

報告番号	※	第	号
------	---	---	---

## 主 論 文 の 要 旨

論文題目: Geochemical Study on isotope ratio of dissolved oxygen and argon anomaly in the northwestern Pacific Ocean

(北西太平洋の溶存酸素同位体比およびアルゴン異常の地球化学的研究)

氏 名: KEEDAKKADAN Habeeb Rahman

## 論 文 内 容 の 要 旨

Isotope ratio of dissolved oxygen has been used to evaluate processes of primary production and oxygen consumption in aquatic ecosystems. After the discovery in 1999 that tropospheric oxygen contains the memory of mass-independent isotope fractionation during stratospheric ozone formation and consumption, dissolved oxygen can be divided into atmospheric and photosynthetic sources using its triple isotopic composition. More recently, exact determination of primary productivity became available by the combined analysis with oxygen to argon ratio which could reduce the uncertainty due to temperature variation and bubble-mediated gas transfer process between air and water.

Oceanographic studies of triple isotopic composition of dissolved oxygen have been conducted in the mixed layer and below to evaluate present ocean primary productivity. On the other hand, behavior of triple isotopic composition of dissolved oxygen in the subsurface ocean below euphotic zone has not been investigated. The subsurface  $\Delta^{17}\text{O}$ , which is defined as a difference from mass dependent raw, was considered as a new tracer to reconstruct past primary productivity.

In this study, (1) development of cryogenic separation of an oxygen-argon mixture in natural air samples for the determination of isotope and molecular ratios, (2) determination of equilibrium isotope fractionation factor of molecular oxygen between gas and liquid phases, and (3) distribution of triple isotopic composition of dissolved oxygen and argon anomaly along 155 °E transect in the northwestern Pacific Ocean were conducted. Argon anomaly is identical to saturation degree of argon and can be obtained from measurements of oxygen to argon ratio and dissolved oxygen concentration.

(1) Development of cryogenic separation of an oxygen-argon mixture in natural air samples

Gas chromatography-based methods have been developed for the separation of oxygen or oxygen-argon mixture from natural air samples; however, these chromatographic methods require ultra-high purity helium as a carrier gas, and the depletion of helium reserves is a growing global concern. We developed simpler, higher portability and helium-free cryogenic separation methods for the determination of isotope and molecular ratio analyses. Atmospheric or dissolved air samples were trapped into a single 5A molecular sieve column at liquid nitrogen temperature, and then only oxygen-argon mixture would be eluted after increasing column temperature to -92 °C. Repeated measurements of atmospheric air yielded a reproducibility ( $1\sigma$ ) of 0.044 ‰, 15 per meg and 1.9 ‰ for  $\delta^{18}\text{O}$ ,  $\Delta^{17}\text{O}$  and  $\delta(\text{O}_2/\text{Ar})$  values, respectively.

(2) Determination of equilibrium isotope fractionation factor of molecular oxygen between gas and liquid phases

Using cryogenic separation method developed, equilibrium isotope fractionation factor of molecular oxygen between gas and liquid phases was determined. The equilibrium isotopic composition of dissolved oxygen with atmosphere is an essential endmember for the estimation of gross primary productivity using triple isotope method. However, present arguments are the existence of temperature dependency and/or the difference of experimentally obtained results due to the approaches of generating equilibrium water. In this study, isotope ratios of equilibrated dissolved oxygen by stirring and bubbling methods were determined with regard to seawater and deionized water. Significant differences were not recognized in  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$  values due to equilibration methods and  $\Delta^{17}\text{O}$  value was in good agreement with recently reported results. On the other hand, significant difference of  $\delta^{18}\text{O}$  value was found between seawater and deionized water.

(3) Distribution of triple isotopic composition of dissolved oxygen and argon anomaly along 155 °E transect in the northwestern Pacific Ocean

To investigate triple isotopic composition of dissolved oxygen and argon anomaly in the subsurface water, seawater samples were collected at depths between surface and 1000 m from 7 stations along 155 °E transect (the equator, 5 °N, 10 °N, 15 °N, 20 °N, 24 °N, 30 °N and 36 °N) in the northwestern Pacific Ocean.

All  $\Delta^{17}\text{O}$  values were ranged between 12 to 190 per meg, which was within the two endmembers of photosynthetic and atmospheric origins. This supports the hypothesis that  $\Delta^{17}\text{O}$  is a conservative tracer in the subsurface ocean below euphotic zone. The maximum values of  $\Delta^{17}\text{O}$  and argon anomaly were found consistently in the thermocline between the

equator and 20 °N. The maximum value of  $\Delta^{17}\text{O}$  was formed by accumulating photosynthetic oxygen in this zone where was shielded from the atmosphere. The maximum value of argon anomaly was formed by vertical diapycnal mixing.

A constant value of  $56 \pm 24$  per meg was found in the North Pacific Intermediate Water (NPIW), which is represented as a potential density of 26.8. In addition to this, an average value of  $120 \pm 37$  per meg was obtained along the Antarctic Intermediate Water (AAIW). These results suggest that subarctic front in the Southern Ocean, where is considered as a origin of AAIW, has kept on holding higher productivity than Okhotsk Sea for the origin of NPIW. A clear contrast in representative values in  $\Delta^{17}\text{O}$  and argon anomaly was first clarified between north and south Pacific.