

10Be/7Be implies the contribution of stratosphere-troposphere transport to the winter-spring surface O3 variation observed on the Tibetan Plateau

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Received July 7, 2010; accepted September 19, 2010

10Be/7Be is a stratospheric sensitive tracer. In this paper, measurements of 10Be/7Be and surface O3 from October 2005 to May 2006 at Mt. Waliguan (hereafter WLG, 100.898°E, 39.287°N, 3810 m, a.s.l.), China global atmospheric watch (GAW) observatory, are introduced and used to investigate the stratosphere-troposphere transport (STT) and its impact on surface O3 on the Tibetan Plateau. The results show that the magnitude of STT is weak in winter, followed by strengthening from the end of winter to the middle of spring (from mid February to mid April) with large increases in 10Be, 7Be, 10Be/7Be and surface O3. At the end of spring (from the end of April to mid May in this paper), the STT weakened, and the continuous increase of surface O3 at WLG is produced by tropospheric photochemistry reactions.

Citation: Zheng X D, Shen C D, Wan G I, et al. 10Be/7Be implies the contribution of stratosphere-troposphere transport to the winter-spring surface O3 variation observed on the Tibetan Plateau. Chinese Sci Bull, 2011, 56: 84~88, doi: 10.1007/s11434-010-4211-3

7Be and 10Be are produced mainly from collisions of cosmic rays with oxygen and nitrogen atoms in the upper atmosphere, including the upper troposphere and stratosphere. Both 7Be and 10Be are absorbed easily by sub-micrometer-size aerosol particles once produced. 7Be as a natural tracer of downward transport from the upper atmosphere had been gradually established since the 1960s, and the first application of 10Be/7Be as a stratospheric tracer was addressed by Rasebeck et al. [1] in 1981. The half-lives of 7Be and 10Be are 53.3 d and 1.5×106 a, respectively, while the average age of the stratospheric air mass is ~1.5 a. In the stratosphere, although the initial production rate of 10Be is lower than that of 7Be, the 10Be/7Be increases as the 7Be isotope naturally decays to a lower concentration until reaching its equilibrium concentration, resulting in higher 10Be/7Be. In the troposphere, the ratio of 10Be/7Be is little influenced by wet deposition scavenging of aerosol particles because they are from the same source, making the ratio a more sensitive tracer of stratosphere than using 7Be or 10Be alone. Research on 10Be measurements is mainly conducted in the field of paleoclimatology. However, as a natural stratospheric tracer, 10Be/7Be effectively indicates the contribution of Stratosphere-Troposphere Transport (STT) to surface-level O3 variations as observed in the European Alps and Arctic regions [2,3]. Jordan et al. [4] reported latitudinal distribution of 10Be/7Be values in the upper troposphere and lower stratosphere over several regions through analysis of extensive aircraft aerosol samples. However, publications of at-
mospheric $^{10}$Be measurements are still limited because of the complexities in $^{10}$Be target preparation and $^{10}$Be detection by Accelerator Mass Spectrometry (AMS). Shen et al. [5] reported short-term $^{10}$Be concentrations in dust deposition sampled in Beijing and Ningbo. Measurements of $^{10}$Be/$^{7}$Be in atmospheric aerosol samples have not yet been reported in China.

Tropospheric $O_3$ is a significant trace gas due its oxidation and greenhouse characteristics. Tropospheric photochemical production and the direct or indirect STT are the two primary sources of tropospheric $O_3$. The debate on which source is dominant is ongoing, especially on the extensive spring peaks in surface $O_3$ in the northern hemisphere [6]. With respect to atmospheric circulation, the seasonally intensified downward transport branch (presented as STT) of the stratospheric Brewer-Dobson circulation in the northern hemisphere increases the fraction of stratospheric $O_3$ in troposphere, contributing to the rise of surface $O_3$ [7]. However, atmospheric chemistry suggests that as the solar radiation seasonally increases in spring, tropospheric $O_3$ may be largely produced in the short-term through photochemical reactions with precursors, such as NOx, which are emitted in significant amounts in winter [8].

Mt. Waliguan (hereafter WLG) is located on the northeast margin of the Tibetan Plateau. It was selected as a site for China’s Global Atmospheric Watch (GAW) observatory. Long-term observations reveal that surface $O_3$ at WLG increases from winter to spring, reaching its maximum in June. There are several publications presenting possible mechanisms of the summer $O_3$ maximum at WLG [9–13]. However, the mechanisms for winter and spring surface variations at WLG require elucidation. In this paper, weekly concentrations of $^7$Be and $^{10}$Be measured on aerosol samples obtained from October 2005 to May 2006 at WLG are presented, and $^{10}$Be/$^7$Be is used as a sensitive stratospheric tracer to investigate the STT and its contribution to winter-spring variation in surface $O_3$.

1 Measurements and data set

Measurements of $^7$Be and $^{210}$Pb analysis were described in an earlier study [14]. Every aerosol particle sample was continuously collected over one week by a pump with flow rate of ~1.3 m$^3$ min$^{-1}$. The collector is a three-layered polypropylene filter. The sampled filters were then sent to the State Key Laboratory of Earth Geochemistry (SKLEG), Chinese Academy of Sciences, to measure $^7$Be and $^{210}$Pb. The total relative measurement errors are from ±1.4% to ±6.4% [14]. Complying with the standard operation procedures issued by the World Meteorological Organization (WMO), surface $O_3$ at WLG is routinely measured by UV absorption analyzers (Thermal Environment, Model 49C) with a precision of ±2×10$^{-9}$ volume mixing ratio [15]. The long-term surface $O_3$ data is also periodically audited by the assigned WMO laboratory with stringent inter-comparison measurements [16].

After $^7$Be and $^{210}$Pb were analyzed, the aerosol samples were sent to the Key Laboratory of Isotope Geochronology and Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, for target preparation for AMS $^{10}$Be analysis. The detailed procedures for making $^{10}$Be targets have been described in other references [5,17]. Briefly, the filters were alternately pulverized and leached to extract final $^{10}$Be residues in BeO. The $^{10}$Be AMS target was made by mixing Nb powder with the BeO. These targets were sent to the 6 MeV EN tandem AMS system, National Key Laboratory of Nuclear Physics and Technology, Peking University for $^{10}$Be measurements. The detection limit of $^{10}$Be in the AMS system is $6×10^{-15}$. The standard, $^{10}$Be/$^{9}$Be, is $2.67×10^{-11}$ with a precision higher than 5‰, and was imported from the US National Institute of Standards and Technology [18]. The total relative error for the $^{10}$Be determination is estimated to within ±5%, including errors caused by the efficiency of leaching filters and $^{10}$Be measurements [17].

2 Results and analysis

Figure 1 shows the weekly concentrations of $^7$Be, $^{10}$Be and $^{210}$Pb at WLG from October 2005 to May 2006. Because precipitation is the most significant sink for the Be and Pb isotopes, weekly precipitation and occurrence fog are also shown in Figure 1. The variations in $^7$Be and $^{10}$Be concentrations are generally consistent. $^{10}$Be concentration was lower than that of $^7$Be before February 2006, and then rose, exceeding $^7$Be concentration. After mid April, both $^{10}$Be and $^7$Be concentrations began to decrease. The weekly variations in Be isotope concentration are somewhat associated with synoptic processes indicated by precipitation and fog records. Be isotope concentration increased almost continuously during two periods with little precipitation, one was from circa December 2005 to February 2006, another was from circa mid of March to mid of April in 2006. However, in the second dry period, Be concentrations increased as a result of STT (Figure 2). Be isotope concentrations began to reduce after mid April as precipitation increased.

The main source of $^{210}$Pb is from land surface emission. Figure 1 shows that $^{210}$Pb concentration in the spring did not increase as did Be isotopes. When maximum $^{210}$Pb concentrations occurred in winter, concentrations of Be isotope did not rise correspondingly. These comparisons suggest that dust or soil emissions have little impact on variation in Be isotope concentration at WLG, and the cause of spring $^{10}$Be and $^7$Be enhancement is only the intensified STT. The temporal increases of $^{210}$Pb, $^{10}$Be and $^7$Be concentration during the two non-precipitation periods are due to weak wet scavenging. To some extent, the general decreasing trend of $^{210}$Pb concentration from winter to spring is associated with
seasonal increase in precipitation.

Figure 2 presents weekly variations of surface O₃ concentration, ¹⁰Be/⁷Be, and ⁷Be/²¹⁰Pb. ⁷Be/²¹⁰Pb is considered to be a tracer unaffected by wet scavenging processes. The STT during the period from 15 February to the end of April is evidenced by the simultaneous elevations of surface O₃ and ¹⁰Be/⁷Be. However, for the last five samples starting from the end of April, the clear reductions of ¹⁰Be/⁷Be reveal a weakening of STT. At the same time, the continuous increase of surface O₃ at WLG supports dominant tropospheric photochemical O₃ production. This transfer is consistent with estimations of monthly average surface O₃ budget using the ⁷Be observation alone. In that study, the contribution from STT to the surface O₃ budget in May 2003 was concluded to be less than that in April and June, and the input from tropospheric chemical production was dominant for the surface O₃ budget [19].

Using high values of ⁷Be/²¹⁰Pb, studies have plausibly interpreted that summer surface O₃ at WLG is influenced by downward transport from the upper atmosphere [12,13]. However, the last four samples in Figure 2 demonstrate the different physical processes implied by ⁷Be/²¹⁰Pb, and ¹⁰Be/⁷Be. Obviously, the implication of strengthening downward transport from the stratosphere is not reasonable based on the observed increase of ⁷Be/²¹⁰Pb alone. Due to differences in the source distribution, ²¹⁰Pb is more sensitive to wet scavenging than Be isotopes [20], and this caused a higher ⁷Be/²¹⁰Pb ratio at the end of spring and even throughout the summer at WLG, but a corresponding strengthening STT did not occur.

The inter-comparisons of ¹⁰Be, and ¹⁰Be/⁷Be ratio between WLG and the other sites are given in Table 1. It has been noted that ⁷Be concentrations tend to have the highest values in comparisons with data obtained at the sites with elevations or latitudes similar to WLG [23]. In Table 1, ¹⁰Be also tends to have the highest concentration at WLG, but the case for ¹⁰Be/⁷Be is much different given the fact that WLG is located at lower latitude. Although being at high elevation,
O3 may also influence the interpretation of 10Be/7Be. To reside in aerosol particles, and the fact that behavior of fluorine is influenced by wet scavenging. However, because Be isotopes are generally higher than those measured at other sites. In winter the relatively lower 10Be/7Be and surface O3 concentration demonstrates the weakness of STT and its impact on surface O3. From the end of winter to the middle of spring (from mid February to mid April), continuous elevations of 10Be, 7Be, and surface O3 concentration and 10Be/7Be support the seasonal intensified STT and its positive contribution to the surface O3 budget. At the end of spring (from the end of April to mid of May in this study), the reductions of 10Be and 7Be concentration and 10Be/7Be suggest weakening of the STT, while the continuous increase of surface O3 at WLG is from the positive input of tropospheric photochemical reactions.

3 Discussion

Some transport processes at time scales of less than one week would be smoothed in the data because of the fixed weekly sampling for 10Be/7Be determination, especially in the case of deep STT that generally persists for just 1–2 d or less. For an individual sampling week with a lasting precipitation event, the correlations between surface O3 and 10Be/7Be were generally higher than those measured at other sites. However, in winter the relatively lower 10Be/7Be and surface O3 concentration demonstrates the weakness of STT and its impact on surface O3. From the end of winter to the middle of spring (from mid February to mid April), continuous elevations of 10Be, 7Be, and surface O3 concentration and 10Be/7Be support the seasonal intensified STT and its positive contribution to the surface O3 budget. At the end of spring (from the end of April to mid of May in this study), the reductions of 10Be and 7Be concentration and 10Be/7Be suggest weakening of the STT, while the continuous increase of surface O3 at WLG is from the positive input of tropospheric photochemical reactions.

| Location       | Lat., Long., and altitude a.s.l. | Location Lat., Long., and altitude a.s.l. |
|----------------|---------------------------------|------------------------------------------|
| Jungfraujoch   | 46.533°N, 7.983°E, 3.58 km      | WLG (Fall and Winter) 36.287°N, 100.89°E, 3.81 km |
| Zugspitze      | 47.416°N, 10.983°E, 2.962 km    | WLG (for all samples) 36.287°N, 100.89°E, 3.81 km |
| Alert          | 2.5°N, 62.3°W                  | PEM-B, Flight#17 39°–44°N, 136°–139°E, troposphere |
| Ljungbyhed     | 56.08°N, 13.23°E,              | SONEX, Flight#8 55°–68°N, 5.4°W–11.9°E, troposphere |
| Visby          | 57.63°N, 18.32°E,              | Northern Hemisphere North to 50°N, West Pacific Ocean |
| Kiruna         | 67.84°N, 20.34°E,              | Southern Hemisphere South to 60°S, Pacific Ocean |
| Antarctica     | South Pole, 2.8 km             | N/A                                      |
| WLG            | 3.81 km                        | N/A                                      |
| WLG (for all samples) | 36.287°N, 100.89°E, 3.81 km | 7.53–25.4                               |
| WLG (Fall and Winter) | 36.287°N, 100.89°E, 3.81 km | 7.53–12.3                               |
| PEM-B, Flight#17 | 39°–44°N, 136°–139°E, troposphere | 0.9–3.6 [4]                               |
| SONEX, Flight#8 | 55°–68°N, 5.4°W–11.9°E, troposphere | 1.1–126 [4]                               |
| Northern Hemisphere | North to 50°N, West Pacific Ocean | N/A                                      |
| Southern Hemisphere | South to 60°S, Pacific Ocean   | N/A                                      |

4 Conclusion

Winter and spring concentrations of 10Be and 7Be at WLG are generally higher than those measured at other sites. However, in winter the relatively lower 10Be/7Be and surface O3 concentration demonstrates the weakness of STT and its impact on surface O3. From the end of winter to the middle of spring (from mid February to mid April), continuous elevations of 10Be, 7Be, and surface O3 concentration and 10Be/7Be support the seasonal intensified STT and its positive contribution to the surface O3 budget. At the end of spring (from the end of April to mid of May in this study), the reductions of 10Be and 7Be concentration and 10Be/7Be suggest weakening of the STT, while the continuous increase of surface O3 at WLG is from the positive input of tropospheric photochemical reactions.

We thank Dr. H. N. Lee from the Environmental Measurements Laboratory, Department of Homeland Security, New York, USA for providing instruments for in-situ aerosol sampling. We acknowledge the operational work done at Mt. Waliguan, China Global Atmospheric Observatory. This work was supported by the National Science Foundation of China (40575013, 40175032 and 40830102).

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