In the following our answers are made in italic.

This publication reads like a solid piece of work, well written, and logically structured. The caveat is that I am not an ice core specialist- and if there are methodological issues in this part, I have probably not spotted that. From a general atmospheric chemistry perspective, however, the manuscript and story make a lot of sense. I can therefore recommend this manuscript for publication in ACP, with some minor suggestions for improvements below.
Minor suggestions: General: As this manuscript is submitted to a more general Atmospheric Chemistry journal, I would recommend to spell out/explain specialized abbreviations used in this manuscript. E.g. I didn't know the meaning of Yr cal BP; also BP, CE may not be known to all readers. Possibly a table ?
We agree and we have now specified in the "Basal ice Dating" section that: "As seen in Table 1, the mean age of the ELB-178-03 sample (1530 yr cal BP, i.e. 1530 years before 1950)…….;"
Also in the first sentence of the abstract: "This study reports on the glaciochemistry of a deep ice core (182 m long) drilled in 2009 at Mount Elbrus in the Caucasus, Russia. Radiocarbon dating of the particulate organic carbon fraction in the ice suggests that the basal ice dates to 280 ± 400 yr CE (Common Era)."

General: it would be useful if in addition to concentrations also the deposition fluxes would be presented, which is the more obvious quantity for comparison with models.
We agree that the knowledge of deposition fluxes would be useful to compare with model simulations. Unfortunately, that is not an easy task. Indeed, what we estimate on the basis of the seasonal dissection (or annual counting) is the annual ice thickness. This annual ice thickness systematically decreases with depth due to ice flow. Ideally, using the annual ice thickness versus depth and a good ice flow model (that does not exist) it would be possible to derive the original accumulation rate. But even with that, you have to consider a possible strong erosion of snow by wind after deposition.

P1 l. 19 focus on dust-free sulfur pollution. (to clarify).
OK done here and throughout the text.

P1 l. 26 I would say also the much later onset is an important piece of information, which confirms knowledge on industrialization.
As now discussed when comparing the three sites (see also our answer to your comment on comparison with other ice cores) in section 5, we also emphasized the difference in the onset: "Long-term dust-free sulfate trends observed in the ELB ice cores are compared with those previously obtained in Alpine and Altai (Siberia) ice, the most important differences consist in a much earlier onset and a more pronounced decrease of the sulfur pollution over the three last decades in western Europe than south-eastern Europe and Siberia."

P2 l 2 In general short lived climate forcers, with one of the most important components being aerosol.
OK done

P 2 l 6 this is somewhat naïve statement, as models will usually calculate the concentrations and verify them with observations. Only from the satellite era onward, aerosol is assimilated but not in 'climate' models.

You are right and we now corrected the sentence as follows: "However, uncertainties still exist in quantifying the climatic impact of aerosols. The spatial distribution of aerosols is very heterogeneous and requires therefore numerous observations to make these parameters useful as inputs and constraints for transport and chemistry models."

P 2 l 6 A number of other continental ice cores are mentioned, but only CDD is explored later in the text. It is not entirely clear, why a comparison with the other icecores is not included in the manuscript.

Yes, in the draft the ELB record was only compared to the CDD (alpine) record. In the revised version we also add a comparison with the one extracted from the Belukha glacier in the Siberian Altai. The abstract was changed consistently.

2 l 26 Another argument is that there is a quite strong seasonal dependency of the oxidation chemistry of SO2, which has probably been oxidant limited in the emission era.

Yes you are right: three factors influence the seasonality: the upward transport intensity (maximum in summer) is the main factor, the second and third are the seasonality in the emission with a slight maximum in winter counteracted by the lowering of the conversion SO_2/SO_4.

P3 l. 15 explain meter water equivalent, and if this information is available how do these precipitation rates compare to a larger footprint around Mt. Elbrus?

Annual firn and ice (density varying from 0.3 to 0.9 g cm^{-3}*) thickness are commonly converted into a water column. As answered above, the link between ice annual thickness and local precipitation rate is anyway quite complex. For your information, Kozachek et al. (Climate of the Past, 13, 1473-489, 2017) reported a mean annual ice thickness close to 1.3 mwe in the recent layers (see also the new Figure 2 in the revised version) against a precipitation rate of 1.7 m of water at the site of Klukhorskiy Pereval located at 2037 m elevation.*

P 3 l 28-32. Later in the text outliers are removed, are these outliers related to these known problems? If not what could be the cause of such outliers ?

Generally speaking single values considered as outliers are very likely due to contamination during the subsampling or due to the poor quality of the ice. To better illustrate these outliers, we report them in Figure 7 together with all raw data.

P 4 l. 12 Again for non experts explain whether the decrease of NH4 with depth is a 'real' signal, or rather related to gradual degradation/oxidation with time.

No, as far as we know there is no evidence from numerous other ice core studies that the decrease of ammonium with depth is due to a degradation. More likely the increase of ammonium in the recent layer (as for nitrate) is related to atmospheric changes but a detail discussion of these trends is out of the scope of this paper that focuses on sulfate.

P 4 l. 34 I understand the chemical stratification is a preferred method compared to radio carbon dating, can you confirm because that is because of higher accuracy?

Yes, definitely when the annual counting is possible the accuracy is typically a few years for a period of 100 years. When not possible because of poor record in ice of the seasonal atmospheric contrast, and in the absence of absolute horizons such as volcanic events, the *unique possibility is the radiocarbon dating (which is far less accurate). In the revised version we report a dating figure (Figure 5) that illustrates fairly well this point.*

P 6 l. 27 the 616 and 67 numbers are the samples influenced by high dust? Sentence is ambiguous. *OK we reworded this sentence: "In this way, 616 (on a total of 2524) summer and 67 (on a total of 1150) winter samples were considered as containing large amount of dust."*

P 7 l. 4 at the best=>at the most :
OK Done

P 7 l. 14 Dust may contain a quite large fraction of CaSO4, which is quite insoluble under alkaline conditions, may be dissolve when more acidic. If I understood well this would not be picked up in the analysis, and can not influence the trend estimates? Please confirm.
Fraction of gypsum (primarily emitted) may indeed be quite insoluble. However the other fraction coming from neutralization of calcium carbonate during transport (sulphuric acid or SO_2) would be more soluble. Also the change of acidity over time in this region is not so large than in the Alps since together with the increase of anthropogenic species (sulfate and nitrate) we have an increase of alkaline calcium (as discussed in the companion paper).

P 8 l15- you can mention here that the corrected values were rather constant as also shown in Figure 9. ???
We are not sure if we understand your question. This figure appears far later in the text.

p. 9 l 1 Please provide some plausible reasons for the outliers, or connect to the statements in the analysis section.
See our previous answer for outliers.

P 9 l. 27 It would be good to mention here which emission database was used.
Yes done: "Using data from Smith et al. (2011), available at http://sedac.ciesin.columbia.edu/data/set/haso2-anthro-sulfur-dioxide-emissions-1850-2005-v2-86, we report in Figure 12 emissions of SO2 from countries located nearby the ELB site: Georgia, Azerbaijan, Syria, Irak, Turkey, Russian, Iran or located further north (Ukraine) and west (Bulgaria)." And we also add to the reference list :" "Smith, SJ, J van Aardenne, Z Klimont, RJ Andres, A Volke, and S Delgado Arias. (2011). Anthropogenic Sulfur Dioxide Emissions: 1850–2005, Atmospheric Chemistry and Physics, 11:1101–1116."

Answer to Referee Margit Schwikowski

We would like at first thank the reviewer for her comments. In the following our answers are made in italic.

This manuscript presents an ice core record of sulfate from a glacier on Mount Elbrus covering the time period 1774-2009. Generally, it is well written and structured and mostly scientifically sound (see comments below). The high-quality data set fills a gap, since it is the first sulfate record from South-Eastern Europe. Regional data on pre-industrial to industrial concentration changes of major aerosol components are essential to constrain emission estimates used in modelling the aerosol effect on climate. I therefore expect that this record will have an impact. The manuscript definitely deserves publication, after taking into account the comments and suggestions listed in the following.

Specific comments: There is very little information about the ice core itself. The coordinates are just given in the abstract and the length in the introduction. I suggest adding a short paragraph about the Elbrus ice core, including some additional information, e.g. name of the glacier, ice thickness, ice temperature, and net accumulation rate. In the abstract it is called a deep ice core, but that is relative. More important is if it reached bedrock or not. In addition, it would also be good to summarize briefly previous work published on this core.

Thanks for this comment, we added a paragraph with more information on the drill site, the ice core and previous works done on this ice core, as follows "A deep ice core was drilled to bedrock (182.6 m, i.e. 142.1 meter water equivalent (mwe)) in 2009 on the western plateau of Mt. Elbrus (43°21'N, 42°26'E; 5115 m above sea level) in the Caucasus, Russia (Fig. 1). Glaciological settings of the drill site are detailed in Mikhalenko et al. (2015). In brief, the surface of the glacier plateau is about 0.5 km^2, and the surface snow accumulation at the drill site is about 1.5 mwe yr^{-1}. Ice-penetrating radar measurements made in 2007 and 2009 revealed a maximum glacier thickness of 255 ± 8 m at the central part of the plateau, and minimum values of ~60 m near the western border of the glacier. Borehole measurements indicated temperatures of -17°C at 10 m depth and -2.4°C at 181.8 m depth. Occasionally melting of surface snow can occur, however, the thickness of the infiltration ice layers, which do not form every year, does not exceed 10 mm. After the overall presentation from Mikhalenko et al. (2015), two other studies of the ELB ice core were dedicated to black carbon (Lim et al., 2017) and water stable isotope composition on the 126 m upper layers (Kozachek et al., 2017). "

Use the term South-Eastern Europe instead of Central Europe for the source area of emissions detected in the Elbrus record.

OK done through the text.

You observe a stronger thinning with depth of the winter layers compared to the summer layer. This is interesting. Is it due to a change of precipitation seasonality or is it an artefact caused by diffusion of chemical tracers or even different flow behaviour of summer and winter layers?

We assume that the reviewer refers here to Figure 1 (mean summer and winter sample length). The initial aim of this figure was to illustrate the fact that we adapted the depth resolution of the ice sampling (from 10 cm at the top to 2 cm at the bottom) to the decrease of annual thickness with depth, in view to minimize the lost of temporal resolution. In fact this aspect is particularly important in the companion paper that deals with changes of the frequency of sporadic dust events over time. In the revised version this figure has been reworked to illustrate the thinning of summer, winter, and annual layers with depth.

As now shown, indeed the winter layer thickness decreases more than the summer ones but only in the lowest part of the core (below 155 mwe, see Figure 1d). Already observed in

Alpine small-scale glaciers we assume that this effect is likely due to more wind erosion of winter than summer snow layers upstream the drill site. Note also that no changes in the seasonal precipitation contributions were observed at least over the last 100 years for which the seasonal precipitation was reconstituted for this ice core (Kozachek et al., 2017). The text in the manuscript in section 2.1. was revised accordingly. "The large decrease of the net snow accumulation in winter below 155 m (Fig. 2), likely due to more wind erosion of winter than summer snow layers upstream the drill site as already observed at other high altitude glacier sites (e.g. Preunkert et al., 2000), leads to a more pronounced loss of resolution in these winter layers compared to the surface layers (12 samples per winter near the surface and 1-2 samples per winter at 157 m depth)."

Dating of the core: This is so central for the interpretation and it was extended compared to the previous publication (Mikhalenko et al., 2015). I therefore suggest including a depth-age figure with the 14C dating points to give an idea about the thinning (can this be fitted with a glaciological flow model?). Also the volcanic horizons used to anchor the counted layers should be shown. You evoke basal melting to explain why the deepest ice is so young. Does this mean, the glacier is not frozen to bedrock at the drilling site? This has implications on the thinning. Please clarify.
Thanks for encouraging us to add a figure, since we were not sure whether the new results are important enough to add a figure or not. We now added a figure (Fig.5) reporting the entire annual layer counting, the most prominent identified time horizons, the ^{14}C data, and a ice flow fit based on the Nye law.
Our speculation on melting was meant in the sense to not exclude that this might had happened in the past, since Mikhalenko et al. (2015) proposed that in present time basal melting might occur below ice thicknesses of more than 220 m at the Elbrus site possibly due to a heat magma chamber. If ever this heat magma chamber had an increased energy in the past this underlying heat source could have melted the lowest ice layers, without influencing significantly above situated ice layers still having negative temperatures.
The manuscript was revised accordingly: "From the observed temperature gradient in the borehole ELB site, Mikhalenko et al. (2015) calculated a heat flux at the bottom glacier that is presently 4-5 times larger than the mean value for the Earth's surface, possibly due to a heat magma chamber of the Elbrus volcano, leading to potential basal ice melting when ice thicknesses exceeds 220 m. Though the ice at the drill site and upstream is at present frozen to bedrock, we can not exclude that in the past, assuming a more active heat chamber due to the eruption of 50 ± 50 CE (located 1.6 km away from the Eastern Elbrus plateau), a temporary basal ice melting had occurred at the drill site. If so, that may explain the young age of basal ice at the volcanic crater site compared to other non-volcanic mountain glaciers."

I am not convinced by the equidistant binning of the summer and winter layers to obtain monthly values. This requires the absence of seasonality in precipitation and snow preservation. Precipitation data from nearest meteorological stations show strong seasonality (Kozachek et al., 2017). Since the monthly data are not really discussed, accept for showing the seasonality of chemical tracers in Fig. 6, I suggest deleting this part and the figure.
We agree and the figure with monthly resolution was skipped. In addition we revised the text accordingly (see paragraph 2.2) and the figure caption of old figure 2 (now figure 3).
Figure 3. ELB ice chronology at depth intervals of 166.2 to 168.5 m (top), 154.4 to 156.5 m (mid), and from 99.8 to 107.3 m (bottom), based on the ammonium and succinate stratigraphy. Vertical red lines denote yearly dissection based on identification of winter layers (see Sect. 2.2). For the two oldest time-periods (1773-1782 and 1850-1859), each sample was 2 cm long whereas for the most recent time period (1925-1934) one sample was on average 4 cm long.

Note that, though being not coherent with the intra seasonal precipitation distribution (see Kozachek et al., 2017), we here assumed that the accumulation is equally distributed within summer and winter seasons. "

Identification of annual layers and attribution of summer and winter layers: You use two criteria for that (ammonium and succinate). To which of the two do you give priority when the two signals do not agree? How does the attribution of summer and winter layers presented in this manuscript agree with the one based on the stable isotope record of the same core (Kozachek et al., 2017)?

As now specified in the text, it is required that at least one of the criteria is fulfilled and the value of the other is below or close to the limit (< 10% above). "Requiring that at least one of the criteria is fulfilled and the value of the other is below or close to the limit (< 10% above) the annual counting was found to be very accurate dating (a 1-year uncertainty) over the last hundred years when anchored with the stratigraphy with the Katmai 1912 horizon (Mikhalenko et al., 2015)."

Kozachek et al. (2017) compared the dating derived from examination of the annual cycle of ^{18}O with the dating obtained with the ammonium-succinic criteria, and found a discrepancy of 2 years at a depth of 126 m (at the end of the examined water isotope profile). The text in paragraph 2.2 was changed as "A good agreement (a 2-year discrepancy) was also found when comparing this dating with the chronology achieved by annual layer counting of the water stable ^{18}O isotope back to 1900 (Kozachek et al., 2017). Though the annual counting becomes less evident prior to 1860, Mikhalenko et al. (2015) reported an ice age of 1825 at 156.6 m depth, what is still consistent with the presence of volcanic horizon at around 1833-1940 such as Coseguina (1835)."

14C-dating: Was the AMS equipped with a gas ion source? You used a rather old version of Oxcal. I suggest using an updated version.

Yes the AMS was equipped with a gas source. The Oxcal version used (4.3) is to our knowledge the actual one (see https://c14.arch.ox.ac.uk/oxcal.html), but the reference we used (Bronk Ramsey, 1995) refers to the overall introduction of Oxcal. In the revised version, we added the reference of Bronk Ramsey (2009), which deals with new features of Oxcal 4.

we reworded the sentences as "After cryogenic extraction of the CO2 content, radiocarbon analyses were done at the accelerator mass spectrometer facility at the Curt-Engelhorn-Center Archaeometry (CEZA) in Mannheim equipped with a Gas Interface System (GIS) (Hoffmann et al., 2017). Calibration of the retrieved 14C ages was done using OxCal version 4.3 (Bronk Ramsey, 1995, Bronk Ramsey, 2009)."

Ion balance: Use the same unit (either ppb or uEq/L) in the text and in Figure 4.

OK done

Attribution of dust sources: This part of the manuscript is not convincing to me. What is the argument to relate high Ca concentrations to Saharan dust and low Ca concentrations to sources in the Middle East?

The argument is given in the paper from Kutuzov et al. (2013) as well as in the companion paper as now referenced in the text.

The plots in Figure 5 show a large scatter and low correlation coefficients, so I wonder if the ion ratios you discuss are significantly different. For the ions with strong anthropogenic influence this correlation analysis is anyway not meaningful without splitting the data set in

the pre-industrial and industrial periods. To me this part of the manuscript is weak, distracts from the main message, and could be omitted.
We agree with you and the whole discussion on the origin of dust (including old Table 2 and old Figure 5) was removed.

Important is to estimate the amount of sulfate originating from dust and correct for that when discussing anthropogenic sulfate. Attribution of sulfate related to mineral dust: Instead of arbitrarily introducing a Ca level to identify dust events, I propose to look at the pre-industrial Ca to sulfate correlation. If both are highly correlated, you can use this ratio to correct for mineral dust sulfate in the industrial period.
Thanks for this very important comment. We agree and follow your suggestion. This part was totally reworked and new dust-free sulfate figures are shown.
"As discussed in section 3, large dust events significantly enhanced the sulfate level of the ELB ice. Since, as detailed in Kutuzov et al. (this issue), their occurrence have changed over the past with more frequent events after 1950, we have examined to what extent they contribute to the sulfate trend. It is difficult to accurately directly correct sulfate concentration from the large dust event contribution since the amount of sulfur trapped by the alkaline material during atmospheric transport towards the site would be very different from event to event. For instance, Kozak et al. (2012) reported non-sea-salt-sulfate to non-sea-salt calcium mass ratios in aerosol collected in the eastern Mediterranean ranging between 0.25 (in case of direct arrival at the site of air mass from the Sahara) to 1.15 (when mineral dust passed through polluted sites located in the Balkans and Turkey before arriving at the site). Instead of corrected sulfate values for the large dust events, we therefore have reported in Figure 8 individual values of total sulfate and sulfate calculated after having removed from the average samples suspected to contain large amount of dust ($SO_4^{2-}{}_{red.}$ values). The influence of large dust events on the long-term SSA winter trend is rather insignificant and if existing (i.e. effect of < 10 ppb) remaining limited to two decades around 1870 and the recent decade (2000-2010) (Fig. 9). Remaining negligible prior to 1850, the large dust event effect on the summer trend gradually increases after 1950, reaching often 100 ppb after 1960. This change of large dust events results from change in the occurrence of drought in North Africa and Middle East regions (Kutuzov et al., this issue).
In addition to the enhanced frequency of large dust events after 1950, the calcium background concentrations (i.e., $Ca^{2+}{}_{red.}$) also change over time with an increase from 68 ± 21 ppb prior to 1900 CE to 194 ± 61 ppb after 1960 CE. As discussed by Kutuzov et al. (this issue), this change may result from changes in precipitation and soil moisture content in Levant region (Syria and Iraq). In view to discuss the free-dust sulfate changes with respect to anthropogenic emissions, we make an attempt to correct the sulfate record from this increase of the background level of dust. To do so, we examined in Figure 10 the relationship between calcium and sulfate concentration in individual summer samples corresponding to pre-industrial time (1774-1900 CE). Although being poor (R^2=0.32), the correlation suggests a mean slope of the linear SO_4red-Cared relationship close to 1. The use of this value to correct sulfate from background dust emissions would lead to an overestimation of the sulfate dust contribution. Indeed, as seen in Figure 10, there are numerous samples that contain more sulfate than what is expected with respect to the presence of pure calcium sulfate (gypsum, see the blue line reported in Figure 10), likely to due the presence of sulfate as ammonium sulfate or sulfuric acid. To correct sulfate from the background dust contribution we here have used a sulfate to calcium ratio close to 0.63 (see the red line drawn as the lower envelope of the relationship in Figure 10) and subtracted this contribution from the $SO_4^{2-}{}_{red.}$ values by using the $Ca^{2+}{}_{red.}$ values."

I recommend adding a map with the Elbrus site, outlining the dust and SO2 emission source areas.
OK, done: we show a map (Figure 1) where countries can be easily identified and dust emission are reported.

Table 5 is mentioned in the text, but does not exist.
Sorry (it was a typographic error: Table 3)

Discussion of outliers: This is hard to follow without seeing the raw data (which should be shown anyway). Can some of the outliers be explained by volcanic events? It is strange that you don't see a signal of the largest eruption in the last centuries (Tambora, 1815) and the largest eruption in the Northern Hemisphere in the last centuries (Laki, 1783).
In the revised version we introduce a raw data figure (now Fig. 7). Well we were also surprised by the lack of evidence for Laki and Tambora.

Comparison with emission estimates: You stress in the manuscript the importance to distinguish between summer and winter sulfate values and trends (to me the trends look similar). And then you compare this with emission estimates, which are annual values (I guess). This is inconsistent. You need to include the total anthropogenic sulfate record, which would also be very valuable for comparison with data sets from other ice cores, which are not resolved in summer and winter values. In addition, you give the impression that SO2 emissions in winter are much lower than in summer. The opposite is the case. The major factor producing the difference in summer and winter values at high-alpine sites is the reduced vertical atmospheric transport in winter (and not the variation in source area). You need to explain this in the manuscript.
Indeed the winter and summer trends appears quite similar at ELB. This contrasts to the case of CDD for which the model EMEP simulations confirmed the finding of a clear difference between summer and winter. We cannot discuss further that since we don't have EMEP simulations for the ELB ice core. Anyway in the revised version we also report annual means and discuss as follows: "Since available at all three sites, we compared in Figure 11 the annual long-term trends of dust-free sulfate from ELB, CDD, and BEL. The ELB and CDD annual values were calculated as arithmetic mean from 5 yr-SSA winter and summer records, whereas the BEL annual data refer to 5 year averaged raw data. Examination of the three annual records reveal three major differences between the three sites: (1) an impact of anthropogenic emissions already significant in 1910-1930 at CDD but neither at ELB nor at BEL, (2) a maximum of the anthropogenic perturbation which is reached in 1970-1980 at CDD and later at the two other sites (10 years after at ELB, and a few years after at BEL), and (3) a far less pronounced re-decrease at the beginning of the 21th century at ELB compared to CDD. The re-decrease of sulfate over the very recent decades is somewhat stronger at BEL than at ELB. Using data from Smith et al. (2011), available at http://sedac.ciesin.columbia.edu/data/set/haso2-anthro-sulfur-dioxide-emissions-1850-2005-v2-86, we report in Figure 12 emissions of SO_2 from countries located nearby the ELB site: Georgia, Azerbaijan, Syria, Irak, Turkey, Russian, Iran or located further north (Ukraine) and west (Bulgaria). In these countries SO_2 emissions became significant after 1930 and reached maximum in the late 80's or later (for Turkey and Iran). This feature clearly differs from the situation at CDD where emissions from countries located around the site (France, Italy, Spain, Switzerland and Germany) were already significant in 1930 and exhibited a maximum between the early 70's and the early 80's (Figure 10). For BEL, Eichler et al. (2009) demonstrated the importance of emissions from eastern Europe for the dust-free sulfate annual record at that site.

Finally, we tentatively examine the cause of the recent decrease of sulfate, focusing on the summer season for which the most relevant source regions are limited to countries located nearby the site. As discussed by Kutuzov et al. (this issue), 10 day backward air mass trajectories calculated for the ELB site using the NOAA HYSPLIT-4 model suggest that, in summer, air masses arriving at ELB mainly originate from the nearby Georgia, Azerbaijan, Syria, Irak, and from Turkey, South Russian, and North of Iran. As previously discussed by Fagerli et al. (2007), the CDD site in summer is mainly influenced by emissions from France, western Germany, Italy and Spain. Consistently with SO_2 emission changes, the recent sulfate decrease is more pronounced at CDD than ELB with a recovered 2005 level (316 ppb) close to the 1950 one (296 ppb) (Figure 13). At the ELB site this is not the case, here the 2005 level (380 ppb in 2005) is found to be still almost two times higher than the one of 1950 (227 ppb in 1950). An intermediate pattern is seen at BEL, likely due to a weak impact of countries like Turkey that significantly contribute to the ELB record but not the BEL one, and a more strong contribution of emissions from Russian at BEL (see also Eichler et al., 2009) than at ELB."

Considering the SO2 emission source areas you identified it is strange that you just compare the Elbrus record with the CDD record from the Alps. I strongly recommend to include the sulphate record from Eastern Europe (from Belukha ice core, Eichler et al., EST 2012).
Thanks to rise this important question. We agree and now compare ELB, CDD, and Belukha records (see our answer above and the new Figure 11).

Figure 1. I don't see the point of showing the mean summer and winter sample length. This should not be so different from the sample resolution.
OK this aspect is very important for the discussion made in the companion paper of the enhanced frequency of sporadic large dust events after 1950. So we remove this to the companion paper and reworded the old figure 1 (showing now annual, half-year summer and winter ice thickness).

Technical corrections
Title: seems too long and a bit cumbersome. Suggestion: Reconstruction of anthropogenic sulfate trends from Elbrus ice core, Caucasus.
OK we changed it: The Elbrus (Caucasus, Russia) sulfate ice core record: reconstruction of past anthropogenic sulfur emissions in south-eastern Europe".

Abstract L. 18: After having examined. . . Rephrase and give the results: dust contribution to sulfate concentrations was identified and subtracted to focus on anthropogenic sulphate (not sulfur).
OK, this sentence has been reworded.

P2L4: Replace Andreae et al., 2015 with a newer estimate e.g. from IPCC.
Well we prefer to cite this reference, which highlighted for the first time this aspect instead of an updated report (we don't discuss further this aspect later in the paper).
P2L8: "impact" instead of "disturb". Ok, we changed to "impact"

P2L13-15: The Altai and Kamchatka are not part of Europe.
We correct: In Eurasia…"

P2L16-19: ice cores have been investigated . . .to examine.
Ok done.

P3L12: Give more details how ice cores were decontaminated (by removing xx cm from the outside of the core. . .)
Ok the section was revised as following: "Ice cores were subsampled and decontaminated at -15°C using the electric plane tool methodology described in Preunkert and Legrand (2013). In brief, in a first step ice samples were cut with a band saw. After that, all surfaces of the cut samples were decontaminated by removing ~ 3 mm with a pre-cleaned electric plane tool under a clean air bench."

P3L17:loss
Ok done

P3L29: Give details, which fluid was used.
Ok we added the name of the drilling fluid: "During the drill operations, an incident occurred at the depth of 31 m and a fluid (Havoline XLC, Texaco company) was poured in the hole to liberate the drill device."

P4L7: For the ammonium seasonality earlier work should be cited (Maupetit et al., Atmos. Environ., 1995; Eichler et al., JGlac., 2000):
OK done

P6L14-15: Replace "disturb the chemistry" by changes the chemical composition Table 1: Include 14C lab sample reference number.
Ok disturb was replaced, and in fact the "Sample name" we gave in Column 1 of Table 1 is the 14Csample name used in the 14C lab. The column was renamed.

The Elbrus (Caucasus, Russia) sulfate ice core record: reconstruction of past anthropogenic sulfur emissions in south-eastern Europe

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Abstract. This study reports on the glaciochemistry of a deep ice core (182 m long) drilled in 2009 at Mount Elbrus (43°21′N, 42°26′E; 5115 m above sea level) in the Caucasus, Russia. Radiocarbon dating of the particulate organic carbon fraction in the ice suggests that the a basal ice age dates to 280of ~1670 ± ± 400 cal yr CEBP (eCommon AeEra). Based on chemical stratigraphy, the upper 168.6 m of the core were dated by counting annual layers. The seasonally resolved chemical records cover the years 1774-2009 (Common Era)CE, thus, being useful to reconstruct many aspects of atmospheric pollution in central south-eastern Europe from pre-industrial times to present-day. After having examined the extent to which the arrival of large dust plumes originating from Sahara and Middle East modifies the chemical composition of the Elbrus (ELB) snow and ice layers, we focus on the dust-free sulfur pollution. The ELB dust-free sulfate levels indicate a foursix- and sixseven-fold increase from 1774-1900 to 1980-1995 in winter and summer, respectively. Remaining close to 116 55 ± 28 10 ppb during the nineteen century, the summer annual dust-free sulfate levels started to rise at a mean rate of ~6 3 ppb per year from 1920 to 1950. The summer annual sulfate increase accelerated between 1950 and 1975 (11 8 ppb per year), levels reaching a maximum between 1980 and 1990 (730 376 ± 152 10 ppb) and subsequently decreasing to 630 270 ± 130 18 ppb at the beginning of the twenty first century. Long-term dust-free sulfate trends observed in the ELB ice cores are compared with those previously obtained in Alpine and Altai (Siberia) ice, the most important differences consists in a much earlier onset and a more pronounced decrease of the sulfur pollution over the three last decades in western western Europe than south-eastern Europe and Siberiathan central Europe.

1 Introduction

It is now well recognized that the present climate change is not only related to change of long-lived greenhouses gases but also ~~to~~ of short-lived climate forcers, with one of the most important components being aerosol, ~~aerosols,~~ particularly at regional scales. In this way, it has been suggested that aerosols may have weakened the rate of the global warming during the second part of the last century (Andreae et al., 2005). However, uncertainties still exist in quantifying the climatic impact of aerosols. T~~, because t~~he spatial distribution of aerosols is very heterogeneous and requires therefore numerous observations to make these parameters useful as inputs and constraints for transport and chemistry ~~climate~~ models. An important gap is also related to the fact that direct atmospheric observations are available only from far later (starting with the appearance of the acid rain phenomena in the late 1960s) than man-made activities started to ~~disturb~~ impact the pre-industrial atmosphere. However, to predict future climate the knowledge of atmospheric changes in aerosol load and composition from present-day polluted atmosphere back to preindustrial times is required. Chemical records of species trapped in snow deposited on cold glaciers provide a unique and powerful way to reconstruct past atmospheric chemistry changes including aerosol load and composition (see Legrand and Mayewski (1997) for a review).

In Eurasia~~ope~~, a largely industrialized continent, ice cores were extracted from high-elevation glaciers located at various places, including the Alps (Preunkert and Legrand, 2013; Schwikowski et al., 2004), the continental Siberian Altai (Eichler et al., 2009; Eichler et al., ~~2011~~2012; Olivier et al., 2006), and Kamchatka (Kawamura et al., 2012). In the Alps, intimately connected to western European emissions, ice cores have been ~~performed~~ investigated at Col du Dôme (CDD, Mont Blanc, Preunkert, 2001), Fiescherhorn (Bernese Alps, Jenk, 2006), and Colle Gnifetti (CG) in the Monte Rosa region (Schwikowski, 2006; Wagenbach et al., 2012) in view to examine various aspects of atmospheric pollution. The exceptionally high net snow accumulation at the CDD site permitted the extraction of seasonally resolved records of various chemical species over the last 100 years (Preunkert and Legrand, 2013). In older ice layers preservation of winter layers at CDD becomes very limited and summer layers become very thin. Conversely, the low and incomplete net snow accumulation rate at CG, which is controlled by wind erosion, highly limits the preservation of winter ice layers (Wagenbach et al., 2012), but is low enough to provide access to an extended time period, at least over the last millennium. Using the EMEP (European Monitoring and Evaluation Programme) regional chemistry-transport model and past emission inventories of SO2 in Europe, observed CDD long-term trends of sulfate were fairly well reproduced, leading Fagerli et al., (2007) to conclude that the seasonal changes seen at the CDD alpine site are associated with geographical changes in source regions impacting the site. This is a strong argument for a separate examination of summer and winter data, extracted from alpine ice cores. However, until now, Alpine ice cores document only the last hundred years (at the best back to 1890, Legrand et al., 2018) on a seasonal basis, whereas the early stage of the industrialization time period, which is generally considered to have started around 1850, is missed. An ice core recently extracted from the Elbrus (the highest summit of the Caucasus) indicated excellent preservation of summer and winter layers at least back to 1820 (Mikhalenko et al., 2015). Thus, the ELB ice may contain very valuable information on past atmospheric pollution in south-eastern~~central~~ Europe since the beginning of the industrialization.

Here we report on the glaciochemistry of a deep ice core ~~(182 m long) drilled drilled to bedrock at 182.6 m (142.1 mwe)~~ in 2009 ~~on the western plateau of Mt. Elbrusat Mount Elbrus (43°21′N, 42°26′E; 5115 m above sea level)~~ in the Caucasus, Russia. ~~Glaciological settings of the drill site are detailed in (Mikhalenko et al., 2015). In Brief, the spatial size of the glacier plateau is about 0,5km^2, and the surface snow accumulation at the drill site is about 1,5 mwe yr^{-1}. Ice-penetrating radar measurements made in 2007 and 2009 revealed a maximum glacier thickness of 255 ± 8 m at the central part of the plateau, and minimum values of about 60 m near the western border of the glacier. Borehole temperature measurements ranged from −17 °C at 10 m depth to −2.4 °C at 181.8 m. Occasionally melting of surface snow can occur, however, the thickness of the infiltration ice layers, which do not form every year, does not exceed 10 mm.~~

~~After the drill site overview study of Mikhalenko et al. (2015), two more specific studies on the black carbon content of the ice core (Lim et al., 2017), and the water stable isotope composition over the upper 126m (Kozachek et al., 2017) respectively, were achieved so far.~~

~~In the present study, The ss~~Seasonally resolved chemical records were obtained back to 1774 (i.e., well prior to the onset of the industrial period). Data are discussed in two companion papers of which this one. The present paper examines first of all the impact of large dust plumes, which arrive sporadically from Sahara and Middle East, on the chemical composition of the Elbrus (ELB) snow and ice layers. It then focuses on long-term dust-free sulfate trends in relation to growing sulfur pollution. The long-term summer and winter trends of dust-free sulfate are discussed with respect to past SO_2 emissions in south-eastern ~~central~~ Europe and compared to those extracted at the Alpine site of CDD ~~in relation to SO_2 emissions from western Europe~~ and the Siberian Altai (Belukha glacier) in relation to SO_2 emissions from western and eastern Europe, respectively. The second paper focuses on calcium (a dust tracer) long-term trend (Kutuzov et al., this issue), discussing its past changes in relation with natural variability, as well as climatic and land use changes in the dust source regions Middle East and North Africa.

2 Methods and Dating

A deep ice core was drilled to bedrock (182.6 m, i.e. 142.1 meter water equivalent (mwe)) in 2009 on the western plateau of Mt. Elbrus (43°21′N, 42°26′E; 5115 m above sea level) in the Caucasus, Russia (Fig. 1). Glaciological settings of the drill site are detailed in Mikhalenko et al. (2015). In brief, the surface of the glacier plateau is about 0.5 km^2, and the surface snow accumulation at the drill site is about 1.5 mwe yr^{-1}. Ice-penetrating radar measurements made in 2007 and 2009 revealed a maximum glacier thickness of 255 ± 8 m at the central part of the plateau, and minimum values of ~60 m near the western border of the glacier. Borehole measurements indicated temperatures of -17°C at 10 m depth and -2.4°C at 181.8 m depth. Occasionally melting of surface snow can occur, however, the thickness of the infiltration ice layers, which do not form every year, does not exceed 10 mm. After the overall presentation from Mikhalenko et al. (2015), two other studies of the

ELB ice core were dedicated to black carbon (Lim et al., 2017) and water stable isotope composition on the 126 m upper layers (Kozachek et al., 2017).

2.1 Discrete Subsampling of firn and ice, and Chemical Analysis

Ice cores were subsampled and decontaminated at -15°C using the electric plane tool methodology described in Preunkert and Legrand (2013). In brief, in a first step ice samples were cut with a band saw. After that, all surfaces of the cut samples were decontaminated by removing ~ 3 mm with a pre-cleaned electric plane tool under a clean air bench. ~~Pieces of cores were cleaned under a clean air bench located in a cold room (-15°C) using an electric plane tool previously developed to process Alpine firn and ice samples.~~ A total of 3724 subsamples were obtained along the upper 168.6 ~~m~~ m (131.6 m-we) of the Elbrus core. ~~The depth resolution decreased from 10 cm at the top to 5 cm at 70 m, and 2 cm at 157 m depth and below.~~ As expected from ~~the~~ glaciers ice flow (e.g. ~~(e.g.~~ Paterson and Waddington, 1984), a decrease of ~~Given the decrease of~~ the ~~net~~ annual ice thickness~~snow accumulation accumulation~~ with depth is observed (~~see~~ Fig. ~~1~~2). Annual layer thicknesses decreases ~~from~~ from 1.5 mwe (0.8 mwe in summer and 0.7 mwe in winter) near the surface, to ~~to~~0.46 mwe at ~100 m (i.e. 75 mwe) (0.35 mwe in summer and 0.11 mwe in winter), 0.21 mwe at 155 m (i.e. 120 mwe) (0.12 mwe in summer and 0.09 mwe in winter) and ~~-~~0.18 mwe (0.15 mwe in summer and 0.03 mwe in winter) at 157~~57~~ m~~we~~ (i.e. 122 mwe) depth~~,~~. ~~as seen in Figure 1,~~ To minimize the loss~~t~~ of temporal resolution with depth along the core, the sample depth resolution was decreased from 10 cm at the top to 5 cm at 70 m (47 m we)~~-~~, and 2 cm at 157 m (122 mwe) depth and below. ~~this sampling permitted to minimize the lost of temporal resolution with depth along the core, particularly in summer.~~ In this way, an average of 9 summer samples per year were sampled at 157 m depth (compared to 15 summer samples per year near the surface). The large~~r~~ decrease of the net snow accumulation in winter below 155 m (Fig. 2), likely due to more wind erosion of winter than summer snow layers upstream the drill site~~probably due to glacier upstream effects~~ as already observed ~~in~~at other high altitude glacier sites (e.g. Preunkert et al., 2000), ~~than in summer~~ leads to a more pronounced loss of resolution in th~~is~~ese winter layers compared to the surface layers (12 samples per winter near the surface and 1-2 samples per winter at 157 m depth)~~(Figure 1).~~.

For measurements of cations (Na^+, K^+, Mg^{2+}, Ca^{2+}, and NH_4^+), a Dionex ICS 1000 chromatograph equipped with a CS12 separator column was used. For anions, a Dionex 600 equipped with an AS11 separator column was run with a quaternary gradient of eluents (H_2O, NaOH at 2.5 and 100 mM, and CH_3OH). A gradient pump system allows the determination of inorganic species (Cl^-, NO_3^-, and SO_4^{2-}) as well as short-chain carboxylates. Investigated carboxylates include formate (HCO_2^-), lactate ($CH_3CHOHCO_2^-$), acetate ($CH_3CO_2^-$), glycolate ($CH_2OHCO_2^-$), and glyoxylate ($CHOCO_2^-$), oxalate ($C_2O_4^{2-}$), malate ($CO_2CH_2CHOHCO_2^{2-}$), malonate ($CO_2CH_2CO_2^{2-}$), succinate ($CO_2(CH_2)_2CO_2^{2-}$), and glutarate ($CO_2(CH_2)_3CO_2^{2-}$). Details on working conditions are reported in Legrand et al. (2013). For all investigated ions, blanks of the ice decontamination procedure were found to be insignificant with respect to respective levels found in the ice cores.

During the drill operations, an incident occurred at the depth of 31 m and a fluid (Havoline XLC, Texaco company) was poured in the hole to liberate the drill device. This has led contamination of the firn at 31 m down to the firn-ice transition located at 55.7 m depth. Samples covering the 1983-1997 years were contaminated for sodium (124 ± 87 ppb compared to 26 ± 28 ppb over the 16 preceding years) and potassium (35 ± 25 ppb compared to 16 ± 15 ppb over the 1966-1982 years). One core section (denoted ELB-140) that covers winter 1875/76, summer 1876, and winter 1876/1877 was not analysed. Finally, a part of the ELB-138 ice core section that covers winter 1877/1878 was of poor quality (splitted ice).

2.2 Annual Layer Counting

As discussed by Mikhalenko et al. (2015), dating of the Elbrus ice can be done by annual layer counting on the basis of the stratigraphic ammonium and succinic acid records, both exhibiting well-marked winter minima. As previously seen in alpine ice cores, ammonium reveals a well-marked maximum in summer due to a maximum of NH_3 emission together with an efficient upward transport in summer (Maupetit et al., 1995; Preunkert et al., 2000, Eichler et al., 2000~~Fagerli et al., 2007~~). Succinic acid is a light dicarboxylic acid for which a strong summer maximum and a quasi-null winter level can be observed in the present-day atmosphere in Europe (Legrand et al., 2007). The very low winter levels of this organic compound are related to the absence of a winter source of this species, which is mainly photo-chemically produced from biogenic precursors. Mikhalenko et al. (2015) assumed a concentration limit of 100 ppb ammonium and 5 ppb of succinate to separate winter and summer in the upper layers down to 75.6 m depth (i.e., 1963). To account for an observed decreasing trend of ammonium concentrations with depth (i.e., due to a post 1950 increase as also seen for species like nitrate and sulfate, see below), the ammonium winter criterion was adjusted to 50 ppb between 75.6 and 86.8 m depth (i.e., 1950-1963) and 30 ppb below. Since no systematic change of succinate with depth is observed, the succinate concentration limit of 5 ppb was also applied in deeper layers. Requiring that at least one of the criteria is fulfilled and the value of the other is below or close to the limit (< 10% above) ~~In this way,~~ the annual counting was found to be very accurate dating (a 1-year uncertainty) over the last hundred years when anchored with the stratigraphy with the Katmai 1912 horizon (Mikhalenko et al., 2015). ~~Similarly, a~~A good agreement (a 2-year discrepancy) was also found when comparing this ~~e here presented~~ dating ~~to~~with the chronology achieved by annual layer counting of the water stable ^{18}O isotope ~~d^{18}O~~ back to 1900 (Kozachek et al., 2017). Though the annual counting becomes less evident prior to 1860, Mikhalenko et al. (2015) reported an ice age of 1825 at 156.6 m depth, what is still consistent with the presence of volcanic horizon at around 1833-1940 such as Coseguina (1835). We here extended the annual counting down to 168.5 m depth (i.e., 131.6 mwe) by considering a concentration limit of 30 ppb for ammonium and 5 ppb for succinate. With that, ice dates to 1774 CE at the depth of 168.5 m. ~~In the following we will examine individual half-year summer and winter values, as well as monthly means. To calculate monthly means, a uniform snowfall rate is assumed within each half-year. Winter samples were attributed to the last 3 months of the year and the three first months of the following year (i.e., winter 1850/1851 is from 1850.75 to 1851.25). Summer samples are from the fourth to the ninth month (i.e., summer 1850 is from 1850.25 to 1850.75) in each year.~~ In Fig.~~ure 2~~ 3 we report the obtained chronology for three different sequences including the deepest one (1774-1784). It could be seen that in the years prior to

1850, quite often a winter layer is made only of one or two samples, whereas summer layers are made still of more than 6 samples. Below 168.5 m depth, the ice core quality becomes rather bad (numerous small pieces of broken ice) rendering subsampling and ice decontamination not evident. Furthermore, as seen in Fig.~~ure~~ ~~3~~4, in contrary to what is observed above 168~~,~~.5 m, the 30 subsamples obtained along a 1 m long core section at 176.3-177.3 m depth reveal an absence of samples with ammonium and succinate concentrations below the applied winter criterion. This hampered the dating of the basal ice layers of the core by annual counting and therefore another dating approach based on ^{14}C of particulate organic matter was made for this part of the core.

2.3 Basal Ice Dating

Four ice samples located along the deepest 6 m of the core (bottom at 182.65 m, 142.1 mwe) were analysed for radiocarbon in particulate organic carbon ($PO^{14}C$). The lowest 0.5 m of the core were not analyzed due to a large presence of macro-size inorganic particles. To minimize the time interval covered by each sample, sample lengths were kept as short as possible with respect to the detection limit related to working conditions during sampling and analysis. A typical sample length of 26 to 40 cm (available ice core section of 14-21 cm^2) was used leading to an initial ice sample mass of 430-580 g. After having decontaminated ice sample (using a DOC decontamination method according to Preunkert et al., 2011), melted ice was filtered and combusted at 340°C at the Institut de Géophysique Externe (Grenoble) using the inline filtration-oxidation-unit REFILOX (Reinigungs-Filtrations-Oxidationssystem, Hoffmann et al., 2018). Hereby, the resulting ice mass was reduced to 260-320 g containing 4.4 to 6.5 µgC of POC (Table 1). After cryogenic extraction of the CO_2 content, radiocarbon analyses were done at the accelerator mass spectrometer facility at the Curt-Engelhorn-Center Archaeometry (CEZA) in Mannheim equipped with a ~~a~~ Gas Interface System (GIS) (Hoffmann et al., 2017). Calibration of the retrieved 14C ages was done using OxCal version 4.3 (Bronk Ramsey, 1995, Bronk Ramsey, 2009).

To test the reliability of the DOC decontamination method (Preunkert et al., 2011) for POC analysis, a 340 °C REFILOX mass combustion comparison was made between ultrapure water and decontaminated blank ice (3 samples of 200 to 500 mL). To achieve an impurity-free solid ice the ultra-pure water was slowly frozen in polyethylene (PE) foil (Hoffmann et al., 2018~~7~~ and references in there). The comparison showed that whatever the blank ice volume, the blank values were in the same range than the ultrapure water POC blanks (~0.4 ± 0.25 µgC) which were determined during the course of the ELB radiocarbon sample measurements. Thus, the ice decontamination procedure used for DOC ice measurement is also valid for POC ice decontamination.

Since the CO_2 collection line was recently extended to allow sample pooling, we were now able to directly determine the fraction modern carbon ($F^{14}C$) in blanks done with ultrapure water. A $F^{14}C$ value of 0.71 ± 0.07 was found, measured on three blank samples in total (each consisting of four pooled samples). This value is in agreement with $F^{14}C$ blank values found in previous studies (as reviewed and adopted in Hoffmann et al., 2018). In Table 1, we report ice sample data after blank correction, including correction of the $F^{14}C$ value as well as correction of the extracted POC mass with the respective ultrapure water blank determined before each ice sample extraction.

Using a mean mass related combustion efficiency of the device of 0.7 (Hoffmann et al., 2018), the mean POC concentrations of the four samples obtained by combustion at 340°C is of 25.4 ± 3.1 ngC g^{-1} with highest concentration of 29.0 ngC g^{-1} for the lowest sample analysed at ~~142~~141.6 mwe (182.0 m). These values are in good agreement with those observed by Hoffmann et al. (~~2017~~2018) in the 340°C POC fraction of the lowest 8 mwe of a CG ice core (37 ± 16 ngC g^{-1}). Since a similarity between CG and ELB was also observed for their preindustrial black carbon content (Lim et al., 2017), we thus exclude significant age errors due to a POC contamination during ^{14}C sample preparation and analysis.

As seen in Table 1, the mean age of the ELB-178-03 sample (1530 yr cal BP, i.e. 1530 years before 1950) is older than the mean age of sample ELB-181-01 located 2.3 m below the ELB-178-03 sample. However, given age uncertainties, it is difficult to conclude that, as observed previously at other mid-latitude glacier sites such as CG (Hoffmann et al., 2018), the ELB radiocarbon ages do not increase monotonically with depth as would be expected from well-behaved ice flow. PO^{14}C measurements suggest that the ELB ice core extends to ~ 1670 ± 400 yr cal BP (Table 1). This is younger than basal ice ages found at Alpine sites, i.e. ~5000 yr BP for Col du Dome (Preunkert et al., ~~in press~~2019), ~ 4000 yr BP (Hoffmann et al., 2018) and >10,000 yr BP (Jenk et al., 2009) for two CG ice cores, and ~7000 yr BP for Mt. Ortles (3905 m asl) (Gabrielli et al., 2016). From the observed temperature gradient in the borehole ELB site, Mikhalenko et al. (2015) calculated a heat flux at the bottom glacier that is presently~~in present times~~ 4-5 times larger than the mean value for the Earth's surface, possibly due to a heat magma chamber of the Elbrus volcano, ~~-~~leading to potential basal ice melting when ice ~~below ice~~ thicknesses exceeds ~~of more than~~ 220 m.

Though~~,~~ the ice at the drill site and upstream ~~of it~~ is at present frozen to bedrock, we can ~~thus~~ not exclude that in the past, assuming a more active heat chamber ~~e.g. arriving in combination with~~due to the eruption of 50 ± 50 CE (located 1~~,~~.6 km away ~~situated~~from the Eastern Elbrus plateau)~~ in 50 ± 50 CE~~, a temporary ~~bottom up~~basal ice -melting had occurred ~~also~~ at the drill site. ~~That may have letad to to a melting and removing of the basal ice being in contact with the bedrock, ice melting and removal of the oldest basal layers~~~~without influencing the above situated ice layers and~~ ~~. If so, that may~~If so, that may explain the young age of basal ice at the volcanic crater site compared to other non-volcanic mountain glaciers. The age of the basal ELB ice is nevertheless largely greater than expected by ice flow model calculations, estimating a basal ice age of less than 400 years at the drill site (Mikhalenko et al. 2015). Fig. ~~xx~~5 summarizes ~~presents~~ the extended depth--age relation, including annual layer counting back to ~~xxxx~~1774 CE, the prominent time horizons, and PO^{14}C ~~measurements~~data. To interpolate data to a continuous age-depth relation, a two--parameter fit (based on a simple analytical expression for the decrease of the annual layer thickness with depth) was used (Nye, 1963; Jenk et al., 2009~~,~~; Preunkert et al., 2019).

3 The Effect of large Dust events on the Chemistry of ELB Ice

Large dust plumes originating from Middle East and less frequently from Sahara reach the Caucasus (Kutuzov et al., 2013). As seen in the Alps, these dust events disturb modify the chemistry of snow deposits, in particular with calcium rich alkaline snow layers (Wagenbach et al., 1996). Depositions of these plumes disturb enhance the level of numerous chemical species in Alpine ice because either they are present in dust at the emission stage or, being acidic, they were uptake by the alkaline dust material during transport (Usher et al., 2003). Preunkert (2001) showed that the arrival of dust plumes at CDD enhanced depositions of several cations (sodium, potassium, magnesium, and sodium) as well as acidic anions (sulfate, nitrate, chloride, fluoride, and carboxylates). To identify these layers in the ELB snow and ice we have estimated the acidity (or alkalinity) of samples by checking the ionic balance between anions and cations with concentrations expressed in micro-equivalents per liter, μEq L^{-1}):

$$[H^+] = ([F^-] + [Cl^-] + [NO_3^-] + [SO_4^{2-}] + [MonoAc^-] + [DiAc^{2-}]) - ([Na^+] + [K^+] + [Mg^{2+}] + [Ca^{2+}] + [NH_4^+]) \quad (1)$$

$$\text{with } [MonoAc^-] = [HCO_2^-] + [CH_3CHOHCO_2^-] + [CH_3CO_2^-] + [CH_2OHCO_2^-] + [CHOCO_2^-] \quad (2)$$

$$\text{and } [DiAc^{2-}] = [C_2O_4^{2-}] + [CO_2CH_2CHOHCO_2^{2-}] + [CO_2CH_2CO_2^{2-}] + [CO_2(CH_2)_2CO_2^{2-}] + [CO_2(CH_2)_3CO_2^{2-}] \quad (3)$$

In this work, samples whichsamples that are below the 25% quartile of a robust spline through the calculated raw acidity profile and contain more than 120 ppb of calcium and which are below the 25% quartile of a robust spline through the calculated raw acidity profile, were considered as impacted by dust events. In this way, 616 (on a total of 2524) summer and 67 (on a total of 1150) winter samples were considered consideredas containing large amount of dust. Note that the results are quite similar when changing the calcium concentration criteria from 120 ppb to 100 or 140 ppb. Since the frequency of these events has changed over time (Kutuzov et al., this issue) the significance of their impact on the deposition of chemical species is examined. Figure 4 6 shows the mean ionic budget of samples considered as contaminated by dust and containing high and moderate content of calcium compared to samples assumed to be free of dust events, over the 1950-1980 period. For the largest events (Ca^{2+} > 600 ppb30 μEq L^{-1}, Fig. 4A6A), the increase of calcium, accompanied by a strong increase of the alkalinity, reaches a factor of 7.4 compared to dust-free samples (Fig. 64C). In addition, this calcium enhancement is accompanied by an increase of a factor close to 8 for chloride, sodium, potassium and magnesium, whereas ammonium, nitrate, sulfate, and carboxylates are, at the bestmost, enhanced by a factor of 2. When comparing dust samples containing weaker calcium contents (i.e. Ca^{2+} < 30 μEq L^{-1}600 ppb, Fig. 4B6B) with dust-free samples (Fig. 4C6C), in addition to the increase of calcium (factor of 2) the most significant changes are seen for magnesium (x1.5), sodium and chloride (x1.6), and potassium (x1.3), respectively. In brief, all cations (except ammonium) and chloride are present in dust at the emission stage. Furthermore, acidic chloride can be taken up by dust during transport.

For species present in dust at the emissions stage, it is interesting to compare their ratio to calcium in ELB dust layers (Figure 5) with atmospheric aerosol data obtained at sites impacted by dust events. For magnesium, a species predominantly originating from dust in ELB ice, the mean $[Mg^{2+}]/[Ca^{2+}]$ ratio in ELB dust events is 0.035 (Figure 5). Koçak et al. (2012)

reported dust event related aerosol concentrations of sodium, magnesium, and calcium from two Eastern Mediterranean sites, i.e. from Erdemli (Turkey) with dust arriving from Middle East and from Heraklion (Crete) with dust from Sahara. It is important to emphasize that, as for the ELB ice data, the atmospheric concentrations of these cations correspond to their water-soluble fraction (not the total fraction), which were measured with IC. In the case of Erdemli during Middle East dust events, Koçak et al. (2012) reported atmospheric concentrations of 7085 ng m^{-3} for Ca^{2+} and 423 ng m^{-3} for Mg^{2+} (Table 2). Since Erdemli is located at 22 m above sea level and 10 m away from the sea, in addition to the leachable fraction of magnesium from dust, a fraction of magnesium would here come from sea-salt. To correct concentration from the sea-salt contribution, we have used the Na^+ concentration (1148 ng m^{-3}) and assumed a mean $[Na^+]/[Ca^{2+}]$ ratio in dust of 0.08 as observed in ELB ice samples containing dust (see below). Thus, neglecting the sea-salt calcium contribution, we estimate a dust sodium contribution of 567 ng m^{-3} (0.08 x 7085 ng m^{-3}). With that, and using the $[Mg^{2+}]/[Na^+]$ ratio in seawater (0.12), we estimate that 70 ng m^{-3} of magnesium are originated from sea-salt and calculate a $[Mg^{2+}]/[Ca^{2+}]$ ratio for dust aerosol close to 0.05 (Table 2). A similar value is obtained for aerosol at Heraklion during a Saharan dust event (0.043, Table 2). The content of Mg^{2+} in ELB samples impacted by dust is therefore very consistent with what is observed in atmospheric aerosol from the Eastern Mediterranean region during dust events. Note that the same is true for the Mg^{2+} content of CDD samples impacted by Saharan dust (mean $[Mg^{2+}]/[Ca^{2+}]$ ratio of 0.045, Figure 5).

Figures 5 compares the chemical content of dust deposited in the Caucasus (ELB) and in the Alps (CDD). In the Alps, most of dust events are related to sporadic arrivals of Saharan dust plumes (Wagenbach et al., 1996). As discussed above, whereas Saharan dust events also sporadically reach the Elbrus site and are characterized by very large amount of calcium (see Fig. 4A) more frequent are dust events from Middle East that contain less calcium (Fig. 4B). As seen in Figure 5, ELB samples containing dust indicate a rather similar mean $[K^+]/[Ca^{2+}]$ ratio of 0.030 compared to dust events deposited in the Alps ($[K^+]/[Ca^{2+}]$ ratio of 0.035). The same remains true (not shown) for sodium ($[Na^+]/[Ca^{2+}]$ ratio of 0.08-0.09 at ELB and CDD sites) and chloride ($[Cl^-]/[Ca^{2+}]$ ratio of 0.11 for both ELB and CDD sites), suggesting that dust deposition of dust at the two sites is similar for these species present together with calcium at the emission stage. This conclusion is consistent with the study of dust samples from several Middle East sites and Saharan showing similar chemical and mineralogical constituents in most cases (Engelbrecht et al., 2009).

For nitrate, and to a lesser extent for sulfate, a systematic lower content relative to calcium can be observed at the ELB site ($[NO_3^-]/[Ca^{2+}]$ ratio of 0.28 and $[SO_4^{2+}]/[Ca^{2+}]$ ratio of 0.72) compared to the French Alps site ($[NO_3^-]/[Ca^{2+}]$ ratio of 0.40 and $[SO_4^{2-}]/[Ca^{2+}]$ ratio of 0.90). Such a lower neutralisation of alkaline material by acidic species in dust plumes reaching the ELB site compared to the CDD site is probably related to a reduced availability of acidic species along the transport of the dust plumes towards the site

To evaluate the effect of dust events on the deposition of chemical species, we compare in Table 5 2 averaged chemical concentrations of all samples with those not impacted by dust (denoted X_{red}). Averages were obtained on the base of half-year summers over the half-decades 1996-2000 and 1974-1978 characterized by high and low dust content, respectively (Kutuzov et al., this issue). Though the main impact of dust is as expected, on cations (except ammonium) and chloride, i.e.

the constituents of dust particles, the impact is also significant for acidic species like nitrate and sulfate. For instance the increase of nitrate from 1974-1978 to 1996-2000 AD (144 ppb) in the whole dataset is largely (three quarters) related to the increase of dust as indicated by the smaller increase after removal of dust samples (increase of 31 ppb for the $NO_3^-{}_{red.}$ value). Same is true for sulfate, for which the apparent increase between the two periods (90 ppb) is not due to an increase of pollution but of dust, as indicated by the drop of values when the dust free data set is considered (decrease of 48 ppb for the $SO_4^{2-}{}_{red.}$ value). The effect of changing dust inputs over time has to be therefore considered when discussing long-term trends in view to relate them to growing anthropogenic emissions (see Sect.Sect. 5 for sulfate in relation with SO_2 emissions). Finally, the large effect of dust seen for formate ($HCOO^-$) and not for acetate (CH_3COO^-) is in agreement with previous observations made by Legrand et al. (2003) in Alpine ice and by (Legrand and De Angelis, 1995) in Greenland ice. These studies showed that the presence of formate and acetate in ice follows the uptake of formic and acetic acid from the atmospheric gas phase, and that the incorporation of these weak acids into hydrometeors is pH dependent with a stronger dependence for formic acid, which is a stronger acid than acetic acid. In conclusion, large dust events significantly influence the chemistry of ELB ice for many species, requiring a case by case examination depending on the nature of the dust contribution: primary emissions for sodium and other cations (except ammonium), neutralization of the alkaline material during atmospheric transport for nitrate, and both primary gypsum emissions and neutralization of the alkaline material by acidic sulfur during atmospheric transport for sulfate, for instance.

4 Long-term summer and winter trends of sulfate in the Elbrus ice

~~From the winter/summer dissection made on the basis of the ammonium and succinate stratigraphy (Sect. 2), monthly means as well as half-year summer and winter means were calculated over the 1774 to 2010 period. In Figure 6, we report the seasonal cycle of sulfate, ammonium, and succinate averaged across a pre-industrial period (1775-1825 AD) and two different periods of the industrial period (1940-1960 and 1980-2000 AD). Individual sulfate half-year summer and winter means are reported in Figure 7, considering raw sulfate data and those regarded as free of dust ($SO_4^{2-}{}_{red.}$), respectively.~~

A few outliers of unknown origin were observed in the sulfate raw data set including 22 ppm at 166.65 m depth (summer 1780 AD), 2248 ppb at 146.38 m depth (summer 1862 AD), 1080 ppb at 146.11 m depth (summer 1863 AD), and 864 ppb at 154.73 m depth (winter 1833/34 AD) (Fig. 7). These individual values were removed when calculating the corresponding half-year summer and winter means reported in Fig.ure 78. In addition, single winter samples with sulfate levels of 815 ppb at 160.62 m depth (winter 1810/11 AD) and 3 data points from 150 to 230 ppb corresponding to winters 1786-87, 1827-28, and 1844-45 were not considered and corresponding half-year winter values were not reported.

A few ELB snow and ice layers are impacted by known volcanic eruptions. As discussed by Mikhalenko et al. (2015), ice layers dated to 1911 and 1913 were probably impacted by the 1912 AD Katmai eruption, and summer layers of 1836 and 1837 by the 1835 AD Coseguina eruption, respectively. In addition, we suspect the 1854 AD Shiveluch eruption to have impacted summer 1854 ice layer and finally, although less evident since this part of the core is made up of splitted ice (see

SSeect.ion 2), the Cotopaxi 1877 AD eruption may have influenced the winter 1877/1878 layer. To discuss the long-term trends of sulfate in relation to growing SO_2 emissions, these half-year summer and winters means suspected to be contain volcanic debris, were discarded in Fig.ure 89. To minimize the effect of year-to-year variability due to meteorological transport conditions we added the first component of single spectra analysis (SSA) with a five-year time window in Fig.ure 89, for the total sulfate data and those which are considered to be free of dust input ($SO_4^{2-}$$_{red.}$ values), respectively.

As discussed in Sect. 3, large dust events significantly enhanced the sulfate level of the ELB ice. Since, as detailed in Kutuzov et al. (this issue), their occurrence have changed over the past with more frequent events after 1950, we have examined to what extent they contribute to the sulfate trend. It is difficult to accurately directly correct sulfate concentration from the large dust event contribution since the amount of sulfur trapped by the alkaline material during atmospheric transport towards the site would be very different from event to event. For instance, Kozak et al. (2012) reported non-sea-salt-sulfate to non-sea-salt calcium mass ratios in aerosol collected in the eastern Mediterranean ranging between 0.25 (in case of direct arrival at the site of air mass from the Sahara) to 1.15 (when mineral dust passed through polluted sites located in the Balkans and Turkey before arriving at the site). Instead of corrected sulfate values for the large dust events, we therefore have reported in Fig. 8 individual values of total sulfate and sulfate calculated after having removed from the average samples suspected to contain large amount of dust ($SO_4^{2-}$$_{red.}$ values). The dust influence of large dust events on the long-term SSA winter trend is rather insignificant and if existing (i.e. effect of < 10 ppb) remaining limited to two decades around 1870 and the recent decade (2000-2010) (Fig. 89). Remaining negligible prior to 1850, the large dust event effect on the summer trend gradually increases after 1950, reaching often 100 ppb after 1960. This change of large dust events results from change in the occurrence of drought in North Africa and Middle East regions (Kutuzov et al., this issue). the long-term increasing trend of calcium summer concentrations (from 74 ± 24 ppb prior 1850 to 370 ± 193 ppb between 1960 and 2010), resulting from changes in precipitation and soil moisture content in Levant region (Syria and Iraq) and occurrence of drought in North Africa and Middle East regions (Kutuzov et al., this issue). In addition to the enhanced frequency of large dust events after 1950, the calcium background concentrations (i.e., $Ca^{2+}$$_{red}$) also changed over time with an increase from 68 ± 21 ppb prior to 1900 CE to 194 ± 61 ppb after 1960 CE. As discussed by Kutuzov et al. (this issue), this change may result from changes in precipitation and soil moisture content in Levant region (Syria and Iraq). In view to discuss the free-dust sulfate changes with respect to anthropogenic emissions, we make an attempt to correct the sulfate record from this increase of the background level of dust. To do so, we examined in Fig. 10 the relationship between calcium and sulfate concentration in individual summer samples corresponding to pre-industrial time (1774-1900 CE). Although being poor (R^2=0.32), the correlation suggests a mean slope of the linear SO_4red-Cared relationship close to 1. The use of this value to correct sulfate from background dust emissions would lead to an overestimation of the sulfate dust contribution. Indeed, as seen in Fig. 10, there are numerous samples that contain more sulfate than what is expected with respect to the presence of pure calcium sulfate (gypsum, see the blue line reported in Fig. 10), likely to due the presence of sulfate as ammonium sulfate or sulfuric acid. To correct sulfate from the background dust contribution we here have used a sulfate to calcium ratio close to 0.63 (see the red line drawn as the lower envelope of the relationship in Fig. 10) and subtracted this contribution from the $SO_4^{2-}{}_{red.}$ values by using the $Ca^{2+}{}_{red.}$ values.

As seen in Fig.~~ure~~ ~~8~~9, the derived mean summer and winter pre-industrial free-dust sulfate levels in ELB ice (taken as the mean value observed from 1774 to 1850) is of ~~116~~ 70 ppb and ~~69~~ 40 ppb, respectively ~~(113 ppb and 68 ppb, respectively for $SO_4^{2-}{}_{red.}$ values)~~. In summer as in winter, the free-dust sulfate ~~SO42-red.~~ values remained close to the pre-industrial values until 1910-1920 (~~125~~ 81 ppb instead of ~~113~~ 70 ppb in summer, ~~66~~ 47 ppb in winter). After 1920, dust-free sulfate levels increased at a mean rate of ~~6~~ 5 ppb per year ~~(5.7 ppb yr^{-1} for $SO_4^{2-}{}_{red.}$)~~ in summer, and ~~with~~ 1~~.5~~ ppb yr^{-1} ~~for SO_4^{2-} and $SO_4^{2-}{}_{red.}$~~ in winter. The sulfate increase then accelerated between 1950 and 1975 (~~11~~ 10 ppb yr^{-1}~~, 10.5 ppb yr-1 for SO42-red.~~ in summer, 5 ppb yr^{-1} in winter), until a maximum of ~~730~~ 530 ppb in summer (~~663~~ 255 ppb ~~of $SO_4^{2-}{}_{red.}$~~ in winter) was reached at the end of the 80's~~between 1980 and 1990~~. After 1990, sulfate levels decreased to ~~590~~ 390 ppb in summer (~~490~~ 154 ppb ~~of $SO_4^{2-}{}_{red.}$~~ in winter) during the first decade of the twenty first century. ~~In winter, the sulfate increase accelerated between 1950 and 1975 (4.5 ppb yr^{-1} for SO_4^{2-} and $SO_4^{2-}{}_{red.}$), to reach a maximum of 267 ppb (267 ppb of $SO_4^{2-}{}_{red.}$) between 1980 and 1990, followed by a subsequent decrease to 208 ppb (190 ppb of $SO_4^{2-}{}_{red.}$) in the first decade of the twenty first century.~~

5 Comparison between Elbrus, ~~and~~ Alpine, and Siberian Altai long-term sulfate trends

5.1 The Alpine CDD and Siberian Altai (Belukha, BEL) ice core Sulfate Records

The ELB dust-free sulfate long-term trend is compared with those previously extracted from the Alpine CDD site (ice cores denoted C10 and CDK in Fig.~~ure~~ ~~9~~11). C10 sulfate data were presented in Preunkert et al. (2001), and those form CDK in (Legrand et al., 2013). Since winter data from CDD are more limited (only a few pure winter layers are available between 1890 and 1930, Legrand et al., (2018) we here focus on the comparison of summer levels. The two CDD cores were dated by annual layer counting using the pronounced seasonal variations of ammonium. The two chronologies were in excellent agreement over their overlapping period from 1925-1990 (Legrand et al., 2013; Preunkert et al., 2000). A re-evaluation of the C10 chronology based on very recently made continuous measurements of heavy metals, as well as a comparison to a well-dated Greenland ice core record (McConnell and Edwards, 2008), resulted in a revised C10 chronology (Legrand et al., 2018). As for C10, continuous measurements of heavy metals are also available in the lowest part of CDK (Preunkert et al., 2019~~in press~~). It was thus possible to identify the distinct Greenland increases of thallium, lead, and cadmium associated with the widespread start of coal burning at the beginning of the Industrial Revolution in 1890 CE also in the CDK core (at 117.8 m (90.5 mwe)). This time marker was then used to constrain a revised annual layer counting in the early 20th-century part of the CDK record. ~~In the following we compare summer trends of both Alpine CDD cores with the ELB ice core record, considering long term sulfate trends regarded to be free of dust influence (i.e., the $SO_4^{2-}{}_{red.}$ values).~~The dust-free ELB sulfate long-term trend is also compared with the one previously extracted from the Siberian Altai (Belukha glacier, denoted BEL in Fig. 11) by Eichler et al. (2009 and 2012).

5.2 ELB versus CDD and BEL sulfate trends

Since available at all three sites, we compared in Fig. 11 the annual long-term trends of dust-free sulfate from ELB, CDD, and BEL. The ELB and CDD annual values were calculated as arithmetic mean from 5 yr-SSA winter and summer records, whereas the BEL annual data refer to 5 year averaged raw data. Examination of the three annual records reveal three major differences between the three sites: (1) an impact of anthropogenic emissions already significant in 1910-1930 at CDD but neither at ELB nor at BEL, (2) a maximum of the anthropogenic perturbation which is reached in 1970-1980 at CDD and later at the two other sites (10 years after at ELB, and a few years after at BEL), and (3) a far less pronounced re-decrease at the beginning of the 21th century at ELB compared to CDD. The re-decrease of sulfate over the very recent decades is somewhat stronger at BEL than at ELB.

Using data from Smith et al. (2011), available at http://sedac.ciesin.columbia.edu/data/set/haso2-anthro-sulfur-dioxide-emissions-1850-2005-v2-86, we report in Fig. 12 emissions of SO_2 from countries located nearby the ELB site: Georgia, Azerbaijan, Syria, Irak, Turkey, Russian, Iran or located further north (Ukraine) and west (Bulgaria). In these countries SO_2 emissions became significant after 1930 and reached maximum in the late 80's or later (for Turkey and Iran). This feature clearly differs from the situation at CDD where emissions from countries located around the site (France, Italy, Spain, Switzerland and Germany) were already significant in 1930 and exhibited a maximum between the early 70's and the early 80's (Fig. 10). For BEL, Eichler et al. (2009) demonstrated the importance of emissions from eastern Europe for the dust-free sulfate annual record at that site.

~~For summer (see Figure 9 a and b), the pre-industrial sulfate ELB value ($SO_4^{2-}{}_{red.}$ = 113 ppb) thus exceeded the CDD one (66 ppb) (Preunkert et al., 2000). A similar difference is observed for winter with $SO_4^{2-}{}_{red.}$ close to 68 ppb at ELB (Figure 7) compared to 20 ppb observed by Preunkert et al. (2000) at CDD. It is out of the scope of this work to discuss the cause of this difference between the two ice cores but we can first mention the existence of local volcanic sulfur emissions (as evidenced by direct on site observations of a sulfur smell nearby the ELB drill site). The pre-industrial summer level of dust free calcium samples at ELB (74 ppb, Kutuzov et al., this issue) is higher than the one at CDD (45 ppb, Legrand, 2002). That may also contribute to the ELB/CDD difference of the sulfate pre-industrial level. Clearly, more work, including simulations with transport and chemistry models considering also oceanic emissions of DMS may help here.~~

~~Figure 9 compares the increasing summer sulfate trends of the ELB and CDD sites. Three major differences between the two sites are revealed: (1) an impact of anthropogenic emissions already significant in 1910 at CDD and not at ELB, (2) a maximum of the anthropogenic perturbation from 1970 to 1980 at CDD and 10 years after (1980-1990) at ELB, and (3) a far less pronounced re-decrease at the beginning of the 21th century at ELB compared to CDD.~~ Finally, we tentatively examine the cause of the recent decrease of sulfate, focusing on the summer season for which the most relevant source regions are limited to countries located nearby the site.

As discussed by Kutuzov et al. (this issue), 10 day backward air mass trajectories calculated for the ELB site using the NOAA HYSPLIT-4 model suggest that, in summer, air masses arriving at ELB mainly originate from the nearby Georgia, Azerbaijan, Syria, Irak, and from Turkey, South Russian, and North of Iran. As previously discussed by Fagerli et al. (2007), the CDD site in summer is mainly influenced by emissions from France, western Germany, Italy and Spain. Consistently with SO_2 emission changes, the recent sulfate decrease is more pronounced at CDD than ELB with a recovered 2005 level (316 ppb) close to the 1950 one (296 ppb) (Fig. 13). At the ELB site this is not the case, here the 2005 level (380 ppb in 2005) is found to be still almost two times higher than the one of 1950 (227 ppb in 1950). An intermediate pattern is seen at BEL, likely due to a weak impact of countries like Turkey that significantly contribute to the ELB record but not the BEL one, and a more strong contribution of emissions from Russian at BEL (see also Eichler et al., 2009) than at ELB.

~~We report in Figure 10 emissions of SO_2 from these countries and from a few others located further north (Ukraine) and west (Bulgaria). In these countries SO_2 emissions reached maximum in the late 80's or later (for Turkey and Iran). This feature clearly differs from the situation at CDD where countries around the site (France, Italy, Spain, Switzerland and Germany), thought to be the main contributors for sulfate in CDD ice (Fagerli et al., 2007), exhibit a maximum between the early 70's and the early 80's (Figure 10).~~

~~On this basis and as a first attempt, we compare the ELB and CDD summer sulfate trends with SO_2 emissions from surrounding countries. It can be seen that the impact of growing anthropogenic SO_2 emissions started later at ELB (after 1920) compared to CDD (after 1900). The 10-year delay of the sulfate maximum at ELB compared to CDD is also well seen in the enhancement course of SO_2 emissions. Note also that as indicated by the emissions, the maximum enhancement at ELB (550 ppb between 1980 and 1990) is slightly weaker that the one at CDD (665 ppb between 1974 and 1984) (Table 3). Finally, consistently with SO_2 emission changes, the recent sulfate decrease is more pronounced at CDD than ELB with a recovered 2005 level (254 ppb) close to the 1950 one (234 ppb). At the ELB site this is not the case, here the 2005 level (380 ppb in 2005) is found to be still around two times higher than the one of 1950 (180 ppb in 1950).~~

6. Conclusions

Based on the ammonium and succinate stratigraphy, the upper 168.6 m of the deep ice core extracted at Mt Elbrus (Caucasus) in 2009 were dated by counting annual layers back to 1774 CE. The derived seasonally resolved chemical records cover the years 1774-2009 making this ice core particularly useful to reconstruct many aspects of atmospheric pollution in south-eastern ~~central~~ Europe from pre-industrial times (1850 CE) to present-day. Below 169 m depth the annual counting is not possible but radiocarbon analysis of the particulate organic carbon fraction in the basal ice of the glacier suggests an age of ~1670 ± 400 cal yr BP. We have examined the impact on the chemical composition of the Elbrus ice layers of arrival at the site of large dust plumes originating from Sahara and Middle East. We then report on the dust-free sulfate records~~sulfur pollution~~. The ELB dust-free sulfate record indicates a ~~four~~six- and ~~six~~seven-fold increase from prior to 1900 to 1980-1995 in winter and summer, respectively. Still moderate at the beginning of the 20th century, the sulfate increase accelerated after 1950, dust-free annual levels reaching a maximum in 1980-1990 (376 ± 10 ppb~~730 ± 152 ppb in summer~~) and subsequently decreasing to 270 ± 18 ppb~~630 ± 130 ppb in summer~~ at the beginning of the 21th century. These long-term sulfate changes observed in the ELB ice cores are compared with those previously obtained in Alpine and Siberian Altai ice. Consistently with past SO_2 emission inventories, a much earlier onset and a more pronounced decrease of the sulfur pollution over the three last decades ~~is~~ are observed in western than south-eastern and eastern ~~central~~ Europe.

Data availability

Sulfate and calcium data can be made available for scientific purposes upon request to the authors (contact: suzanne.Preunkert@univ-grenoble-alpes.fr or michel.legrand@univ-grenoble-alpes).

Author contributions

S. Preunkert and M. Legrand performed research, analyzed ice samples and data, and wrote the original manuscript. S. Kutuzov performed research, analyzed data, and commented original manuscript. P. Ginot and V. Mikhalenko performed analysis and commented original manuscript. R. Friedrich analyzed ice samples and commented original manuscript.

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Table 1. Overview of masses (corrected for blanks but not for combustion efficiency) and conventional ^{14}C ages of the Elbrus ice core samples combusted in the REFILOX system. Calibrated date ranges are shown at 68.2% confidence level and are rounded ac-cording to (Millard, 2014).

^{14}C sSample name	Depth	Ice mass [g]	POC mass corrected [µgC]	^{14}C corrected [$F^{14}C$]	Calibrated 14C date BCE/CE at 68.2%	Calibrated ^{14}C-age* range at 68.2% [yr cal BP]	Calibrated ^{14}C-age* [yr cal BP] mean
ELB-176-03	177.11 ± 0.22 m (137.89 ± 0.18 mwe)	295	4.5±0.5	0.914± 0.043	670 CE – 1245 CE	1280 - 705	1040
ELB-178-03	179.19 ± 0.14 m (139.59 ± 0.12 mwe)	300	5.6±0.5	0.955± 0.098	130 CE – 770 CE	1820 - 1180	1530
ELB-181-01	181.50 ±0.13 m (141.19 ± 0.11 mwe)	260	4.4±0.5	0.932± 0.020	440 CE – 1290 CE	1510 - 660	1110
ELB-181-03	182.02 ± 0.13 m (141.62 ± 0.11 mwe)	320	6.5±0.5	0.875± 0.021	90 BCE – 680 CE	2040 - 1270	1670

* age before 1950 CE

Table 32. Mean chemical composition of snow layers deposited in periods characterized by low and high dust inputs (1974-1978 and 1996-2000, respectively). Values in parenthesis are mean values calculated after removal of samples containing dust (denoted red.). Δ refer to the difference between total and dust reduced (red.) values (i.e., $[X] - [X_{red.}]$ for the X species).

	1974-1978 AD	1996-2000 AD
Ca^{2+} ($Ca^{2+}_{red.}$)	286 ppb (169 ppb) Δ = 117 ppb	544 ppb (186 ppb) Δ = 358 ppb
Mg^{2+} ($Mg^{2+}_{red.}$)	25.0 ppb (19.5 ppb) Δ = 5.5 ppb	29.5 ppb (18.0 ppb) Δ = 11.5 ppb
K^{+} ($K^{+}_{red.}$)	24 ppb (20 ppb) Δ = 4 ppb	30 ppb (20 ppb) Δ = 10 ppb
Na^{+} ($Na^{+}_{red.}$)	31 ppb (25 ppb) Δ = 6 ppb	40 ppb (24 ppb) Δ = 16 ppb
Cl^{-} ($Cl^{-}_{red.}$)	67 ppb (55 ppb) Δ = 12 ppb	88 ppb (46 ppb) Δ = 22 ppb
NH_4^{+} ($NH_4^{+}{}_{red.}$)	177 ppb (165 ppb) Δ = 12 ppb	199 ppb (149 ppb) Δ = 50 ppb
NO_3^{-} ($NO_3^{-}{}_{red.}$)	292 ppb (279 ppb) Δ = 13 ppb	436 ppb (310 ppb) Δ = 126 ppb
SO_4^{2-} ($SO_4^{2-}{}_{red.}$)	649 ppb (598 ppb) Δ = 51 ppb	738 ppb (550 ppb) Δ = 188 ppb
$HCOO^{-}$ ($HCOO^{-}_{red.}$)	168 ppb (135 ppb) Δ = 33 ppb	184 ppb (113 ppb) Δ = 71 ppb
CH_3COO^{-} ($CH_3COO^{-}_{red.}$)	48 ppb (37 ppb) Δ = 11 ppb	49 ppb (39 ppb) Δ = 10 ppb

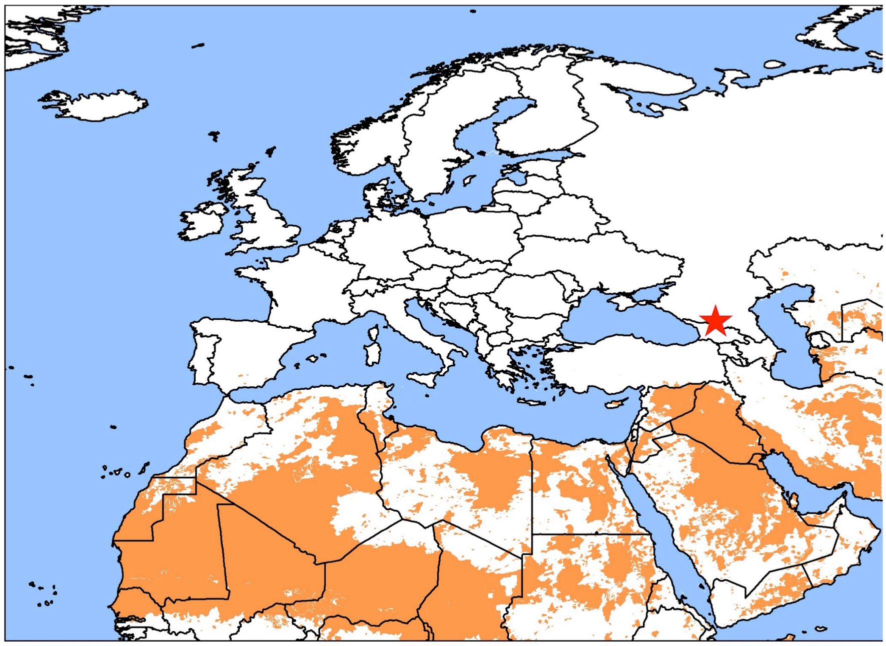


Figure 1. Map showing the location of the Elbrus site (red star) and dust sources (orange shading, based on Kutuzov et al. (this issue) and references therein).

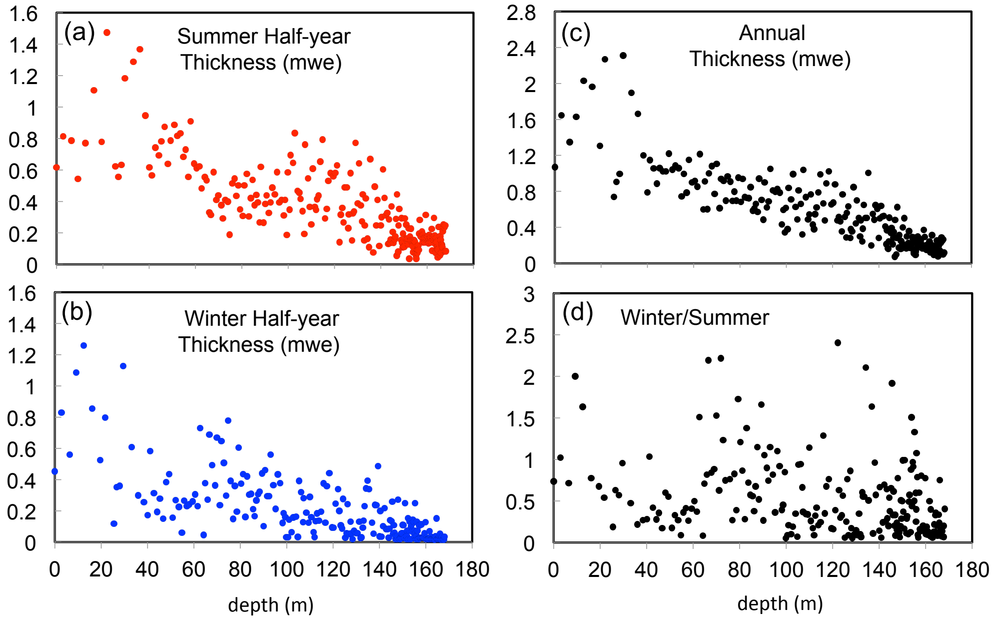


Figure ~~1~~2.~~:~~ **(a) and (b):** Mean summer (a) and winter (b) half-**year** ice **thickness** along the Elbrus deep ice core. (c) Mean **annual** ice **thickness** and (d) summer to winter ratio **of** ice **th**ickness~~**(a) and (c): Mean length of individual samples in summer and winter layers (in mwe). (b) and (d): Numbers of samples (N) spanning summer and winter half-years**~~**.**

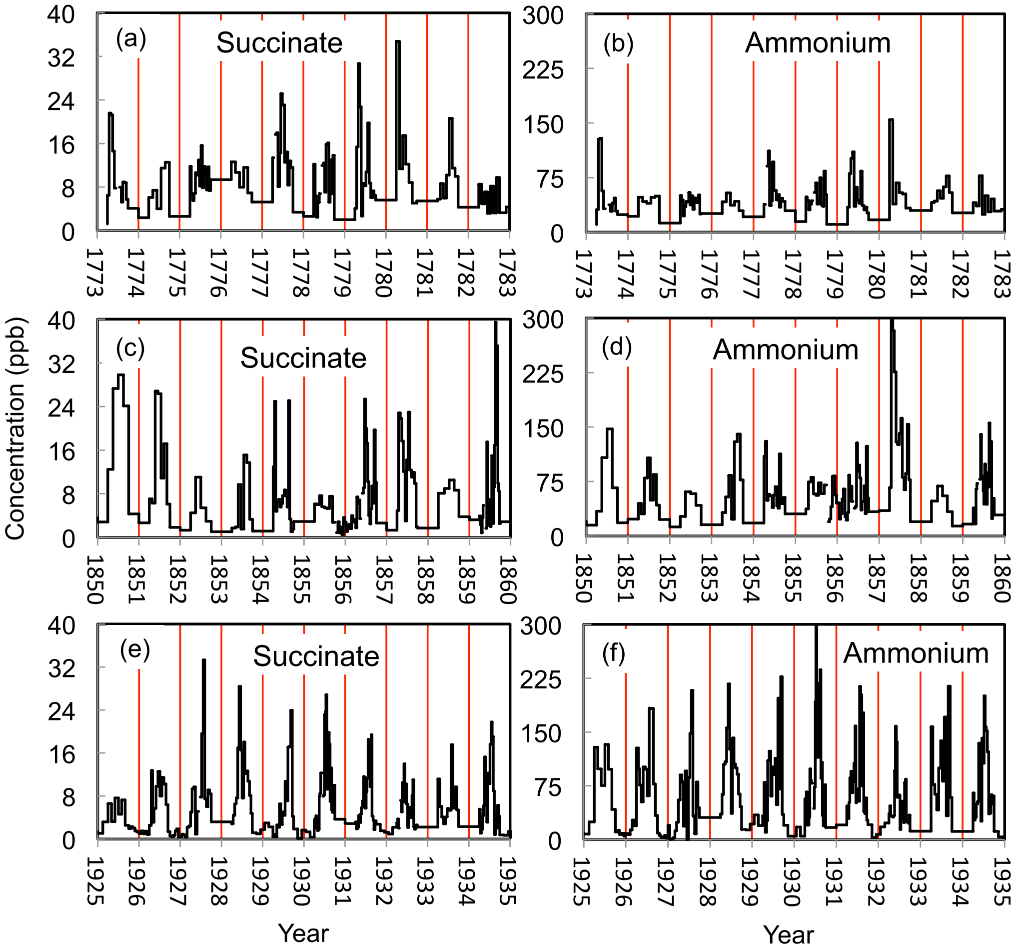


Figure 23. ELB ice chronology at depth intervals of 166.2 to 168.5 m (top), 154.4 to 156.5 m (mid), and from 99.8 to 107.3 m (bottom), based on the ammonium and succinate stratigraphy. Vertical red lines denote yearly dissection based on identification of winter layers (see Sect.Sect. 2.2). For the two oldest time-periods (1773-1782 and 1850-1859), each sample was 2 cm long whereas for the most recent time period (1925-1934) one sample was on average 4 cm long. Note that, though being not coherent with the intra seasonal precipitation distribution (see Kozachek et al., 2017), we here assumed that the accumulation is equally distributed within summer and winter seasons.

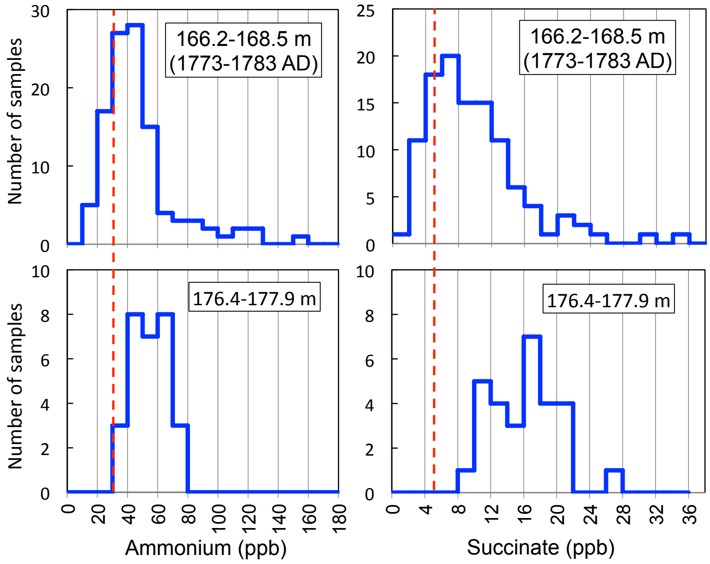


Figure ~~3~~4. Distribution of succinate and ammonium concentrations observed in the deepest ice layers for which annual counting was possible (i.e., above 168.5 m depth, top) and 10 m below (bottom). The vertical red dashed bars denote the values of the winter criteria.

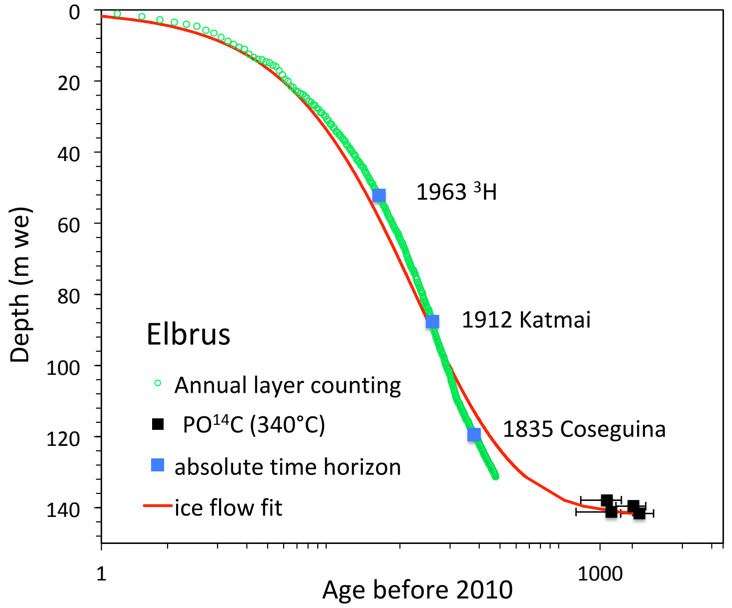


Figure 5. Depth (in mwe) age-relation of the ELB ice core derived from annual layer counting, prominent time horizons, and mean blank corrected and calibrated $PO^{14}C$ data with 1σ age ranges. To interpolate data to a continuous age-depth relation a two-parameter fit was used following Nye (1963).

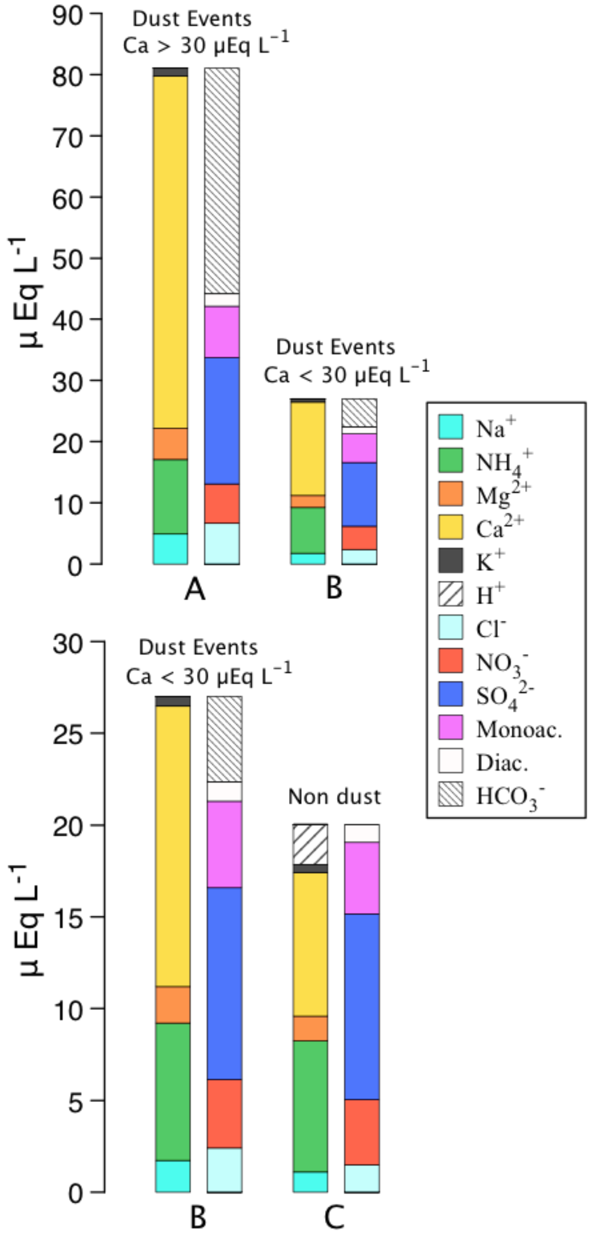


Figure 46. Mean ionic content of ELB layers deposited between 1950 and 1980. A and B: Mean composition of dust event samples containing more and less than 600 ppb (i.e., 30 µEq L^{-1}) of calcium. B and C: Mean composition of dust event samples containing less than 600 ppb of calcium compared to samples free of dust. Abbreviations Monoac. and Diac. stand for C_1-C_3 monocarboxylates and C_2-C_5 dicarboxylates, respectively (see Eqs. 2 and 3 in Sect.Sect. 3).

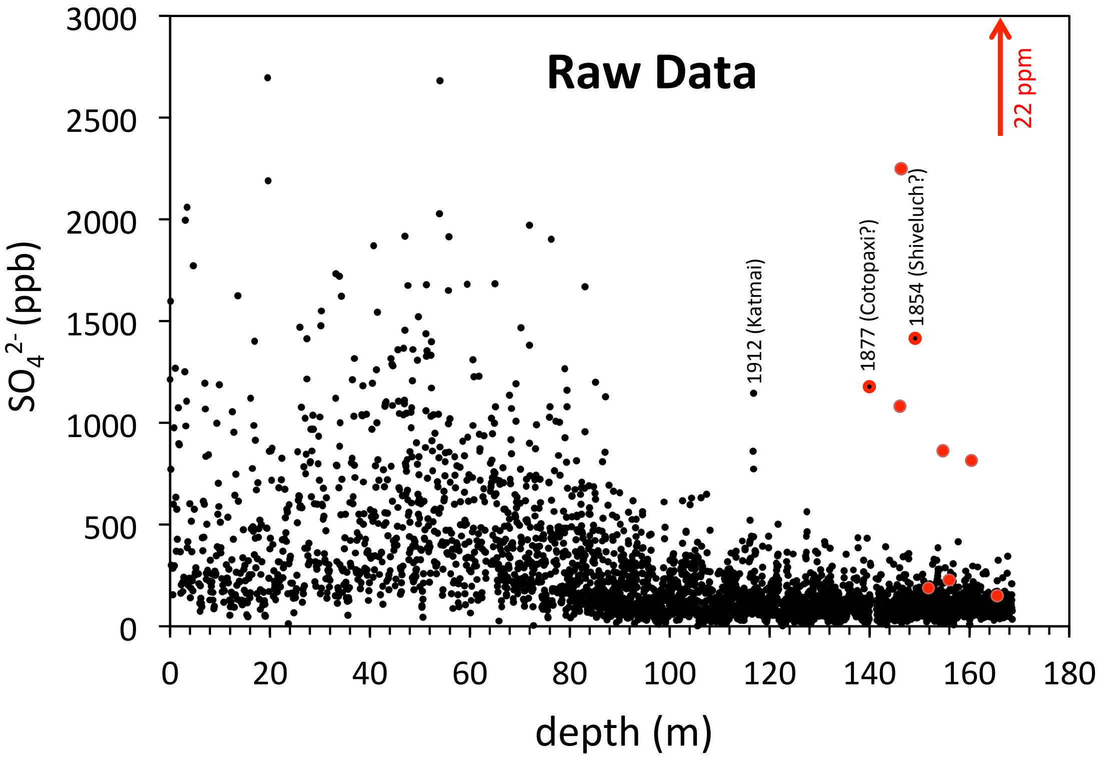


Figure 7. Raw sulfate data. The red dots denote the outliers, which were removed prior to calculation of the half-year summer and winter means. We also indicate samples possibly impacted by the volcanic eruptions of Cotopaxi and Shiveluch (see text).

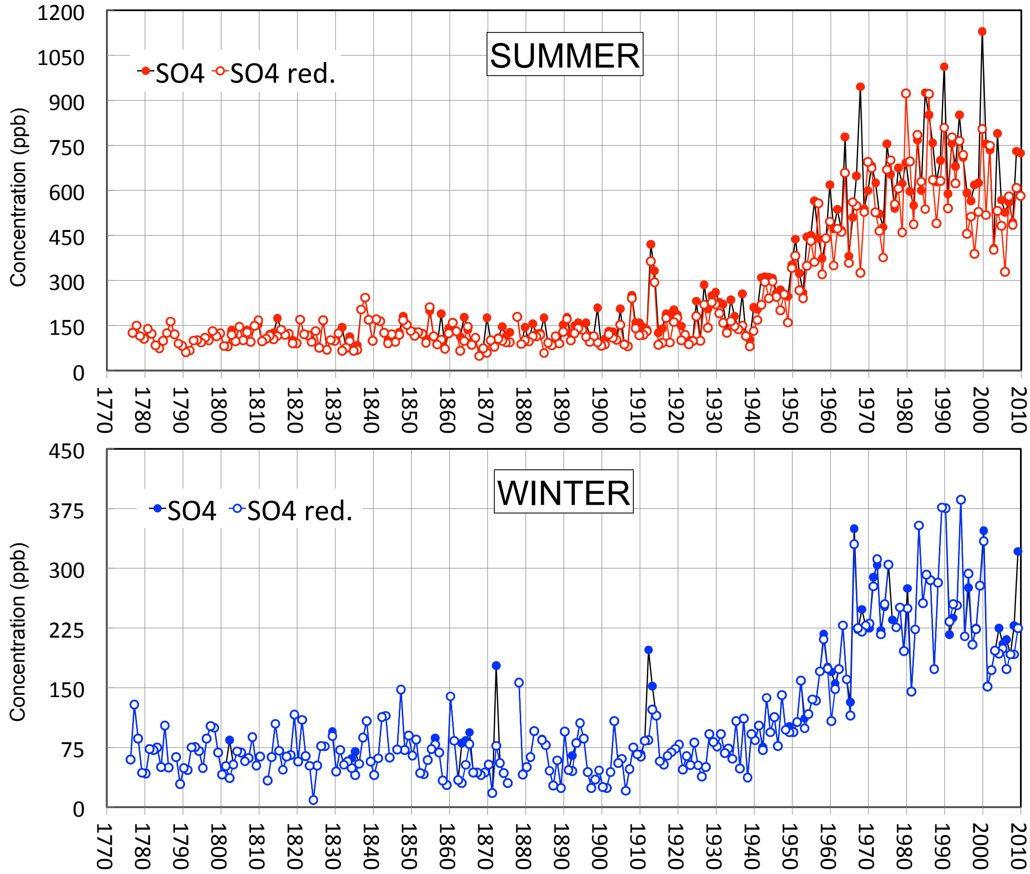


Figure 78. Individual summer (red) and winter (blue) half-year means of sulfate along the ELB ice core. Solid circles refer to values calculated considering all samples. Open circle data (SO4 red.) were calculated after having removed samples considered to be impacted by large dust events (see SSect.- 43).

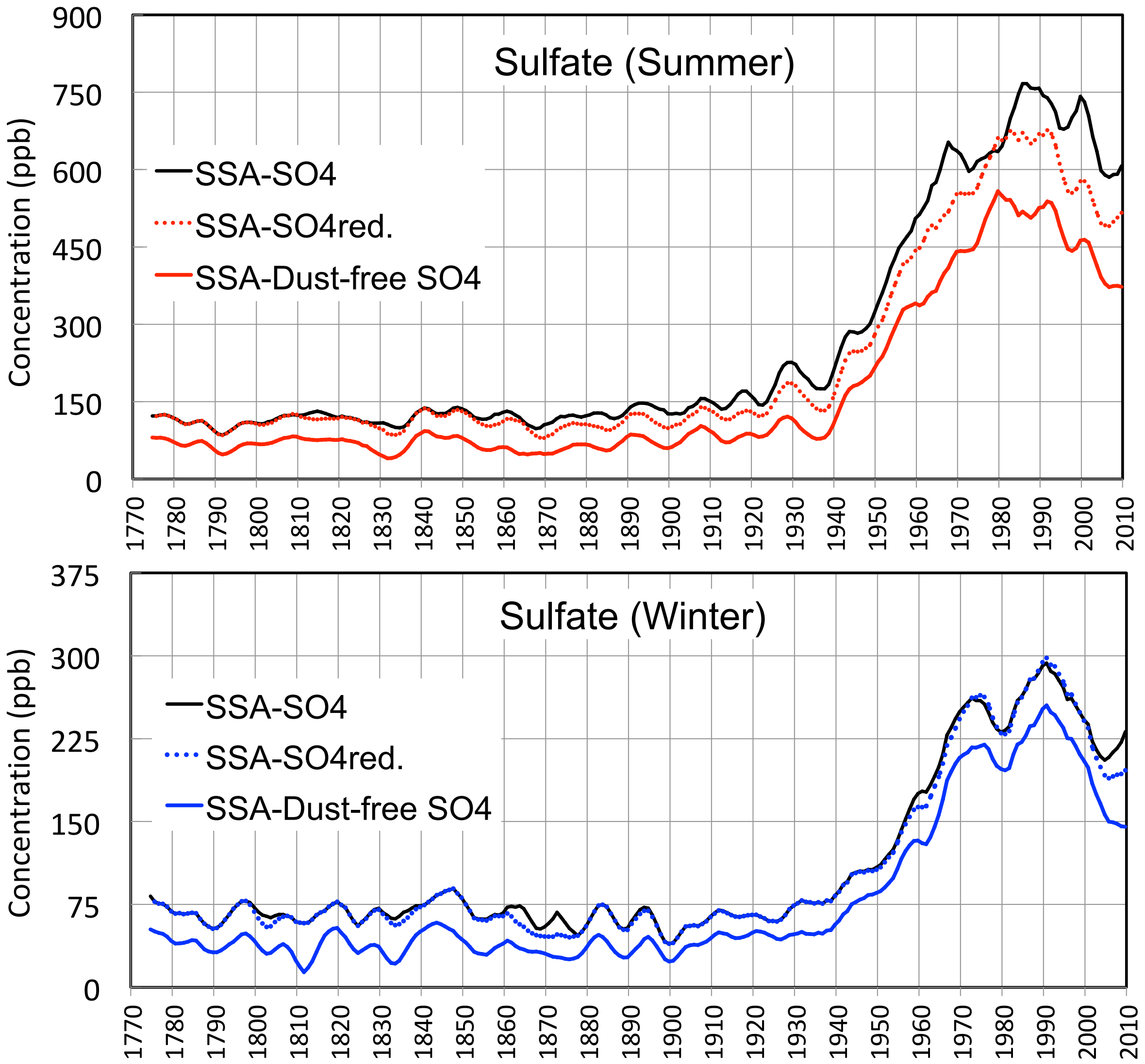


Figure ~~8~~9. ELB half-year ~~sulfate~~ summer and winter sulfate ~~means~~ trends from 1774 to 2010 (the first SSA component with a five-year time window, see text). The black lines refer to raw sulfate values, the dashed lines to sulfate means ~~(triangles)~~ calculated after removal of dust samples ($SO4_{red.}$), the solid red and blue lines to sulfate values after having corrected $SO4_{red}$ values from the background dust contribution (see Sect. 3). ~~The solid thick lines (blue for winter, red for summer) are the first SSA component with a five-year time window (see section 6) calculated for the dust free considered dataset. The solid thin lines (blue for winter, red for summer) represent the first SSA component (five-year time window) when dust events were not removed from calculations.~~ Samples suspected to be impacted by volcanoes were removed.

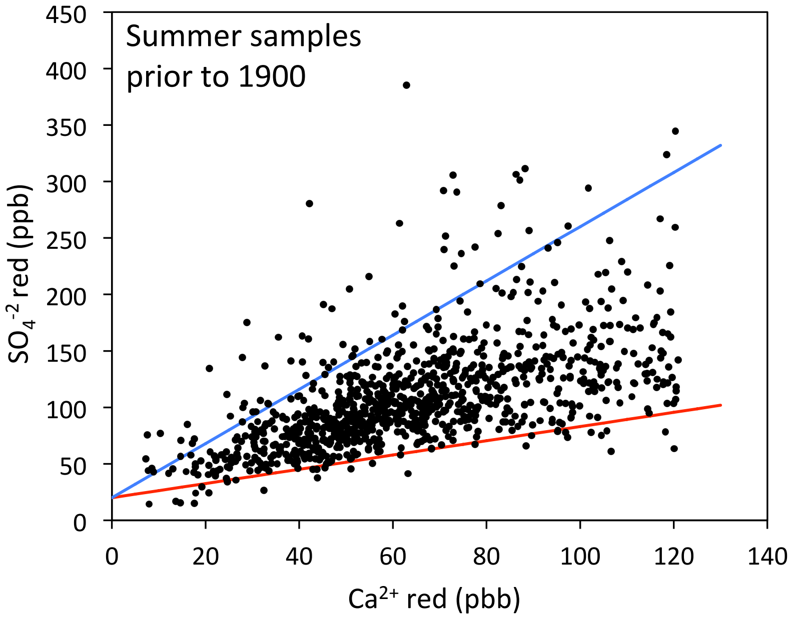


Figure 10. Sulfate versus calcium concentrations in summer samples free of large dust events (Red. values) in ice deposited prior to 1900. The blue line refers to a pure gypsum composition. The red line illustrates a lower envelope of the sulfate to calcium relationship.

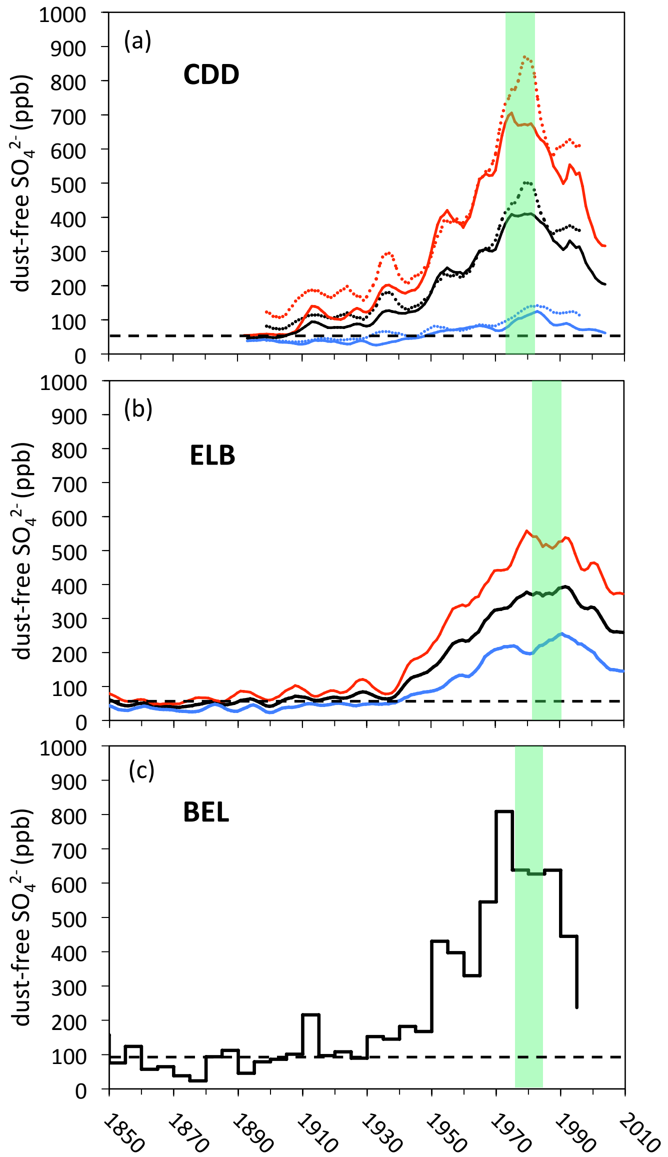
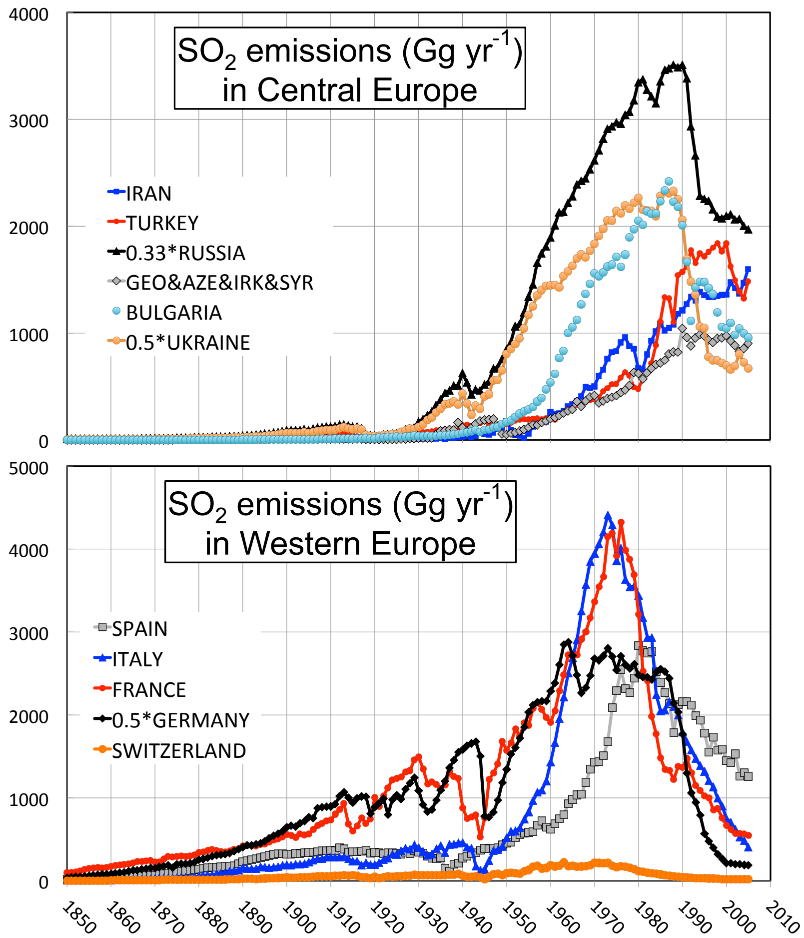


Figure 11. Dust-free sulfate (annual values in black, summer in red, and winter in blue) trends at the CDD (a), ELB (b), and BEL (c) sites. For CDD we report the records derived from the C10 (dashed lines) and CDK (solid lines) ice cores (see Sect. 5.1). Green areas indicate the decades in which the sulfate levels reached their maxima.

Figure 9. Comparison of the dust corrected long-term sulfate summer trends ($SO_4^{2-}{}_{red.}$ values) from two CDD ice cores (C10 and CDK) (a) and the ELB ice core (b) with SO_2 emissions from countries suspected to contribute to sulfate depositions at the two sites (c for CDD, d for ELB, see discussions in Section 5). (a) and (b): solid lines refer to the first SSA component with a five-year time window. Dashed blue lines refer to the respective pre-industrial sulfate levels (see section 5). (c): SO_2 emissions from France, Italy, Spain, Switzerland and half from Germany. (d): SO_2 emissions from Turkey, Georgia and Azerbaijan, half from Russia, a quarter from Ukraine, Bulgaria, and Iran. Green areas indicate the decades in which the sulfate levels reached their maxima.



SO$_2$ emissions (Gg yr^{-1}) in Central Europe
IRAN
TURKEY
0.33*RUSSIA
GEO&AZE&IRK&SYR
BULGARIA
0.5*UKRAINE
4000
3000
2000
1000
0
SO$_2$ emissions (Gg yr^{-1}) in Western Europe
SPAIN
ITALY
FRANCE
0.5*GERMANY
SWITZERLAND
5000
4000
3000
2000
1000
0
1850
1860
1870
1880
1890
1900
1910
1920
1930
1940
1950
1960
1970
1980
1990
2000
2010

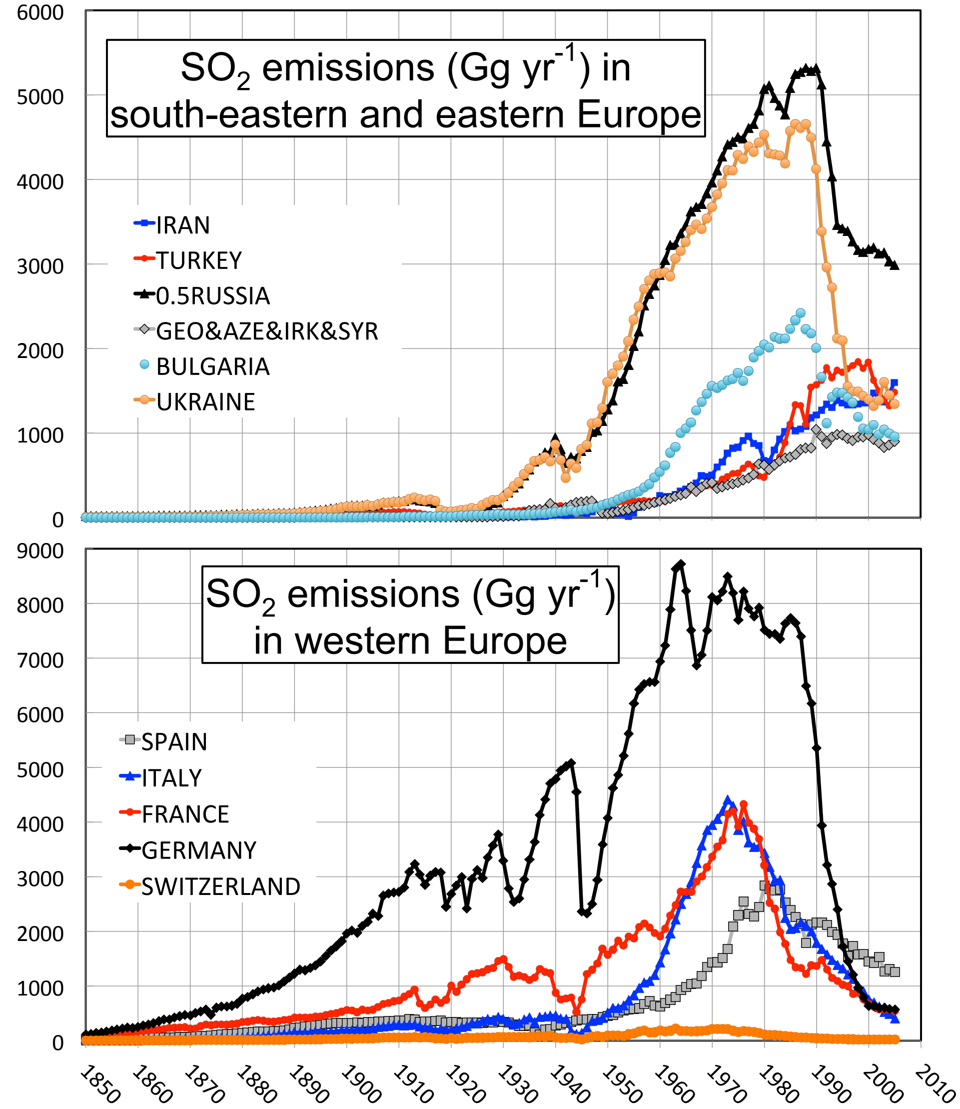


Figure 1012. SO_2 emissions (from 1850 to 2005) from various countries located around the Caucasus (top) and the Alps (bottom). GEO&AZE&IRK&SYR denotes emissions from Georgia, AzerbaidjanAzerbaijan, Irak, and Syria. Data are from Smith et al. (2011).

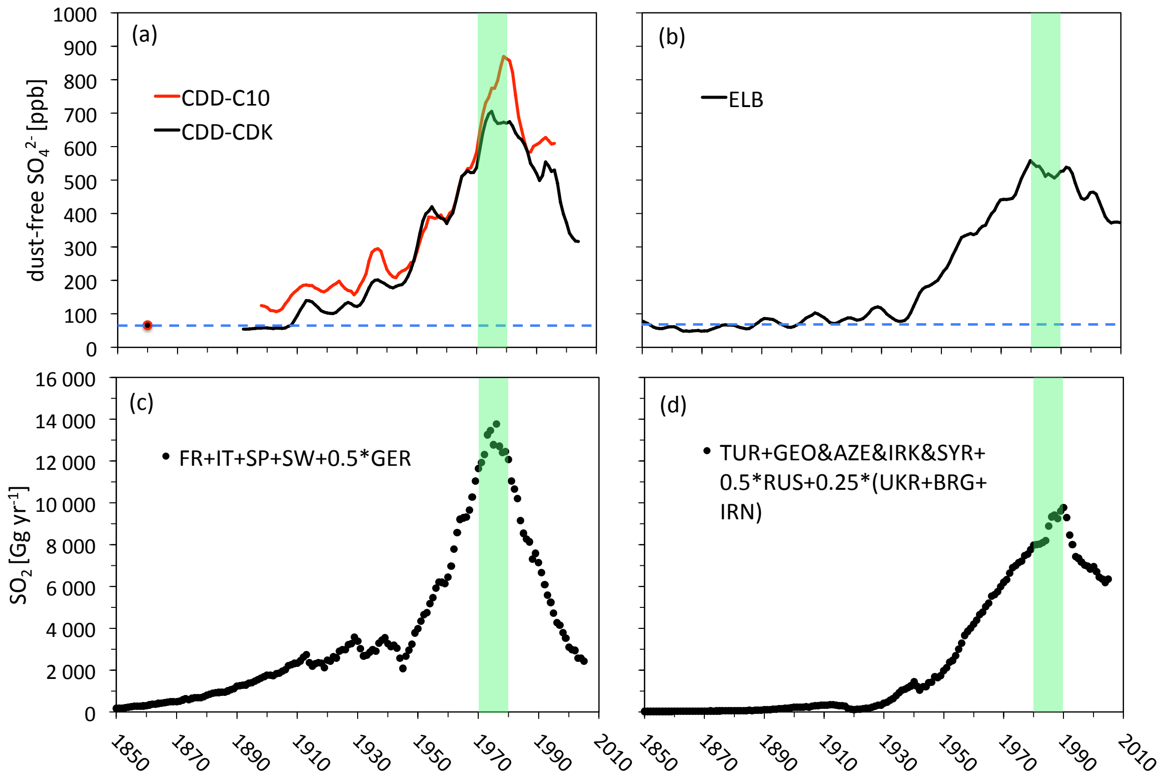


Figure 13. Comparison of the dust-free sulfate summer trends (SO42-red. values) from two CDD ice cores (C10 and CDK) (a) and the ELB ice core (b) with SO2 emissions from countries suspected to contribute to sulfate depositions at the two sites (c for CDD, d for ELB, see discussions in Sect. 5.2). (a) and (b): solid lines refer to the first SSA component with a five-year time window. Horizontal dashed blue lines refer to the respective pre-industrial sulfate levels. (c): SO2 emissions from France, Italy, Spain, Switzerland and half from Germany. (d): SO2 emissions from Turkey, Georgia and Azerbaijan, half from Russia, a quarter from Ukraine, Bulgaria, and Iran. Green areas indicate the decades in which the sulfate levels reached their maxima.