

ELEMENTAL AND ISOTOPIC COMPOSITION OF O₂ AND N₂ GASES IN ICE CORES (Abstract)

by

T.A. Sowers and M.L. Bender

(Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, U.S.A.)

and

D. Raynaud and C. Lorius

(Laboratoire de Glaciologie et Géophysique de l'Environnement,
B.P. 96, 38402 St Martin d'Hères Cédex, France)

ABSTRACT

A procedure has been developed to extract and measure the relative concentrations of O₂ and ¹⁵N¹⁴N, as well as the isotopic abundance of these occluded gases, in ice cores. A wet-extraction procedure is used to extract 99.995% of the gas from the ice. The gas is removed from the extraction vessel by helium cryogenic trapping of all its constituents in a stainless-steel sample tube immersed in liquid helium. The elemental O₂/N₂ ratio is determined by measuring the ratio of masses ¹⁶O¹⁶O (O₂) and ¹⁵N¹⁴N (N₂) simultaneously, using a Finnigan MAT 251 isotope-ratio mass spectrometer. Mass 29 is used because the instrument cannot be configured to measure masses 28 and 32 simultaneously. The δ¹⁸O of O₂ and δ¹⁵N of N₂ are also measured on the same ice sample. The bubble composition is compared to a dry-air standard admitted to the reference side of the inlet system. The notation used to report the O₂/N₂ ratio is the delta notation:

$$\delta(O_2/N_2) = \left[\frac{R(32/29)_{sa} - 1}{R(32/29)_{st}} \right] \times 10^3$$

$$\text{where } R(32/29) = \left[\frac{(\text{conc. of } ^{16}\text{O}^{16}\text{O})}{(\text{conc. of } ^{15}\text{N}^{14}\text{N})} \right]$$

Applying these methods both to shallow and to deep ice cores will help us to understand global carbon cycling during the period covered by the ice cores. Changes in the distribution of carbon within the biosphere, atmosphere, oceans, and sediments will produce changes in the O₂/N₂ ratio of the recent atmosphere. Thus measurements of the O₂/N₂ ratio in ice will increase our understanding of the distribution of carbon within various reservoirs.

The δ¹⁸O of O₂ in the atmosphere has been shown to be coupled with the δ¹⁸O of the water used during

photosynthesis. The δ¹⁸O_{water} of the whole ocean was 1.3‰ heavier during the last glacial maximum, which has been shown to correspond to a 1.3‰ enrichment in the δ¹⁸O of atmospheric O₂ (Bender and others 1985). Thus the measurements of the δ¹⁸O of O₂ in ice will give an insight into the coupling between biological and hydrological cycles. Measurements of the δ¹⁵N of N₂ serve as a fractionation indicator. Any change in the δ¹⁵N must be due to some fractionation process, as δ¹⁵N cannot have changed over the time-scales in question.

To date, we have analyzed recent (approximately 200 years B.P.) bubble samples from Crête, D10 and Byrd Station ice cores. For the δ(O₂/N₂) analysis, the range of averaged values from each core was from -0.051 to -7.5‰ relative to present-day air. We believe that the large range is due to separation of O₂ relative to N₂, either during bubble close-off or during storage of the collected cores. For δ¹⁸O of the O₂, the average values ranged from +0.37 to +0.71‰. The δ¹⁵N results ranged from +0.18 to +0.33‰. The results indicate that there has been some fractionation of the gases, based on the δ¹⁵N of the N₂ in the bubbles. There is a striking covariance between δ¹⁸O and δ¹⁵N. The correlation coefficient *r* = 0.96. The slope of δ¹⁸O versus δ¹⁵N is 2.2, which is slightly greater than the slope which would be expected if the two isotopes were fractionated in a mass-dependent fashion. Possible explanations for the isotopic fractionation are: (1) the gases were fractionated during close-off in the firn, or (2) the composition of the bubbles has been changed since coring by diffusion through small cracks in the core. Radial sampling of gases in the core is in progress in order to investigate possible gas diffusion from the core during post-coring relaxation of the ice.

REFERENCE

Bender M L, Labeyrie L D, Raynaud D, Lorius C 1985
Isotopic composition of atmospheric O₂ in ice linked with deglaciation and global primary productivity. *Nature* 318(6044): 349-352