# スバールバル諸島ニーオルスンにおける大気中酸素/窒素比の高精度連続観測

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# High-precision continuous measurement of the atmospheric O2/N2 ratio at Ny-Ålesund, Svalbard

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#### Introduction

Simultaneous observations of atmospheric  $O_2$  (defined as  $O_2/N_2$  ratio) and  $CO_2$  concentrations provide valuable information about the global carbon cycle. For example, data from long-term observations allows us to estimate land biotic and oceanic  $CO_2$  sinks sepatrately. For a better understanding of the global carbon cycle in terms of atmospheric  $O_2$ , several laboratories have developed precise measurement system for the atmospheric  $O_2/N_2$  ratio and have conducted simultaneous observations of the atmospheric  $O_2/N_2$  ratio and  $CO_2$  concentration mainly using descrete flask samping with subsequent laboratory analysis (e.g. Maning and Keeling, 2006). To elucidate the variations of the atmospheric  $O_2/N_2$  ratio in more detail, continuous measurements have been made recently (e.g. Stephens et al., 2007, van der Laan-Luijkx et al., 2010). We have also developed a high-precision continuous measurement system for the atmospheric  $O_2/N_2$  ratio, and initiated systematic observation at Ny-Ålesund (78°55'N, 11°56'E), Svalbard since November 2012 (Goto et al., 2013a), which is the first continuous observation in the Arctic region. Here, we present our measurement system and the results obtained so far.

#### Method

A differential fuel-cell oxygen analyzer (Oxizilla II, Sable Systems) is employed for our measurement system. In this analyzer, sample air or standard air pass through one fuel cell, flowing a reference air through another cell. To obtain highly precise values of the atmospheric  $O_2/N_2$  ratio, pressure fluctuations of the sample air, standard air and reference air were controlled to within an order of  $10^{-3}$  Pa by using flow regulation valves and differential pressure sensors, with the temperature inside of the analyzer stabilized to  $32.0 \pm 0.1$  °C (Goto et al., 2013b). This system is also equipped with a NDIR analyzer to measure  $CO_2$  concentration simultaneously. To calibrate the analyzer, we use two working standard air prepared by adjusting the  $O_2/N_2$  ratio of dried and compressed natural air. Their  $O_2/N_2$  ratios are determined against our primary standard air system (Ishidoya et al., 2003). Considering the remoteness of the observation site, special attention was paid to the measurement system, in that: (1) the system can be controlled remotely from Japan via the Internet; (2) all of the output data from the system can be monitored and collected in Japan via the Internet; and (3) a specially designed water trap based on a Stirling cooler is employed to automate the removal of the water vapor contains in the sample air. The analytical precision of the system was estimated to be within 4.0 per meg (1\sigma) of replicate analyses of the same sample air.

### **Results and discussion**

Caracteristic events of the atmospheric  $O_2/N_2$  ratio were sometimes observed at Ny-Ålesund. For example, on November 14–21, 2012, the  $O_2/N_2$  ratio decreased by about 22 per meg (=4.6 ppm) and then returned to its original level, while the CO<sub>2</sub> concentration increased by about 3 ppm and then decreased by about 45 per meg (=9.4 ppm) and CO<sub>2</sub> concentration increased by about 6 ppm. The  $O_2:CO_2$  exchange ratio defined as the slope of a liner regression line between the measured values of  $O_2/N_2$  ratio and CO<sub>2</sub> concentration were calcurated to be  $-1.53 \pm 0.12$  ppm/ppm for the former event and  $-1.59 \pm 0.46$  ppm/ppm for the later event. It is known that the  $O_2:CO_2$  exchange ratio depends on the process that controls their variation. For example, the  $O_2:CO_2$  exchange ratio associated with fossil fuel burning is estimated to be 1.83-2.00 ppm/ppm for natural gas, 1.52-1.56 ppm/ppm for gasline, 1.39-1.44 ppm/ppm for oil, and 1.17 for coal (Keeling, 1988). The values of  $O_2:CO_2$  exchange ratio associated two events at Ny-Ålesund are close to that for gasoline. Therefore, the cause of those variations of  $O_2/N_2$  ratio and CO<sub>2</sub> concentration would be attributable to the transport of polluted air affected by fossil fuel combustion in urban areas. In fact, the results of the backward trajectory analysis indicated that the air masses arrived at Ny-Ålesund on November 14–21, 2012 and February 5–9, 2013 passed near or over Oslo, Norway and Moscow, Russia,

respectively. Because CO<sub>2</sub> emission data for indivisual fossil fuel type in each countory are available from the Carbon Dioxide Information Analysis Center (CDIAC), we can estimate an average O<sub>2</sub>:CO<sub>2</sub> exchange ratio for each country. We actually calculated the average O<sub>2</sub>:CO<sub>2</sub> exchange ratio in Norway and Russia to be -1.54 ppm/ppm and -1.62 ppm/ppm, respectively, and these ratios are in good agreement with  $-1.53 \pm 0.12$  ppm/ppm and  $-1.59 \pm 0.46$  ppm/ppm observed at Ny-Ålesund on Nobember 14–21, 2012 and February 5–9, 2013.

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