Development of a noble pretreatment system for the determination on the triple oxygen isotopes of dissolved oxygen

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The triple oxygen isotopic compositions ($\Delta^{17}O = \ln(\delta^{17}O + 1) - 0.518\ln(\delta^{17}O + 1)$) of photosynthetic O_2 are about +150 to 250 per meg higher than those of atmospheric O_2. While both $\delta^{17}O$ and $\delta^{18}O$ of O_2 fractionate during respiration along with "the mass-dependent relation", $\Delta^{17}O$ value is stable during respiration. As a result, measurements on the $\Delta^{17}O$ values for dissolved O_2 in hydrospheric samples enabled us to estimate the mixing ratios between photosynthetic O_2 and atmospheric O_2 in each dissolved O_2 and thus to estimate either gross primary production rate or air-water gas exchange coefficient in each hydrosphereric system.

In most of the previous studies, however, $\Delta^{17}O$ values of dissolved O_2 had been measured together with Ar during mass spectrometric analyses, because of the similarities between O_2 and Ar in the physical characteristics such as boiling points, which made them difficult to separate each other cryogenically. Therefore, additional corrections must be needed subsequent to the mass spectrometric analyses on O_2 isotopes for the samples having O_2/Ar ratios deviated from the atmospheric O_2/Ar ratios, leading poor accuracy on the $\Delta^{17}O$ measurements.

In order to determine accurate $\Delta^{17}O$ values for dissolved O_2 in various types of water samples including those having different O_2/Ar ratios from the atmosphere, we constructed a fully automated pretreatment system. In this system, dissolved gases including O_2 and Ar are extracted from water samples effectively. Then, extracted O_2 is separated from the other gases including Ar using GC column, and then obtained pure O_2 is concentrated in a cryogenic trap held at 10K. In this study, we would like to present the $\Delta^{17}O$ values of dissolved O_2 measured using the system for the samples showing substantially lower O_2/Ar ratios than that of atmosphere, such as those taken in the water column of Lake Biwa where hypoxia had been developed in summer hypolimnion in recent years.