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Evaluations of the ocean heat contents and marine biospheric activities based on long-term observations of the atmospheric constituents
（Abstract of the Interim Report）

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1. Introduction

Variations in the Ar/N_2 ratio in air are driven principally by air-sea Ar and N_2 fluxes associated with changes in seawater solubility. On the other hand, the Atmospheric Potential Oxygen ($APO = O_2 + 1.1xCO_2$), derived from the O_2/N_2 ratio and CO_2 concentration measurements, varies due mainly to the marine biospheric and solubility-driven air-sea O_2 and N_2 fluxes. Therefore, simultaneous observations of the Ar/N_2 ratio and APO will provide useful information for detecting changes in the spatiotemporally-integrated air-sea heat flux or ocean heat content (OHC) and the marine biospheric activities. For this purpose, not only precise atmospheric observations but also developments of precise Ar and O_2 standard mixtures traceable to SI (International System of Units) are necessary to determine changes in atmospheric Ar/N_2 and O_2/N_2 ratios accurately. Simultaneous observations of the O_2/N_2 ratio, CO_2 concentration and its stable isotopic ratios ($\delta^{13}C$ and $\delta^{18}O$) are also useful for quantifying the oceanic and terrestrial biospheric carbon cycles. Rn indicates characteristic of continental air transport so that it is a useful tracer to distinguish short-term pollutant air from the background air. N_2O includes information of ocean ventilation. Therefore, we conduct observations of the above-mentioned atmospheric constituents at the stations of Minamitorishima (MNM; 24°17'N, 153°59'E) and Ryori (RYO; 39°02'N, 141°49'E), operated by the Japan Meteorological Agency for the long-term operational observations of major trace gases such as CO_2, CH_4, CO, and O_3 concentrations.

2. Research Objectives

In this study, we will conduct synthetic analyses for evaluating changes in the ocean heat contents and marine biospheric activities by using long-term observational data of the atmospheric Ar/N_2 ratio, O_2/N_2 ratio, $\delta^{13}C$ and $\delta^{18}O$ of CO_2, Rn and N_2O concentrations at MNM and RYO. We continue continuous measurements and/or flask-based observations of O_2/N_2, $\delta^{13}C$ and $\delta^{18}O$ of CO_2, and Rn and N_2O concentrations at MNM and RYO. The automated air sampling system to collect air samples of which artificial fractionation of Ar and N_2 being minimized will newly be installed at both sites to start precise observations of the Ar/N_2 ratio. We will also develop high-precision Ar and O_2 gravimetric standard mixtures traceable to SI for the precise atmospheric observations.

3. Research Methods

MNM has an area of 1.5 km^2 and is covered with sparse evergreen shrub and grass. Maritime air from easterly winds prevails throughout the year. Continental air masses from East Asia are

sometimes transported by the synoptic-scale weather perturbations, but the influences of local sources and sinks within this small island are negligible for trace gas observations. RYO is located on the east coast of the northeastern part of Japan and the ridge of a hill along the sawtooth coastline facing the Pacific Ocean, at an elevation of 260 m above the sea level. Northwesterly winds from the Siberian high pressure dominate the site throughout the year. In summer, southerly winds associated with the Pacific subtropical high are often observed.

The atmospheric Ar/N_2 is measured by using a mass spectrometer[1]. This year, we have continued observations of the Ar/N_2 at RYO and MNM by analyzing the air samples collected using a newly-developed automated air sampling system to collect air samples of which artificial fractionation of Ar and N_2 were minimized. The air samples at RYO and MNM were also analyzed for the O_2/N_2 ratio by using the mass spectrometer. We also conducted continuous observations of the atmospheric O_2/N_2 ratio at MNM and RYO by employing a paramagnetic oxygen analyzer[2]. The Ar/N_2 and O_2/N_2 observed continuously at TKB since 2012 were also used for the analyses in this research.

Systematic observations of $\delta^{13}C$ and $\delta^{18}O$ in the atmospheric CO_2 at MNM have been carried out by analyzing discrete flask air samples[3]. Air samples were collected once per week, and the measurements of their $\delta^{13}C$ and $\delta^{18}O$ in CO_2 were made using a mass spectrometer at our laboratory. The air samples were also analyzed for N_2O concentration using an Off-axis Integrated Cavity Output Spectroscopy (ICOS) method. We have also made the continuous measurements of CO_2 isotopes using an ICOS method at MNM. In October 2020, the atmospheric CO_2 and its isotopic measurements were also initiated at RYO by analyzing discrete flask air samples.

AIST and MRI developed a high precision Rn measurement system used in this study [4]. It is based on the electrostatic collection method that collects positively charged progenies of Rn in the air on the light-sensitive photodiode (PIN photodiode) for an alpha particle detector charged high-negative voltage. The detection limit of the system is 0.1 Bq m^{-3} and with a temporal resolution of 15 minutes. MRI also conducted continuous observations of N_2O concentration at RYO in 2023, by using a newly introduced mid-infrared laser analyzer.

Four high-precision Ar standard mixtures were prepared in 2023. Reproducibility of Ar concentrations was evaluated by comparing their Ar concentrations in the standard mixtures prepared in 2023 with them in 2022. In high-precision measurement for atmospheric O_2 monitoring, the measured O_2 value may deviate by influence of miner components such as noble gas and CH_4. To identify the influence, we compared the O_2 concentration in standard mixtures with and without the minor components. The paramagnetic oxygen analyzer for the atmosphere observation was improved to achieve precision of the WMO DQO and sufficiently long stability. The precision and stability of the oxygen analyzers were studied when temperature of the oxygen analyzer was stabilized.

4. Results and Discussions

We continued Ar/N_2 observation at MNM and RYO by analyzing the air samples collected using the automated air sampling system. We compared the observed data with simultaneously-measured $\delta^{15}N$ of N_2, and confirmed artificial fractionation of Ar and N_2 was reduced enough to observe variations in the atmospheric Ar/N_2 variations. We also analyzed the secular trend in the Ar/N_2 based on 12-years data at Tsukuba and carried out an estimation of the OHC change for the period[5]. Both the O_2/N_2 and APO observed at MNM and RYO showed a secular decrease accompanied by clear seasonal cycles[6]. The recent oceanic and terrestrial biospheric CO_2 uptakes estimated from the long-term changes in the O_2/N_2 and CO_2 at MNM are consistent with those reported by the Global Carbon Project considering the uncertainties. The peak-to-peak amplitude and the appearance of the maximum of the seasonal APO cycle at RYO are larger and earlier, respectively, than those at MNM, which would be due to latitudinal differences in the air-sea O_2 flux driven by marine biospheric activities and solubility changes. We estimated solubility-driven components of the seasonal APO cycles at TKB, MNM and RYO by using the simultaneously-observed seasonal Ar/N_2 cycles. We found that the average seasonal APO cycles at the sites are driven mainly by net marine biospheric activities including an effect of seasonal change in mixed-layer depth. At TKB, we also found the annual change rate of APO driven by net marine biospheric activities showed maxima during El Niño,

while that driven by solubility changes showed maxima during La Niña periods.

At MNM, the CO_2 concentration showed a clear seasonal cycle in the opposite phase with the $\delta^{13}C$ cycle due mainly to a seasonal-dependent CO_2 exchange with C_3 plants in the land biosphere. $\delta^{18}O$ also showed a clear seasonal cycle, but the cycle was out of phase with those of CO_2 and $\delta^{13}C$. Secular increase of CO_2 and decrease of $\delta^{13}C$ due to anthropogenic CO_2 emission were seen, accompanied by year-to-year variations in opposite phase with each other mainly due to that of net CO_2 uptake by terrestrial biosphere, while $\delta^{18}O$ showed a secular increase trend until 2016 and then a decrease trend. Year-to-year variation in the global carbon budget was also estimated from analyses of the secular trends of CO_2 and $\delta^{13}C$ observed at MNM, showing suppressed CO_2 uptake by the biosphere from 2015 to 2016. Day-to-day variations of CO_2 and its isotopes were also observed by a continuous measurement, which were influenced by long-range atmospheric transport of different airmasses. At RYO, the CO_2 concentration showed a clear seasonal cycle in the opposite phase with the $\delta^{13}C$ cycle, while a clear seasonal cycle was not shown for $\delta^{18}O$.

Atmospheric Rn observation data to the end of 2023 have been obtained at MNM and RYO, with serious data unavailability at RYO in August to October 2023 due to a human PC operation error. Rn variations at MNM were very normal. Test observation of atmospheric N_2O using a mid-infrared laser analyzer has been made for June 2023 to January 2024 at RYO. The laser analyzer shows clear diurnal cycles of N_2O under some meteorological conditions, while GC observation by JMA does not, showing high potential of laser measurements to elucidate more detailed mechanisms of atmospheric N_2O variations. Difference of N_2O mole fractions measured by GC and laser analyzer implies some unknown effect of other species on measured N_2O mole fraction, which should be further investigated.

Ar concentrations in four Ar standard mixtures prepared in 2023 were consistent with them prepared in 2022. This result suggests that an Ar standard mixture can be prepared at target uncertainty. The results measuring highly-precision O_2 standard mixtures with and without miner components such as noble gas and CH_4 were different between a paramagnetic O_2 analyzer and a mass spectrometer, identifying that the influence of miner components differ depends on a measurement technique.

By investigating causes of signal drift of the paramagnetic oxygen analyzer when temperature of the analyzer was controlled by a precision air conditioner, it was found that output of the paramagnetic oxygen analyzer depended mainly on sample and ambient temperatures [6]. Precision less than 2 per meg of the WMO-DQO was achieved for a one-week continuous measurement, and this result suggests that the precision of 2 per meg in at least one-week continuous observation is achievable without calibrating the oxygen analyzer.

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