

## Development of automatic analysis apparatus for triple oxygen isotopes of dissolved oxygen

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Oxygen molecules ( $O_2$ ) consists of triple oxygen isotopes (mass numbers 16, 17 and 18) providing additional unique information such as triple oxygen isotopic compositions ( $\Delta^{17}O = \ln(\delta^{17}O + 1) - 0.518\ln(\delta^{18}O + 1)$ ). In most of the terrestrial processes (e.g. photosynthesis and respiration) fractionate O isotopes in a mass-dependent way, such that  $^{17}O$  enrichment is about half of the  $^{18}O$  enrichment relative to  $^{16}O$ . As a result,  $\delta^{17}O$  and  $\delta^{18}O$  in terrestrial materials plot along a single line with a mass-dependent slope of about 0.52. In contrast to these mass-dependent processes, ultraviolet-induced interactions among  $O_2$ ,  $O_3$ , and  $CO_2$  in the stratosphere cause mass-independent fractionation with equal lowering of  $\delta^{17}O$  and  $\delta^{18}O$  in atmospheric  $O_2$ . Therefore,  $\Delta^{17}O$  of photosynthetically-produced  $O_2$  in the hydrosphere shows higher values of about +150 - 250 per meg compared to atmospheric  $O_2$ . Since the  $\delta^{17}O$  and  $\delta^{18}O$  of  $O_2$  fractionated by respiration vary along a line with a mass-dependent slope, which means the  $\Delta^{17}O$  will not change, we can estimate a mixing ratio of  $O_2$  produced from photosynthesis in the hydrosphere ( $\Delta^{17}O = \text{ca. } +150 \sim 250 \text{ per meg}$ ) and atmospheric  $O_2$  ( $\Delta^{17}O = \text{ca. } +150 \sim 250 \text{ per meg}$ ) dissolved in water. This will make it possible to estimate gross primary production in the lake and ocean or the air-water gas exchange coefficient by measuring the  $\Delta^{17}O$  of dissolved  $O_2$ . In this study, we constructed the new purge and trap system to measure  $\Delta^{17}O$  of dissolved  $O_2$ . The system is fully automated, extracting dissolved gases from the water samples, separate  $O_2$  from all the other gases including Ar, and collecting pure  $O_2$  using a cryogenic temperature cooling sampling device (ca. 10K). We will report  $\Delta^{17}O$  values of dissolved  $O_2$  in Lake Biwa where remarkable eutrophication and hypoxia have been observed in recent years.

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