1 **Century-long Record of Black Carbon in an Ice Core from the**
2 **Eastern Pamirs: Estimated Contributions from Biomass Burning**

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28 Key points:

- 29 ● Refractory black carbon (rBC) concentrations in the Muztagh Ata ice core from the
30 Eastern Pamirs increased four-fold during the mid-1970s to 2000 AD relative to the
31 mid-1870s to mid-1970s.
- 32 ● The rBC deposition was mainly influenced by emissions from Central Asia.
- 33 ● Levoglucosan and rBC co-deposition indicates a largely increased energy-related
34 biomass burning in the 1980s-1990s, which possibly contributes more to rBC
35 deposition.

ABSTRACT

We analyzed refractory black carbon (rBC) in an ice core spanning 1875-2000 AD from Mt. Muztagh Ata, the Eastern Pamirs, using a Single Particle Soot Photometer (SP2). Additionally a pre-existing levoglucosan record from the same ice core was used to differentiate rBC that originated from open fires, energy-related combustion of biomass, and fossil fuel combustion. Mean rBC concentrations increased four-fold since the mid-1970s and reached maximum values at the end of 1980s. The observed decrease of the rBC concentrations during the 1990s was likely driven by the economic recession of former USSR countries in Central Asia. Levoglucosan concentrations showed a similar temporal trend to rBC concentrations, exhibiting a large increase around 1980 AD followed by a decrease in the 1990s that was likely due to a decrease in energy-related biomass combustion. The time evolution of levoglucosan/rBC ratios indicated stronger emissions from open fires during the 1940s-1950s, while the increase in rBC during the 1980s-1990s was caused from an increase in energy-related combustion of biomass and fossil fuels.

Keywords: Pamirs, ice core, black carbon, levoglucosan, combustion sources

1. INTRODUCTION

Black carbon (BC) emitted from the combustion of biomass and fossil fuels plays an important role in the energy budget of the Earth system (Bond et al., 2013). BC can contribute to tropospheric warming and glacier melt because of its strong absorption of solar radiation in the air and at snow surfaces (e.g., Ramanathan et al., 2007; Ramanathan and Carmichael, 2008; Hansen and Nazarenko, 2004; Xu et al., 2009; Painter et al., 2013). BC is the second most important contributor to current global warming after carbon dioxide (Jacobson, 2001; Bond et al., 2013). However, energy-consumption related emissions of BC that are estimated from anthropogenic fuel consumption and emission

factors remain greatly uncertain (Novakov et al., 2003; Ito and Penner, 2005; Bond et al., 2007; Fernandes et al., 2007; Junker and Lioussé, 2008), as they vary with fuel types, changes in combustion technology and contributions from different source regions. Biomass burning is the largest global source of BC, and includes both domestic burning for heating and cooking, and open biomass burning (e.g., forest fires, grassland fires, and agricultural waste fires). Due to uncertainties in the quantity of biomass burning and burning conditions, biomass burning contributes greatly to the uncertainty in global BC emissions (Bond et al., 2013).

Ice cores retrieved from remote mountain glaciers and ice sheets can be used to reconstruct historical BC and aerosol particle emissions as the particles deposited on the glaciers and ice sheets are preserved in the ice. By combining the BC records along with other tracers of biomass burning, the contribution of biomass combustion to BC deposition on snow/ice can be determined. Previous research investigating historical variations in BC includes a record of carbonaceous aerosols from a high-elevation glacier in the Swiss Alps that showed a tight linkage with emissions of fossil fuel combustion from Central Europe (Lavanchy et al., 1999). Ice cores drilled from Antarctica reflect Southern Hemisphere biomass burning influenced by continental hydrology (Bisiaux et al., 2012). McConnell et al. (2007) differentiated for the first time BC emissions from industrial activities and forest fires using an ice core in Greenland using non-sea-salt sulfur and vanillic acid to indicate fossil fuel and biomass combustion, respectively.

Identification of source regions and changes in combustion sources of BC deposited on glaciers of the Tibetan Plateau is especially important because this region is close to major BC source regions, and BC may play a significant role in glacier melt, affecting fresh water supplies to a large population (Flanner et al., 2007; Xu et al., 2009a). Prior studies indicate that BC deposited on glaciers over the Himalayas and southeastern Tibetan Plateau are mainly influenced by the westerlies in winter and Indian monsoon in

summer, which transport emissions from Central and South Asia (Ming et al., 2008; Xu et al., 2009b; Kaspari et al., 2011; Wang et al., 2015), whereas BC deposited on glaciers in the Pamir Mountains originates from Europe, the Middle East, and Central Asia due to transport by the westerlies year round (Liu et al., 2008; Xu et al., 2009a).

Previous research preliminarily attributed BC combustion source in the Pamir Mountains to fossil fuels by using sulfate as an indicator (e.g., Liu et al., 2008). However, sulfate aerosols could also come from natural sources (e.g., dimethyl sulphide emissions, volcano eruptions) besides anthropogenic fossil fuel combustion. Thus, the contributions of fossil fuel and biomass emissions to BC deposition in the Pamirs, especially during pre-industrial time, are still poorly understood. To estimate the relative contributions of biomass burning emissions to BC deposited on the Tibetan Plateau, we investigate the temporal variations of refractory BC (rBC) and levoglucosan concentrations in an ice core spanning 1875-2000 AD from Mt. Muztagh Ata, the Eastern Pamirs. Levoglucosan is exclusively produced by the thermal treatment of carbohydrates like cellulose (Simoneit et al., 1999; Fraser and Lakshmanan, 2000), and it has been used to reflect historical records of biomass burning and forest fires in ice cores (Kehrwald et al., 2010; Kehrwald et al., 2012; Kawamura et al., 2012). By analyzing the two datasets together, we intend to reconstruct temporal variations of historical rBC, and examine whether biomass burning was an important source of rBC deposited at Muztagh Ata.

2. METHODS

2.1 Ice Core Collection and Processing

Mt. Muztagh Ata is located on the eastern Pamir Plateau, central Asia (Figure 1). Glaciers on this high-elevation and remote mountain are influenced by the year-round westerly jet stream, and aerosol particles originate predominantly from the west by mid- and long-range transport (Zhao et al., 2011; Wu et al., 2008; Liu et al., 2008). The

location of Muztagh Ata is well situated to investigate historical emissions of BC from Central Asia and Europe. During the summer of 2002, a 74-meter ice core (9.5 cm in diameter) was drilled from the accumulation zone of Muztagh Ata glacier (38° 17' N, 75° 04' E; 6350 m a.s.l.) (Figure 1) using an electromechanical drill (Tian et al., 2006). The ice core was split lengthwise into halves at -20°C in the State Key Laboratory of Cryospheric Science, Lanzhou, China. One half was further split lengthwise into two quarter-cores for the analysis of rBC and levoglucosan, respectively. One quarter-core was cut at ~7 cm intervals to ensure high temporal resolution of 8 samples per year on average for rBC and stable oxygen isotope ($\delta^{18}\text{O}$) analysis, and the other quarter was cut at ~20 cm intervals to determine levoglucosan concentrations.

The ice samples for rBC and $\delta^{18}\text{O}$ analysis were cut into $\sim 7 \times 2.5 \times 2.5 \text{ cm}^3$ cubes for rBC measurement, with the remaining ice collected in 15-ml polyethylene terephthalate (PET) bottles (Foshan Southern Packaging Co., Ltd., China) for oxygen isotope ratio measurements. The 3-mm outer layer of the ice sections was removed with a pre-cleaned stainless steel scalpel at -5°C in a class 100 laminar flow bench to eliminate contamination that may have occurred during drilling, transport, and storage. The inner section for rBC was sealed in a 50 ml polypropylene vial (BD Falcon, cat. no. 358206) and kept at room temperature ($\sim 15^\circ\text{C}$) before analysis.

2.2 Quantification of rBC, levoglucosan and $\delta^{18}\text{O}$

rBC was analyzed at Central Washington University, Ellensburg, US, using a Single Particle Soot Photometer (SP2) coupled with an ultrasonic nebulization system (CETAC UT5000). The SP2 uses laser-induced incandescence to measure the mass of rBC in individual particles (Schwarz et al., 2006). rBC particles are directed by a jet stream through an Nd:YAG laser. The intensity of the intra-cavity light ($\sim 10^6 \text{ W cm}^{-2}$) is strong enough to vaporize light-absorbing particles. Once an rBC particle absorbs light and

reaches its vaporization temperature (i.e., ~2038 to 2371°C), it incandesces (Stephens et al., 2003; Baumgardner et al., 2004). The incandescence signal, which is detected by photomultiplier tube detectors, can be converted to rBC mass. This analytical method was previously applied to ice cores by McConnell et al. (2007), Kaspari et al. (2011), and Bisiaux et al. (2012). The rBC samples were ultrasonic agitated for 15 minutes right before being analyzed. In this study the samples were not acidified. Detailed information on the SP2 analytical process and calibration procedures are described in Wendl et al. (2014). The rBC concentrations are likely to be systematically underestimated due to the following: 1) Samples were stored in the liquid phase after melting, and prior findings indicate that storage in the liquid phase can result in as great as 80% reduction in measured BC concentrations (Wendl et al., 2014). This reduction is hypothesized to be caused by rBC particles sticking onto the container wall during storage in the liquid phase, or rBC particles agglomerating beyond the size range at which particles are nebulized (Wendl et al., 2014; Wang et al., 2012; Lim et al., 2014; Kaspari et al., 2014). 2) The Cetac UT5000 nebulization efficiency is size dependent, with large (> 500 nm) and small (< 200-250 nm) BC particles nebulized with lower efficiency than mid-sized particles (Lim et al., 2014; Wendl et al., 2014; Ohata et al., 2011; Schwarz et al., 2012). Nevertheless, because we focus on the temporal variation of in rBC rather than on absolute concentrations, the systematic underestimation of rBC does not affect the conclusions herein.

Levoglucosan concentrations were previously analyzed using high-performance liquid chromatography with electrospray ionization mass spectrometry (HPLC-ESI/MS) at the Max Planck Institute for Biogeochemistry, Jena, Germany. Further details on the analysis of levoglucosan are documented in Yao et al. (2013).

Stable oxygen isotopes ($\delta^{18}\text{O}$ values) were analyzed in the Laboratory of Tibetan Environment Changes and Land Surface Processes, Institute of Tibetan Plateau Research,

CAS, Beijing, China. The ice samples were melted at room temperature, and measured using a Picarro L2130-i Cavity Ring-Down Spectrometer. $\delta^{18}\text{O}$ measurements were provided as per mil deviations relative to the Vienna Standard Mean Ocean Water (VSMOW2). The analytical precision was 0.05‰. Stable oxygen isotope measurements from 64.18 to 68.57 m core depth were not available as the samples were lost during transport from Lanzhou to Beijing.

2.3 Ice Core Dating

Precipitation $\delta^{18}\text{O}$ on the northern Tibetan Plateau exhibits a distinct seasonal cycle with high values in the summer season and low values in the winter (Yao et al., 2013b and references therein). Modern observations at Muztagh Ata also show that precipitation $\delta^{18}\text{O}$ is significantly positively correlated with local air temperature (Yu et al., 2006; Li et al., 2006). Several ice cores retrieved from Muztagh Ata have been dated using $\delta^{18}\text{O}$, with reference layer of β activity peak in 1963 AD (e.g. Tian et al., 2006; Zhao et al., 2011; Wu et al., 2008; Liu et al., 2008). The Muztagh Ata ice core in the present study was also dated using seasonal variations in $\delta^{18}\text{O}$.

The upper snow pit samples of the Muztagh Ata ice core used in the present study were lost during transport from the mountain. Fortunately, the $\delta^{18}\text{O}$ profile of the upper sections of this ice core is very similar to that of another ice core (Wu et al., 2006; 2008) that was drilled at the same elevation in 2001. Based on the comparison with the $\delta^{18}\text{O}$ profile in Wu et al. (2006; 2008), the most recent annual layer in the Muztagh Ata ice core herein is dated to 2000 AD, and the top 64.18 m ice core is accordingly dated to cover the period 1875-2000 AD by annual layer counting of $\delta^{18}\text{O}$ (Figure 2). Dating uncertainty from 1963-2000 AD with a high resolution of $\delta^{18}\text{O}$ (9 samples per year on average) is estimated to be less than 3 years based on the depth of 1963 AD in another Muztagh Ata ice core from 6350 m a.s.l. (Liu et al., 2008), indicated by the β activity

peak associated with nuclear bomb tests. The dating uncertainty from 1875-1962 AD is larger due to lower resolution in the $\delta^{18}\text{O}$ record (4 to 9 samples per year). The annual ice thickness shows a thinning trend from the top to the bottom of ice core, consistent with thinning with depth that occurs in the glacier due to flow. Because we are predominantly interested in changes in BC on the decadal scale and relative changes in the rBC to levoglucosan records, the dating uncertainties do not affect the main conclusions of this study.

3. RESULTS AND DISCUSSION

3.1 Seasonal Dependence of rBC

High-resolution measurements of rBC concentrations show seasonal dependence with higher values during summer that are identified by a less negative value of $\delta^{18}\text{O}$ (Figure 2). This seasonal dependence is the same as that of airborne carbonaceous particles observed at the same site by Cao et al. (2009), who attributed the higher summertime concentrations to increased convective events in distant source regions and, therefore, more long-range transport to the site. Airborne BC particles can fall onto the ice/snow surface through either dry or wet deposition. The latter is more efficient and globally it accounts for 77% of carbonaceous aerosols removed from the atmosphere (Textor et al., 2006). More frequent local summer precipitation (two thirds of annual precipitation near this site fall between May and August) favors wet deposition of rBC on the glacier.

To further understand the influence of transport and deposition on the seasonal variation of rBC, we analyze results from a 10-year (1996-2005) Community Atmosphere Model version 5 (CAM5) simulation that was conducted to study the global source-receptor relationship of BC (Wang et al., 2014). The treatment of aerosol transport and wet removal in CAM5 has recently been modified to improve the model prediction of

global distributions of aerosols, especially for BC (Wang et al., 2013). The CAM5 simulated airborne BC concentrations during 1996-2005 in the model grid cell, where the Muztagh Ata ice-core drilling site is located, peak during summer (June, July and August) and/or autumn (September, October and November), and are lowest during spring (March, April and May), which agrees with the observed seasonal dependence of airborne BC concentrations from the Muztagh Ata Mountain (Cao et al., 2009). Additionally, the seasonal dependence of BC deposition flux in the Southeastern Tibetan Plateau in the CAM5 simulation is consistent with observations based on an ice core record (Wang et al., 2015). Because the ice-core drilling site is located in a remote and elevated area over the Pamirs, local emissions are minimal. The seasonal dependence of airborne BC is related to long-range transport of BC from remote source regions. As the monthly emissions used in the simulation vary little with seasons (e.g., in the surrounding regions, such as Central Asia, East Asia and South Asia, emissions in spring are either 10-30% higher or about 10% lower than in summer), differences in emissions cannot explain the large seasonal contrast of airborne BC concentrations between summer/autumn and spring (on average 74% higher in summer/autumn). Thus, the higher BC concentration in summer is most likely because of less BC removal during transport, as opposed to higher emissions. Moreover, the 10-year simulation of BC deposition flux at the ice-core drilling site also peaks in summer with much lower values in other seasons. This is also closely related to the high airborne BC concentrations in summer.

The seasonal dependence of rBC in the Eastern Pamirs differs from that reported for elsewhere over the Tibetan Plateau. As addressed above, rBC in this ice core presents high concentrations during summer and low during winter, whereas in the Himalayas and on the southeastern Tibetan Plateau BC concentrations in the atmosphere and recorded in glaciers are low during the summer monsoon season and high during the non-monsoon season (Nair et al., 2013; Ram et al., 2010; Hyvärinen et al., 2009; Kaspari et al., 2011;

Zhao et al., 2013; Xu et al., 2009b; Wang et al., 2015). Atmospheric BC over Waliguan Mountain on the northern Tibetan Plateau and over the Taklimakan Desert also has higher concentrations during the winter and spring seasons (Tang et al., 1999; Li et al., 2010). The seasonal dependence of BC at different locations of Tibetan Plateau to various extents is determined by seasonal variations in emissions, circulation patterns and rate of removal during transport. For example, in the southeastern Tibetan Plateau the seasonal dependence is primarily due to heavy precipitation in the summer monsoon, and relatively weak removal but stronger emissions from South Asia during winter and early spring (Wang et al., 2015). Unlike elsewhere over the Tibetan Plateau, the prevailing wind in the Eastern Pamirs is typically westerly year round, and the peak rBC in summer is likely because of more efficient transport from the Central Asia.

3.2 Temporal variation in rBC

According to the annual layer thickness and its depth in the ice core, the annual mean concentrations of BC were calculated. The annual rBC concentrations started increasing post 1960 AD, with a rapid increase beginning in ~1975 AD (Figure 3b). Peak annual rBC occurred at the end of the 1980s, followed by a drop during the 1990s and then an increase around 2000 AD. The measured rBC concentration had an annual average of 0.62 ng g^{-1} with the range from 0.05 to 3.51 ng g^{-1} during 1875 to 2000 AD. The average rBC concentration of 1.53 ng g^{-1} after 1975 AD was approximately four times higher than the average value before 1975 AD, which was 0.39 ng g^{-1} . This rapid increase is in agreement with results from the southeastern Tibetan Plateau and from Mt. Everest ice cores, which both indicate BC and/or rBC concentrations have increased threefold during the 1980s and 1990s relative to pre-1980s (Xu et al., 2009a; Kaspari et al., 2011). The timing of this increase is consistent with the annual BC flux recorded in Nam Co lake sediments, located in the southern Tibetan Plateau, which showed a rapid increasing trend after 1960 (Cong et al., 2013).

3.3 Differences in rBC and EC

The rBC in the present study is compared with the elemental carbon (EC) in a 41-meter Muztagh Ata ice core (Liu et al., 2008), measured by a two-step heating-gas chromatography system. The two records differ both in mass concentrations and in trends. EC in Liu et al. (2008) is about one magnitude higher than the rBC concentrations reported herein, and Liu et al. (2008) showed peak EC values during the 1950s-1960s, as opposed to during the 1980s in the present study. As the two ice cores were drilled close to each other, spatial variability is unlikely to account for the significant differences.

The differences in the analytical techniques likely account for some of the differences between the two Muztagh Ata ice cores. As mentioned in the previous section, the SP2 underestimates rBC concentrations due to losses of rBC during storage and in the nebulizer (Kaspari, et al., 2014; Wendl et al., 2014). Additionally, because the mass-size distribution of BC particles in snow is larger than in the atmosphere, some of the larger BC particles in snow are likely outside of the size range measured by the SP2 (~80-500 nm) in the current study (Schwarz et al., 2013; Lim et al., 2014). Schwarz et al. (2013) reported that the size distribution of rBC in fresh snow has a similar peak size to that of typical atmospheric BC particles but the size distribution tends to skew toward larger-BC size fraction; less than 1% (in mass) atmospheric BC particles have larger than 600 nm volume-equivalent diameter, whereas ~28% of BC particles in fresh snow do. Although these larger BC particles have much lower mass absorption efficiency and weaker absorption than smaller particles (Schwarz et al., 2013), they were not measured by the SP2, resulting in an underestimation of total BC mass concentrations. In contrast, the two-step heating-gas chromatography system used by Liu et al. (2008) preferentially measures large particles, whereas it has poorly characterized filtration efficiency and small particles may penetrate through the filters (Torres et al., 2014). The two-step heating-gas chromatography system can result in higher measured EC values than the

SP2 because: (1) Filter based thermal methods may overestimate EC and underestimate organic carbon (OC) as pyrolyzed OC was not monitored in this thermal method (Xu et al., 2006); and (2) High dust loads may result in positive biases of EC and OC because of inefficient removal of carbonates by acidifying the filters, although it may also result in negative biases by blocking carbon release (Wang et al., 2012). In addition to these uncertainties in the methods, differences in the measured concentrations may be due to the two methods not measuring the same carbon fraction. The thermal method used by Liu et al. (2008) measures all carbon oxidized at a temperature of 650°C, including non-EC components, including carbonates and brown carbon (light-absorbing organic carbon) (Rowland et al., 1952; Andreae and Gelencser, 2006; Bond et al., 2013). In contrast, the SP2 measures BC particles with a very high vaporization temperature (~2038 to 2371°C) that are often associated with very strong light absorption, hydrophobicity (Schwarz et al., 2006; Moteki and Kondo, 2010; Schwarz et al., 2010; Bond et al., 2013) and are representative of carbonaceous material produced by combustion (Schwarz et al., 2006; Slowik et al., 2007; Cross et al., 2010; Schwarz et al., 2010). Thus, the temporal variation of rBC concentration in the present study most likely represents the trend of combustion-generated BC, even though the nebulizer-SP2 system gives an underestimated rBC mass as discussed above.

To examine the temporal trends of rBC in the present study and EC in Liu et al. (2008), concentration annual anomalies (z-scores) in these two ice-core records were calculated by the following equation:

$$z_i = \frac{C_i - \bar{C}}{\sigma}$$

where C_i represents the annual concentration of rBC or EC in a specific year i ; $\bar{C}$ is the mean of annual concentrations in the entire time period, and σ is the standard deviation of annual concentrations. z-scores of rBC and EC concentrations were compared in

Figure 4. The differences in the trends of rBC and EC are greatest during the 1950s-60s when EC peaked, whereas rBC presented herein has relatively low concentrations. These differences are more likely due to differences in the particle sizes analyzed by both methods than due to the dust interference or pyrolyzed OC in the two-step heating-gas chromatography system. The Ca^{2+} record used as a dust indicator from a Muztagh Ata ice core (retrieved at 7010 m a.s.l.) was relatively low during the 1950s-60s (Zhao et al., 2011) when both EC and OC increased. This suggests that the higher EC concentrations are not caused by dust-induced analytical problems. Lastly, the simultaneous increases of EC and OC suggest a negligible contribution of pyrolyzed OC to the EC trend. Although there are substantial differences between the two records, both exhibit an increase in the mid-1970s and an obvious decrease starting at the end of 1980s.

3.4 Source Region Analysis

To identify source regions of air masses reaching the drilling site, backward trajectory analysis was conducted using the NOAA HYSPLIT model and the NCEP/NCAR global reanalysis meteorological dataset (Draxler and Rolph, 2003). The model was run every 6 hours for the whole year 2000. The frequency plot of 5-day back trajectories at the Muztagh Ata drilling site at 1000 m above ground level suggests that the high-level air masses over the Eastern Pamirs were most likely from Central Asia (Figure 5). Additionally, north Pakistan and the northwestern India, the Middle East and western Russia are also potential source regions.

To quantify the contribution of BC emissions from different source regions to BC deposition at the drilling site, the 10-year CAM5 simulation with BC emissions in potential source regions is explicitly tracked. The surrounding source regions include Central Asia (50°E–95°E, 35°N–50°N), North Asia (50°E–180°E, 50°N–66.5°N), South Asia (50°E–95°E, 5°N–35°N), East Asia (95°E–150°E, 15°N–50°N), and Europe

(25°W–50°E, 35°N–66.5°N). Details of model setup and experimental design can be found in Wang et al. (2014) and Wang et al. (2015). The model results show that BC emissions from Central Asia account for 81.9% of annual mean BC deposition at the ice-core drilling site, with a seasonal minimum of 78.9% in spring (March to May) and maximum of 86.6% in winter (December to February). Lesser annual mean BC contributions are from Europe (5.2%), South Asia (4.7%), and North Asia (4.0%). Emissions in East Asia, predominantly located downwind of the Eastern Pamirs, contribute only 1.3% to the annual mean BC deposition at the site. BC emissions from all of the above regions account for more than 97.2% of BC deposition at the drilling site, with only 2.8% from the rest of the world. Thus we conclude that Central Asia is the dominant source region for BC deposition at the Eastern Pamirs, which is consistent with the short-term back trajectory analysis.

The temporal variation of rBC in the ice core record is synchronous with energy-related BC emissions from the former USSR (including Russia and the countries of Central Asia) estimated by Bond et al. (2007) from 1980-2000 (Figure 3a). However, the ice core record does not exhibit a continuous increase in rBC concentration in the first half of the 20th century shown in energy-related emissions from the former USSR. In addition to the former USSR, emissions from South Asia and the Middle East may also contribute to the post-1960 AD rBC increase. Even though BC emissions in East Asia show a simultaneous increase with Muztagh Ata BC from 1960 AD to the end of 1980s, during the 1990s BC emissions from these regions continued increasing, whereas Muztagh Ata rBC concentrations decrease (Figure 3a). Thus BC emissions in East Asia likely play a minimal role in rBC deposition on Muztagh Ata glacier. Therefore, we believe that rBC deposition on the Muztagh Ata glacier is most likely dominated by transport of emissions from Central Asia, along with a minor contribution from western Russia and South Asia.

3.5 Contribution of Biomass Burning

To investigate the sources of rBC deposited on Muztagh Ata glacier, levoglucosan concentrations were measured. As a source-specific and environmentally stable molecular tracer of cellulose and hemi-cellulose burning, levoglucosan can be used as a molecular indicator for the long-range transport of biomass-burning emissions (Fraser and Lakshmanan, 2000). We note that “biomass-burning” in the present study includes open fires (i.e., forest fires, grass/wood land fires and agricultural waste fires) and energy-related combustion of biomass, including wood, agricultural waste, animal waste, charcoal, etc. Based on the ice core dating results, the annual mean concentration of levoglucosan is calculated (Figure 3c).

The average levoglucosan concentration over the length of the record is 26.5 ng g^{-1} . The levoglucosan concentration had a prominent increasing trend since the late 1970s, reached its maximum value (244.3 ng g^{-1}) at the beginning of the 1990s, and decreased after 1994 AD (Figure 3c). The levoglucosan concentration was also elevated during 1938-1954 AD with an average value of 35.4 ng g^{-1} , though the concentration during this time period was much lower than the average value during the period of 1978-2000 AD (76.9 ng g^{-1}). The rapid increase in levoglucosan concentration from the late 1970s to the early 1990s is consistent with the increase in levoglucosan from the mid-1970s to the mid-1990s detected in the ice core from the Ushkovsky ice cap (Kawamura et al., 2012). The low concentrations of levoglucosan (around 12.0 ng g^{-1}) during the two time periods, 1875-1937 AD and 1955-1977 AD, likely indicate the background level.

A similarity is shown in the temporal variation of levoglucosan concentrations with rBC (Figure 3). The significant correlation between rBC and levoglucosan concentrations at the 0.001 significant level ($R = 0.43$, $N = 341$) for the entire period 1875-2000 AD suggests that biomass burning emissions likely played an important role in contributing to

rBC deposited in this region. rBC and levoglucosan concentrations in the Muztagh Ata ice core reached their maximum values in the beginning of the 1990s, and decreased simultaneously during the 1990s, which was possibly due to a drop of energy demand associated with the breakup of the former USSR and economic recession in Eastern Europe and Central Asia. Anthropogenic sulfur emissions derived from fossil fuel (i.e., coal and crude oil) consumption by the former USSR and Eastern Europe show rapid decreases near the end of 1980s and the beginning of 1990s (Smith et al., 2011). A large decrease of sulfate in the 1990s has been detected in the ice core record from the Muztagh Ata glacier (Zhao et al., 2011). Acetate (CH_3COO^-) and formate (HCOO^-), which originate from anthropogenic emissions, also show rapid decreases in the 1990s, according to the ice core record from Tianshan mountains (Lee et al., 2003). Likewise, previous research on aerosol deposition on Belukha glacier in the Siberian Altai, which records mostly Eastern European sources, showed increases in anthropogenic emissions associated with industrialization starting in 1940 AD, reached maximum concentrations during the 1970s, and then decreased after 1990 AD (Eichler et al., 2012; Eichler et al., 2009; Olivier et al., 2006; Olivier et al., 2003). At Muztagh Ata the substantial increase in BC beginning in 1960 AD followed by even stronger increase during the mid-1970s was likely dominated by the increase in anthropogenic BC emissions during the industrial period.

It has been widely reported that emissions of levoglucosan from biomass burning vary with region, combustion conditions and fuel types (Simoneit et al., 1999; Fine et al., 2001; 2002; Sheesley et al., 2003; Oros and Simoneit, 2001a; 2001b; 2006; Zhang et al., 2006; Schauer et al., 2001; Mazzoleni et al., 2007; Sullivan et al., 2008; Puxbaum et al., 2007). Previous studies have used the ratios of levoglucosan to organic carbon (OC) or total carbon (TC, i.e., sum of OC and BC) to determine the contributions of wood burning and wild/agricultural fires to the atmospheric OC and BC (Puxbaum et al., 2007;

Yttri et al., 2009; 2011; 2014). In the current study, to investigate and discriminate open-fire BC emissions from anthropogenic energy-related BC emissions, the ratio of levoglucosan and rBC is used, based on an assumption that levoglucosan/rBC ratios have different and stable values in particulate emissions from open fires and energy-related biomass combustion. The levoglucosan/rBC ratio varied significantly from 1875-2000 AD with sporadic peaks (Figure 3d). The ratio was elevated during 1938-1954 AD, but relatively low during 1875-1937 AD and 1955-2000 AD. The peaks may indicate large forest fires/wildfires in western Siberia and/or Central Asia, as Siberia and European Russia are important source regions of total particulate matter emissions from fires (Randerson et al., 2007) (Figure 1).

The substantial increase in the levoglucosan/rBC ratio in the 1940s-50s reveals a significant influence of biomass burning during this time (Figure 3d). This may be influenced by enhanced fires during the Second World War from 1939-1945 AD, and increased agriculture burning during the 1950s due to cropland expansion in Central Asia (Kawamura et al., 2012). Another possible reason for the significant biomass burning in the 1940s-50s may be associated with forest fires, as the timing is consistent with the fire frequency variation in central Siberia reconstructed using dendrochronology (Panyushkina and Arbatskaya, 1999; Furyaev et al., 2001) and the fire history in Central Asia (Mouillot and Field, 2005). Additionally, the systematic increase in the levoglucosan/rBC ratio in the 1940s-1950s may relate to the warm period in the Northern Hemisphere around 1940 AD, when more frequent forest fires/wildfires in Siberia/Central Asia might have potentially occurred. However, even though levoglucosan increased significantly in the 1980s-1990s when the temperature of the Northern Hemisphere increased, the ratio did not show high values during the 1980s-1990s, as rBC increased rapid during the same time. Energy-related combustion of biomass as opposed to open fires was likely the main contributor to levoglucosan

variations after ~1980, because variations in levoglucosan were coincident with variations in rBC, which is associated with the sudden decrease of energy consumption and anthropogenic aerosol emissions at the beginning of 1990s. The Northern Hemisphere warming during the 1980s-1990s unlikely resulted in an increase in open fires because during the 1990s, when anthropogenic emissions (including fossil fuel combustion and energy-related biomass burning) decreased, the levoglucosan/rBC ratio did not show a significant increase as in the 1940s-1950s, but remained stable. Thus the significant increase of levoglucosan during the 1980s-1990s was mainly from the energy-related combustion of biomass. The lower levoglucosan/rBC ratio during the 1980s-1990s suggests that either there was less of an influence of open-fire emissions at this time, or larger contributions from fossil fuel emissions. If the lower levoglucosan/rBC ratio at that time was due to lower contributions from open fire emissions, higher precipitation in north Asia since the 1950s may have contributed to the less open burning (Bradley et al., 1987; Harris et al., 2014). Interestingly, Kawamura et al. (2012) found that the peaks of levoglucosan in an ice core drilled from the Ushkovsky ice cap on the Kamchatka Peninsula correspond to higher ambient temperature in the high latitudes of North Hemisphere. They attributed the peaks to increased transport of biomass burning emissions from the low and mid latitudes as the Arctic was warmed up.

In summary, the levoglucosan record suggests that biomass burning from open fires was significant during the 1940s-1950s; however, low rBC concentrations during the same time period indicate that open fires were not a major source of rBC deposited on the glaciers in the Pamirs at that time. Conversely, the elevated levoglucosan and relatively low and stable levoglucosan/rBC ratio during the 1980s-90s suggest an increase in energy-related combustion of biomass and fossil fuel at that time. Provided that energy-related biomass burning produces a smaller ratio of levoglucosan/rBC than open fires, the greatly increased levoglucosan concentrations in the 1980s-1990s likely

suggests that energy-related combustion of biomass was a more important contributor to rBC deposited on the glacier during the 1980s-1990s than before (i.e., from 1875-1978 AD). Energy-related human activities also consume fossil fuels and contribute to rBC deposited on the glacier. However, there is no further evidence from the ice-core measurements that can be used to differentiate contributions to the rBC concentrations from energy-related biomass burning versus fossil fuel combustion.

4. CONCLUSIONS

We measured rBC in an ice core from Muztagh Ata spanning 1875-2000 to reconstruct temporal variations in rBC deposition, and utilized levoglucosan measurements from the same ice core (Yao et al. 2013) to identify contributions to the rBC record from biomass burning. The rBC concentrations increased rapidly beginning in 1960 AD, peaked at the end of the 1980s, and then decreased. Based on the analysis of back trajectories and the regional BC energy-related emission inventories, the source region of rBC over east Pamirs is identified to be mainly the Former USSR, especially Central Asia. The similar trends in rBC and levoglucosan suggest that biomass burning, including open fires and anthropogenic energy-related biomass combustion, played an important role in contributing to rBC deposition on the Muztagh Ata glacier. The temporal variations in the levoglucosan/rBC ratio suggest that open fires peaked during the 1940s-1950s, however open fires did not result in a large increase in rBC concentrations recorded in the ice core. During the 1980s to 1990s, energy-related combustion of biomass and fossil fuels, as opposed to open fires, was the dominant source of rBC in the glacier.

This is the first time that changes in biomass-burning contributions to BC deposition spanning more than 100 years have been investigated on the Tibetan Plateau. This study highlights a possibly more important role that anthropogenic biomass combustion played

in contributing to historical BC emissions in recent decades, i.e., the 1980s-1990s. Reduction of biomass fuel burning may decrease BC emissions and deposition on the Tibetan glacier efficiently, and as a consequence reduce the effects of BC on climate change.

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508

509 References

- 510 Andreae, M. O. and Gelencsér, A.: Black carbon or brown carbon? The nature of light-absorbing
 511 carbonaceous aerosols, *Atmospheric Chemistry and Physics*, 6, 3131-3148,
 512 doi:10.5194/acp-6-3131-2006, 2006.
- 513 Bisiaux, M. M., R. Edwards, J. R. McConnell, M. A. J. Curran, T. D. Van Ommen, A. M. Smith, T. A.
 514 Neumann, D. R. Pasteris, J. E. Penner, and K. Taylor, Changes in black carbon deposition to
 515 Antarctica from two high-resolution ice core records, 1850–2000 AD. *Atmospheric Chemistry and*
 516 *Physics*, 12, 4107-4115, doi:10.5194/acp-12-4107-2012, 2012.
- 517 Baumgardner, D., G. L. Kok, and G. B. Raga. On the diurnal variability of particle properties related to
 518 light absorbing carbon in Mexico City. *Atmospheric Chemistry and Physics*, 7, 2517-2526, 2007.
- 519 Bond, T. C., S. J. Doherty, D. W. Fahey, P. M. Forster, T. Berntsen, B. J. DeAngelo, M. G. Flanner, S.
 520 Ghan, B. Kärcher, D. Koch, S. Kinne, Y. Kondo, P. K. Quinn, M. C. Sarofim, M. G. Schultz, M.
 521 Schulz, C. Venkataraman, H. Zhang, S. Zhang, N. Bellouin, S. K. Guttikunda, P. K. Hopke, M. Z.
 522 Jacobson, J. W. Kaiser, Z. Klimont, U. Lohmann, J. P. Schwarz, D. Shindell, T. Storelvmo, S. G.
 523 Warren, and Zender, C. S., Bounding the role of black carbon in the climate system: A scientific
 524 assessment. *Journal of Geophysical Research-Atmosphere*, 118, 5380–5552, doi:10.1002/jgrd.50171,
 525 2013.
- 526 Bond, T.C., E. Bhardwaj, R. Dong, R. Jogani, S. Jung, C. Roden, D.G. Street, and N.M. Trautmann,
 527 Historical emissions of black and organic carbon aerosol from energy-related combustion, 1850-2000.
 528 *Global Biogeochemical Cycles*, 21, GB2018, doi:10.1029/2006GB002840, 2007.
- 529 Bradley, R. S., H. F. Diaz, J. K. Eischeid, P. D. Jones, P. M. Kelly, and C. M. Goodess, Precipitation
 530 fluctuations over Northern Hemisphere land areas since the mid-19th century. *Science*, 237(4811),
 531 171-175, 1987.
- 532 Cao, J., B. Xu, J. He, X. Liu, Y. Han, G. Wang, and C. Zhu, Concentrations, seasonal variations, and
 533 transport of carbonaceous aerosols at a remote Mountainous region in western China. *Atmospheric*
 534 *Environment*, 43(29), 4444-4452, 2009.
- 535 Cong, Z., S. Kang, S. Gao, Y. Zhang, Q. Li, and K. Kawamura, Historical Trends of Atmospheric Black
 536 Carbon on Tibetan Plateau As Reconstructed from a 150-Year Lake Sediment Record. *Environmental*
 537 *science and technology*, 47(6), 2579-2586, 2013.
- 538 Cross, E. S., T. B. Onasch, A. Ahern, W. Wrobel, J. G. Slowik, J. Olfert, D. A. Lack, P. Massoli, C. D.
 539 Cappa, J. P. Schwarz, J. R. Spackman, D. W. Fahey, A. Sedlacek, A. Trimborn, J. T. Jayne, A.
 540 Freedman, L. R. Williams, N. L. Ng, C. Mazzoleni, M. Dubey, B. Brem, G. Kok, R. Subramanian, S.
 541 Freitag, A. Clarke, D. Thornhill, L. C. Marr, C. E. Kolb, D. R. Worsnop, and P. Davidovits. Soot
 542 particle studies—instrument inter-comparison—project overview. *Aerosol Science and*
 543 *Technology*, 44(8), 592-611, 2010.
- 544 Draxler, R. R., and G. D. Rolph, HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory)
 545 Model; NOAA Air Resources Laboratory: Silver Spring, MD, 2003. Available online:
 546 <http://www.arl.noaa.gov/ready/hysplit4.html>.
- 547 Eichler, A., L. Tobler, S. Eyrikh, G. Gramlich, N. Malygina, T. Papina, and M. Schwikowski, Three
 548 Centuries of Eastern European and Altai Lead Emissions Recorded in a Belukha Ice Core.
 549 *Environmental science and technology*, 46(8), 4323-4330, 2012.
- 550 Eichler, A., S. Brüttsch, S. Olivier, T. Papina, and M. Schwikowski, A 750 year ice core record of past
 551 biogenic emissions from Siberian boreal forests. *Geophysical Research Letters*, 36(18), 2009.
- 552 Fernandes, S. D., N. M. Trautmann, D. G. Streets, C. A. Roden, and T. C. Bond, Global biofuel use,

1850–2000. *Global Biogeochemical Cycles* 21, GB2019, doi:10.1029/2006GB002836, 2007.

Fine, P. M., G. R. Cass, and B. R. T. Simoneit, Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the northeastern United States. *Environmental Science and Technology* 35, no. 13 (2001): 2665-2675.

Fine, P. M., G. R. Cass, and B. R. T. Simoneit, Organic compounds in biomass smoke from residential wood combustion: Emissions characterization at a continental scale. *Journal of Geophysical Research: Atmospheres* (1984–2012) 107(D21), ICC-11, 2002.

Flanner, M. G., C. S. Zender, J. T. Randerson, and P. J. Rasch, Present-day climate forcing and response from black carbon in snow. *Journal of Geophysical Research: Atmospheres* (1984–2012), 112(D11), doi: 10.1029/2006JD008003, 2007.

Fraser, M. P., and K. Lakshmanan, Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols. *Environmental Science and Technology*, 34 (21), 4560–4564, 2000.

Furyaev, V. V., E. A. Vaganov, N. M. Tchebakova, and E. N. Valendik, Effects of fire and climate on successions and structural changes in the Siberian boreal forest. *Eurasian Journal of Forest Research*, 2, 1-15, 2001.

Hansen, J., and L. Nazarenko, Soot climate forcing via snow and ice albedos. *Proceedings of the National Academy of Sciences of the United States of America*, 101, 423-428, 2004.

Harris, I., P. D. Jones, T. J. Osborn, and D. H. Lister, Updated high - resolution grids of monthly climatic observations—the CRU TS3. 10 Dataset. *International Journal of Climatology*, 34(3), 623-642, 2014.

Hyvärinen, A - P., H. Lihavainen, M. Komppula, V. P. Sharma, V - M. Kerminen, T. S. Panwar, and Y. Viisanen, Continuous measurements of optical properties of atmospheric aerosols in Mukteshwar, northern India. *Journal of Geophysical Research: Atmospheres* (1984–2012), 114, no. D8, 2009.

Ito, A., and J. E. Penner, Historical emissions of carbonaceous aerosols from biomass and fossil fuel burning for the period 1870–2000. *Global Biogeochemical Cycles*, 19, GB2028, doi:10.1029/2004GB002374, 2005.

Jacobson, M. Z., Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature*, 409(6821), 695-697, 2001.

Junker, C., and C. Lioussé, A global emission inventory of carbonaceous aerosol from historic records of fossil fuel and biofuel consumption for the period 1860–1997. *Atmospheric Chemistry and Physics*, 8, 1195-1207, doi: 10.5194/acp-8-1195-2008, 2008.

Kaspari, S. D., M. Schwikowski, M. Gysel, M. G. Flanner, S. Kang, S. Hou, and P. A. Mayewski, Resent increase in black carbon concentrations from a Mt. Everest ice core spanning 1860-2000 AD. *Geophysical Research Letters*, 38, L04703, doi:10.1029/2010GL046096, 2011.

Kaspari, S., T. H. Painter, M. Gysel, S. M. Skiles, and M. Schwikowski, Seasonal and elevational variations of black carbon and dust in snow and ice in the Solu-Khumbu, Nepal and estimated radiative forcings, *Atmospheric Chemistry and Physics*, 14, 8089-8103, doi:10.5194/acp-14-8089-2014, 2014.

Kawamura, K., Y. Izawa, M. Mochida, and T. Shiraiwa, Ice core records of biomass burning tracers (levoglucosan and dehydroabietic, vanillic and p-hydroxybenzoic acids) and total organic carbon for past 300 years in the Kamchatka Peninsula, Northeast Asia. *Geochimica et Cosmochimica Acta*, 99, 317-329, 2012.

Kehrwald, N., R. Zangrando, A. Gambaro, and C. Barbante, Fire and climate: Biomass burning recorded in ice and lake cores, *EPJ Web Conf.*, 9, 105–114, 2010.

Kehrwald, N., R. Zangrando, P. Gabrielli, J. L. Jaffrezo, C. Boutron, C. Barbante, and A. Gambaro, Levoglucosan as a specific marker of fire events in Greenland snow, *Tellus Series B*, 64, 18196, 2012.

598 Lavanchy, V. M. H., H. W. Gäggeler, U. Schotterer, M. Schwikowski, and U. Baltensperger, Historical
 599 record of carbonaceous particle concentrations from a European high-alpine glacier (Colle Gnifetti,
 600 Switzerland). *Journal of Geophysical Research: Atmospheres*, 104(D17), 21227-21236, 1999.

601 Lee, X., D. Qin, G. Jiang, K. Duan, and H. Zhou, Atmospheric pollution of a remote area of Tianshan
 602 Mountain: Ice core record, *Journal of Geophysical Research: Atmospheres*, 108(D14), 4406,
 603 doi:10.1029/2002JD002181, 2003.

604 Li, J., K. Huang, Q. Wang, Y. Lin, F. Xue, J. Huang, S. J. Fu, and G. Zhuang, Characteristics and source of
 605 black carbon aerosol over Taklimakan Desert. *Science China Chemistry*, 53(5), 1202-1209, 2010.

606 Li, Z., T. Yao, L. Tian, B. Xu, and G. Wu., Variations of $\delta^{18}\text{O}$ in precipitation from the Muztagata Glacier,
 607 East Pamirs. *Science in China Series D*, 49(1), 36-42, 2006.

608 Lim, S., X. Faïn, M. Zanatta, J. Cozic, J.-L. Jaffrezo, P. Ginot, and P. Laj, Refractory black carbon mass
 609 concentrations in snow and ice: method evaluation and inter-comparison with elemental carbon
 610 measurement. *Atmospheric Measurement Techniques*, 7, 3549-3589, doi:10.5194/amtd-7-3549-2014,
 611 2014.

612 Liu, X., B. Xu, T. Yao, N. Wang, and G. Wu, Carbonaceous particles in Muztagh Ata ice core, west
 613 Kunlun Mountains, China. *Chinese Science Bulletin*, 53(21), 3379-3386, 2008.

614 Mazzoleni, L. R., B. Zielinska, and H. Moosmüller, Emissions of levoglucosan, methoxy phenols, and
 615 organic acids from prescribed burns, laboratory combustion of wildland fuels, and residential wood
 616 combustion. *Environmental science and technology*, 41(7), 2115-2122, 2007.

617 McConnell, J. R., R. Edwards, G. L. Kok, M. G. Flanner, C. S. Zender, E. S. Saltzman, J. Ryan Banta, D. R.
 618 Pasteris, M. M. Carter, and J. D. W. Kahl, 20th-century industrial black carbon emissions altered
 619 arctic climate forcing. *Science*, 317(5843), 1381-1384, 2007.

620 Ming, J., H. Cachier, C. Xiao, D. Qin, S. Kang, S. Hou, and J. Xu, Black carbon record based on a shallow
 621 Himalayan ice core and its climatic implications. *Atmospheric Chemistry and Physics* 8(5), 1343-1352,
 622 2008.

623 Moteki, N., and Y. Kondo. Dependence of laser-induced incandescence on physical properties of black
 624 carbon aerosols: Measurements and theoretical interpretation. *Aerosol Science and Technology*, 44(8):
 625 663-675, 2010.

626 Mouillot, F., and C. B. Field, Fire history and the global carbon budget: a 1 degree $\times$ 1 degree fire history
 627 reconstruction for the 20th century. *Global Change Biology*, 11(3), 398-420, doi: 10.1111/j.1365-
 628 2486.2005.00920.x, 2005

629 Nair, V. S., S. S. Babu, K. K. Moorthy, A. K. Sharma, and A. Marinoni, Black carbon aerosols over the
 630 Himalayas: direct and surface albedo forcing, *Tellus B*, 65, 2013.

631 Novakov, T., V. Ramanathan, J. E. Hansen, T. W. Kirchstetter, M. Sato, J. E. Sinton, and J. A. Sathaye,
 632 Large historical changes of fossil-fuel black carbon aerosols. *Geophysical Research Letters*, 30, 1324,
 633 doi: 10.1029/2002GL016345, 2003.

634 Ohata, S., N. Moteki, and Y. Kondo, Evaluation of a method for measurement of the concentration and size
 635 distribution of black carbon particles suspended in rainwater. *Aerosol Science and Technology*, 45(11),
 636 1326-1336, 2011.

637 Olivier, S., C. Blaser, S. Brütsch, N. Frolova, H. W. Gäggeler, K. A. Henderson, A. S. Palmer, T. Papina,
 638 and M. Schwikowski, Temporal variations of mineral dust, biogenic tracers, and anthropogenic
 639 species during the past two centuries from Belukha ice core, Siberian Altai. *Journal of Geophysical
 640 Research: Atmospheres* (1984-2012), 111(D5), 2006.

641 Olivier, S., M. Schwikowski, S. Brütsch, S. Eyrikh, H. W. Gäggeler, M. Lüthi, T. Papina, M. Saurer, U.
 642 Schotterer, L. Tobler and E. Vogel, Glaciochemical investigation of an ice core from Belukha glacier,
 643 Siberian Altai. *Geophysical Research Letters*, 30(19), 2003.

644 Oros, D. R., and B. R. T. Simoneit, Identification and emission factors of molecular tracers in organic
645 aerosols from biomass burning Part 1. Temperate climate conifers. *Applied Geochemistry*, 16(13),
646 1513-1544, 2001a.

647 Oros, D. R., and B. R. T. Simoneit, Identification and emission factors of molecular tracers in organic
648 aerosols from biomass burning Part 2. Deciduous trees. *Applied Geochemistry*, 16(13), 1545-1565,
649 2001b.

650 Oros, D. R., M. Abas, N. Y. M. Omar, N. A. Rahman, and B. R. T. Simoneit, Identification and emission
651 factors of molecular tracers in organic aerosols from biomass burning: Part 3. Grasses. *Applied*
652 *Geochemistry*, 21(6), 919-940, 2006.

653 Painter, T. H., M. G. Flanner, G. Kaser, B. Marzeion, R. A. VanCuren, and W. Abdalati, End of the Little
654 Ice Age in the Alps forced by industrial black carbon. *Proceedings of the National Academy of*
655 *Sciences*, 110(38), 15216-15221, 2013.

656 Panyushkina, I. P., and M. K. Arbatskaya, Dendrochronological approach to study flammability of forests
657 in Evenkia (Siberia). *Siberian Journal of Ecology*, 2, 167-173, 1999.

658 Puxbaum, H., A. Caseiro, A. Sánchez - Ochoa, A. Kasper - Giebl, M. Claeys, A. Gelencsér, M. Legrand, S.
659 Preunkert, and C. Pio, Levoglucosan levels at background sites in Europe for assessing the impact of
660 biomass combustion on the European aerosol background. *Journal of Geophysical Research:*
661 *Atmospheres (1984–2012)*, 112(D23), 2007.

662 Ram, K., M. M. Sarin, and P. Hegde, Long-term record of aerosol optical properties and chemical
663 composition from a high-altitude site (Manora Peak) in Central Himalaya. *Atmospheric Chemistry and*
664 *Physics*, 10(23), 11791-11803, 2010.

665 Ramanathan, V., and G. Carmichael, Global and regional climate changes due to black carbon. *Nature*
666 *Geoscience*, 1, 221–227, 2008.

667 Ramanathan, V., M. V. Ramana, G. Roberts, D. Kim, C. Corrigan, C. Chung, and D. Winker, Warming
668 trends in Asia amplified by brown clouds solar absorption. *Nature*, 448, 575-578, 2007.

669 Randerson, J. T., G. R. van der Werf, L. Giglio, G. J. Collatz, and P. S. Kasibhatla, Global Fire Emissions
670 Database, Version 2 (GFEDv2.1), 2007. Data set. Available on-line [<http://daac.ornl.gov/>] from Oak
671 Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, U.S.A.

672 Rowland, R. A., Differential thermal analysis of clays and carbonates, *Clays and Clay Minerals*, 1(1),
673 151-163, 1952.

674 Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Simoneit, Measurement of emissions from air
675 pollution sources. 3. C1-C29 organic compounds from fireplace combustion of wood. *Environmental*
676 *Science and Technology*, 35(9), 1716-1728, 2001.

677 Schwarz, J. P., J. R. Spackman, R. S. Gao, A. E. Perring, E. Cross, T. B. Onasch, A. Ahern, W. Wrobel, P.
678 Davidovits, J. Olfert, M. K. Dubey, C. Mazzoleni, and D. W. Fahey. The detection efficiency of the
679 single particle soot photometer. *Aerosol Science and Technology*, 44(8), 612-628, 2010.

680 Schwarz, J. P., R. S. Gao, A. E. Perring, J. R. Spackman, and D. W. Fahey, Black carbon aerosol size in
681 snow. *Scientific reports* 3, 2013.

682 Schwarz, J. P., R. S. Gao, D. W. Fahey, D. S. Thomson, L. A. Watts, J. C. Wilson, J. M. Reeves, M.
683 Darbeheshti, D. G. Baumgardner, G. L. Kok, S. H. Chung, M. Schulz, J. Hendricks, A. Lauer, B.
684 Kärcher, J. G. Slowik, K. H. Rosenlof, T. L. Thompson, A. O. Langford, M. Loewenstein, and K. C.
685 Aikin. Single-particle measurements of midlatitude black carbon and light-scattering aerosols from the
686 boundary layer to the lower stratosphere, *Journal of Geophysical Research*, 111, D16207,
687 doi:10.1029/2006JD007076, 2006.

688 Schwarz, J. P., S. J. Doherty, F. Li, S. T. Ruggiero, C. E. Tanner, A. E. Perring, R. S. Gao, and D. W.
689 Fahey, Assessing Single Particle Soot Photometer and Integrating Sphere/Integrating Sandwich

690 Spectrophotometer measurement techniques for quantifying black carbon concentration in snow.
691 *Atmospheric Measurement Techniques*, 5(11), 2581-2592, 2012.

692 Sheesley, R. J., J. J. Schauer, Z. Chowdhury, G. R. Cass, and B. R. T. Simoneit, Characterization of organic
693 aerosols emitted from the combustion of biomass indigenous to South Asia. *Journal of Geophysical*
694 *Research: Atmospheres* (1984–2012), 108(D9), 2003.

695 Simoneit, B. R., J. J. Schauer, C. G. Nolte, D. R. Oros, V. O. Elias, M. P. Fraser, W. F. Rogge, and G. R.
696 Cass, Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmospheric*
697 *Environment*, 33(2), 173-182, 1999.

698 Slowik, J. G., E. S. Cross, J.-H. Han, P. Davidovits, T. B. Onasch, J. T. Jayne, L. R. Williams, M. R.
699 Canagaratna, D. R. Worsnop, R. K. Chakrabarty, H. Moosmüller, W. P. Arnott, J. P. Schwarz, R.-S.
700 Gao, D. W. Fahey, G. L. Kok, and A. Petzold. An inter-comparison of instruments measuring black
701 carbon content of soot particles. *Aerosol Science and Technology*, 41(3), 295-314, 2007.

702 Smith, S. J., J. V. Aardenne, Z. Klimont, R. J. Andres, A. Volke, and S. Delgado Arias, Anthropogenic
703 sulfur dioxide emissions: 1850–2005. *Atmospheric Chemistry and Physics*, 11(3), 1101-1116, 2011.

704 Stephens, M., N. Turner, and J. Sandberg. Particle identification by laser-induced incandescence in a
705 solid-state laser cavity. *Applied Optics*, 42(19), 3726-3736, doi:10.1364/AO.42.003726, 2003.

706 Sullivan, A. P., A. S. Holden, L. A. Patterson, G. R. McMeeking, S. M. Kreidenweis, W. C. Malm, W. M.
707 Hao, C. E. Wold, and J. L. Collett. A method for smoke marker measurements and its potential
708 application for determining the contribution of biomass burning from wildfires and prescribed fires to
709 ambient PM_{2.5} organic carbon. *Journal of Geophysical Research: Atmospheres* (1984–2012),
710 113(D22), 2008.

711 Tang, J., Y. Wen, L. Zhou, D. Qi, M. Zheng, N. Trivett, and E. Wallgren, Observational study of black
712 carbon in clean air area of western China. *Quarterly Journal Of Applied Meteorology*, 10(2), 160-170,
713 1999. (in Chinese with English abstract)

714 Textor, C, M. Schulz, S. Guibert, S. Kinne, Y. Balkanski, S. Bauer, T. Berntsen, T. Berglen, O. Boucher, M.
715 Chin, F. Dentener, T. Diehl, R. Easter, H. Feichter, D. Fillmore, S. Ghan, P. Ginoux, S. Gong, A.
716 Grini, J. Hendricks, L. Horowitz, P. Huang, I. Isaksen, I. Iversen, S. Kloster, D. Koch, A. Kirkevåg, J.
717 E. Kristjansson, M. Krol, A. Lauer, J. F. Lamarque, X. Liu, V. Montanaro, G. Myhre, J. Penner, G.
718 Pitari, S. Reddy, Ø. Seland, P. Stier, T. Takemura, and X. Tie, Analysis and quantification of the
719 diversities of aerosol life cycles within AeroCom. *Atmospheric Chemistry and Physics*, 6(7),
720 1777-1813, 2006.

721 Thompson, L. G., E. Mosley-Thompson, M. E. Davis, J. F. Bolzan, J. Dai, T. Yao, N. Gundestrup, X. Wu,
722 L. Klein, and Z. XieKlein. Holocene—Late Pleistocene Climatic Ice Core Records from
723 Qinghai-Tibetan Plateau. *Science*, 246(4929), 474-477, 1989.

724 Tian, L., T. Yao, Z. Li, K. MacClune, G. Wu, B. Xu, Y. Li, A. Lu, and Y. Shen, Recent rapid warming
725 trend revealed from the isotopic record in Muztagata ice core, eastern Pamirs. *Journal of Geophysical*
726 *Research: Atmospheres*, 111(D13103), doi:10.1029/2005JD006249, 2006.

727 Torres, A., T. C. Bond, C. M. B. Lehmann, R. Subramanian, and O. L. Hadley, Measuring Organic Carbon
728 and Black Carbon in Rainwater: Evaluation of Methods, *Aerosol Science and Technology*, 48(3),
729 239-250, 2014.

730 Wang, H., P. J. Rasch, R. C. Easter, B. Singh, R. Zhang, P.-L. Ma, Y. Qian, S. J. Ghan, and N. Beagley.
731 Using an explicit emission tagging method in global modeling of source-receptor relationships for
732 black carbon in the Arctic: Variations, sources, and transport pathways, *Journal of Geophysical*
733 *Research*, 119, doi:10.1002/2014JD022297, 2014.

734 Wang, H., R. C. Easter, P. J. Rasch, M. Wang, X. Liu, S. J. Ghan, Y. Qian, J.-H. Yoon, P.-L. Ma, and V.
735 Vinoj. Sensitivity of remote aerosol distributions to representation of cloud–aerosol interactions in a
736 global climate model. *Geoscientific Model Development*, 6(3), 765-782, 2013.

737 Wang, M., B. Xu, H. Zhao, J. Cao, D. Joswiak, G. Wu, and S. Lin, The influence of dust on quantitative
738 measurements of black carbon in ice and snow when using a thermal optical method. *Aerosol Science*
739 *and Technology* 46(1), 60-69, 2012.

740 Wang, M., B. Xu, J. Cao, X. Tie, H. Wang, R. Zhang, Y. Qian, P. J. Rasch, S. Zhao, G. Wu, H. Zhao, D. R.
741 Joswiak, J. Li, and Y. Xie, Carbonaceous aerosols recorded in a southeastern Tibetan glacier: analysis
742 of temporal variations and model estimates of sources and radiative forcing, *Atmospheric Chemistry*
743 *and Physics*, 15, 1191-1204, doi:10.5194/acp-15-1191-2015, 2015

744 Wendl, I. A., J. A. Menking, R. Färber, M. Gysel, S. D. Kaspari, M. J. G. Laborde, and M. Schwikowski,
745 Optimized method for black carbon analysis in ice and snow using the Single Particle Soot Photometer,
746 *Atmospheric Measurement Techniques Discussions*, 7(3), 3075-3111, 2014.

747 B. Xu, C. Zhang, and S. Gao, Atmospheric dust aerosols over the Eastern Pamirs: major element
748 concentrations and composition. *Environmental Earth Sciences*, 61(6), 1227-1237, 2010.

749 Wu, G., T. Yao, B. Xu, L. Tian, Z. Li, and K. Duan, Seasonal variations of dust record in the Muztagata ice
750 cores. *Chinese Science Bulletin*, 53(16), 2506-2512, 2008.

751 Wu, G., T. Yao, B. Xu, Z. Li, L. Tian, K. Duan, and L. Wen, Grain size record of microparticles in the
752 Muztagata ice core. *Science in China Series D*, 49(1), 10-17, 2006.

753 Xu, B., J. Cao, J. Hansen, T. Yao, D. R. Joswiak, N. Wang, G. J. Wu, M. Wang, H. B. Zhao, W. Yang, X.
754 Liu, and J. He, Black soot and the survival of Tibetan glaciers. *Proceedings of the National Academy*
755 *of Sciences of United States of America*, 106, 22114-22118, 2009a.

756 Xu, B., M. Wang, D. R. Joswiak, J. Cao, T. Yao, G. Wu, W. Yang, and H. Zhao, Deposition of
757 anthropogenic aerosols in a southeastern Tibetan glacier. *Journal of Geophysical Research:*
758 *Atmospheres (1984–2012)*, 114(D17), 2009.

759 Xu, B., T. Yao, X. Liu, and N. Wang, Elemental and organic carbon measurements with a two-step
760 heating–gas chromatography system in snow samples from the Tibetan Plateau. *Annals of Glaciology*,
761 43(1), 257-262, 2006.

762 Yao, P., V. F. Schwab, V.-N. Roth, B. Xu, T. Yao, and G. Gleixner, Levoglucosan concentrations in
763 ice-core samples from the Tibetan Plateau determined by reverse-phase high-performance liquid
764 chromatography–mass spectrometry. *Journal of Glaciology*, 59(216), 599, 2013a.

765 Yao, T., V. Masson - Delmotte, J. Gao, W. Yu, X. Yang, C. Risi, C. Sturm, M. Werner, H. Zhao, Y. He, W.
766 Ren, L. Tian., C. Shi, and S. Hou, A review of climatic controls on $\delta^{18}\text{O}$ in precipitation over the
767 Tibetan Plateau: Observations and simulations. *Reviews of Geophysics*, 51(4), 525-548, 2013b.

768 Yttri, K. E., C. Dye, O.-A. Braathen, D. Simpson, and E. Steinnes, Carbonaceous aerosols in Norwegian
769 urban areas. *Atmospheric Chemistry and Physics*, 9(6), 2007-2020, 2009.

770 Yttri, K. E., C. Lund Myhre, S. Eckhardt, M. Fiebig, C. Dye, D. Hirdman, J. Ström, Z. Klimont, and A.
771 Stohl, Quantifying black carbon from biomass burning by means of levoglucosan – a one-year time
772 series at the Arctic observatory Zeppelin, *Atmospheric Chemistry and Physics*, 14, 6427-6442,
773 doi:10.5194/acp-14-6427-2014, 2014.

774 Yttri, K. E., D. Simpson, K. Stenström, H. Puxbaum, and T. Svendby, Source apportionment of the
775 carbonaceous aerosol in Norway–quantitative estimates based on ^{14}C , thermal-optical and organic
776 tracer analysis. *Atmospheric Chemistry and Physics*, 11(17), 9375-9394, 2011.

777 Yu, W., T. Yao, L. Tian, Z. Li, W. Sun, and Y. Wang, Relationships between $\delta^{18}\text{O}$ in summer precipitation
778 and temperature and moisture trajectories at Muztagata, western China. *Science in China Series D*,
779 49(1), 27-35, 2006.

780 Zhang, Y., M. Shao, Y. Zhang, L. Zeng, L. He, B. Zhu, Y. Wei, and X. Zhu, Source profiles of particulate
781 organic matters emitted from cereal straw burnings. *Journal of Environmental Sciences*, 19(2007),
782 167-175, 2006.

- 783 Zhao, H., B. Xu, T. Yao, L. Tian, and Z. Li, Records of sulfate and nitrate in an ice core from Mount
784 Muztagata, central Asia. *Journal of Geophysical Research: Atmospheres* (1984–2012), 116(D13),
785 2011.
- 786 Zhao, Z., J. Cao, Z. Shen, B. Xu, C. Zhu, L. - W. Antony Chen, X. Su, S. Liu, Y. Han, G. Wang, and K.
787 Ho. Aerosol particles at a high - altitude site on the Southeast Tibetan Plateau, China: Implications for
788 pollution transport from South Asia. *Journal of Geophysical Research: Atmospheres*, 118(19), 11-360,
789 2013.

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792 Figure 1. Location of the Muztagh Ata ice core drill site (black square), and spatial
793 distribution of total particle matter emissions from fires (red) (Randerson et al.,
794 2007).

Figure 2. The Muztagh Ata $\delta^{18}\text{O}$ and rBC concentrations corresponding to ice core depth. Gray dashed lines with dots illustrate $\delta^{18}\text{O}$ and rBC concentration of each sample, and solid lines are 5-value averages ($\delta^{18}\text{O}$ in red; rBC in black). The vertical cyan dashed lines identify ice core annual layers.

Figure 3. (a) Temporal variations of regional BC emissions (Bond et al., 2007), (b) Muztagh Ata rBC concentrations, (c) levoglucosan concentrations (from Yao et al., 2013), and (d) The levoglucosan/rBC ratio from the Muztagh Ata ice core spanning 1875-2000. Gray bars illustrate annual concentrations, and red bold lines indicate 5-year running averages. Cyan bars show the annual ratios, and the dark blue solid line is the 5-year running average.

Figure 4. Temporal patterns of rBC (this study) and EC concentrations (Liu et al., 2008) from two Muztagh Ata ice cores shown as anomalies (z-scores).

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Figure 5. 5-day backward air mass trajectory frequency for Muztagh Ata at 1000 m above ground level in 2000 AD based on HYSPLIT results. The red square indicates the location of the Muztagh Ata ice core drill site.