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Chapter 1 .

Precise and systematic measurements of the concentration of atmospheric greenhouse gases were first begun in 1957 for CO₂ , in 1978 for CH₄ and in 1976 for N₂O and extended to various places around the world. These measurements established that the atmospheric concentrations of greenhouse gases have been increased rapidly due to human activities so that global climate change is likely to occur in the near future. It is however difficult to predict future concentration levels of greenhouse gases, because the causes of their concentration increase are not well understood quantitatively. To solve this problem, the cycle of these gases on the earth's surface should be elucidated. For this purpose, it is extremely important to know how the concentrations of these gases distributed spatially and varied temporally in the past atmosphere, in addition to such a knowledge in the present atmosphere. Analysis of air extracted from polar ice cores is thought to be the most promising method for the above purpose, because air bubbles in ice sheet preserve the atmosphere at the time of formation of their surrounding ice. In this study, four ice cores, three from the Antarctica and one from Greenland, were analyzed to reconstruct the CO₂ , CH₄ and N₂O concentrations and $\delta^{13}\text{C}$ of C O₂ in the past atmosphere, using new and precise experimental techniques.

Chapter 2 .

Precise analysis technique with dry and wet air extractions for the CO₂ , CH₄ and N₂O concentrations and $\delta^{13}\text{C}$ of CO₂ from polar ice core was newly developed independently to reconstruct their ancient levels. A dry extraction system was capable of crushing an ice sample of 1000 g into fine powder within 2 min, and its air extraction efficiency was found to be 98%. The overall precision of the present measurements, including air extraction, was estimated to be better than ± 1.0 ppmv for CO₂ , ± 10 ppbv for CH₄ , ± 2 ppbv for N₂O and 0.05 ‰ for $\delta^{13}\text{C}$; these are precise enough to resolve variations of the ancient atmospheric CO₂ , CH₄ , N₂O concentrations and $\delta^{13}\text{C}$ of CO₂ .

Chapter 3 .

In this chapter, the CO₂ , CH₄ and N₂O concentrations over almost all periods of the Holocene, obtained by analyzing a 700 m-long ice core drilled at Mizuho Station, Antarctica, are discussed.

The CO₂ , CH₄ and N₂O concentrations were fairly stable between 9000 and 3000 years before present (BP), average values being 280.9 ± 4.6 ppmv for CO₂ , 729 ± 30 ppbv for CH₄ and 265 ± 8 ppbv for N₂O. However, somewhat high values of the respective concentrations were found around 9000-8000 years BP, presumably being related to high air temperature during

that period. High air temperature possibly rose the ocean water temperature and enhanced to release CO_2 , CH_4 and N_2O from the oceans into the atmosphere by lowering their solubilities. It is also thought that emission from land surfaces was intensified by oxidation of organic matter in soil for CO_2 , by transmethylation of acetic acid or methyl alcohol in wetland and defrosting of polar permafrost for CH_4 and by denitrification in aerobic soils or nitrification in anaerobic soils for N_2O .

The CO_2 concentrations during the period 645-350 years BP were higher by about 7 ppmv than 277 ppmv before and after this period, which is probably related to changes in the carbon cycle during the Little Ice Age. In general, under circumstance with low temperatures, land plants wither and oxidize, oxidation of organic matter is deactivated and oceanic CO_2 uptake is increased due to higher CO_2 solubility in ocean water. Taking these into account, it may be expected that the first effect took precedence over others especially during 700-400 years BP and the second and third effects over the 400-300 years BP.

After 250 years BP, the CO_2 , CH_4 and N_2O concentrations increase significantly with time, due to human activities such as fossil fuel combustion, deforestation, rice cultivation, ruminants, landfills, venting of natural gas at wells, pipeline leakage of natural gas, coal mining and biomass burning, cultivation and use of fertilizers.

Chapter 4.

In this chapter, concentration variations of greenhouse gases in the glacial period are discussed using the results from ice core collected at bare ice field in the southern part of the Yamato Mountains, Antarctica, which was named South Yamato core.

The CO_2 , CH_4 and N_2O concentrations from an ice core near the Yamato Mountains were obviously lower, the average values being 213.3 ± 8.7 ppmv, 484 ± 44 ppbv and 243 ± 10 ppbv, respectively, than the pre-industrial Holocene values, suggesting that this ice core was formed in the glacial period.

During the glacial period, the CO_2 concentrations varied almost out of phase with $\delta^{13}\text{C}$, implies that CO_2 with isotopically light carbon was added to or subtracted from the atmosphere. Considering the relation between the CO_2 concentration and the $\delta^{13}\text{C}$ value, the fluctuations of the atmospheric CO_2 concentration during the glacial period may be arisen mainly from C O_2 exchange with the land biosphere, unless ^{13}C of CO_2 in the surface ocean was extremely diluted relative to ^{12}C .

By comparing measured CO_2 and CH_4 concentrations with those from the Vostok core, the air age in surface part of the South Yamato core is thought to be older than 30 kyrs BP and younger than 50 kyrs BP.

Chapter 5 .

In this chapter, we estimated variations of the past concentration of atmospheric CH₄ in the Arctic region by analyzing ice core drilled at Site J, Greenland, and north-south CH₄ differences in the pre-industrial/pre-agricultural era were derived supplementing by the results from the Mizuho core and were compared with those from recent systematic measurements.

The pre-industrial/pre-agricultural levels of the CH₄ concentration obtained from an Arctic core were higher by 54 ± 20 ppbv than those from an Antarctic cores, which is suggested that natural CH₄ sources had been stronger in the northern hemisphere than in the southern hemisphere, reflecting the greater extent of boreal compared with austral lands.

The present concentration difference of atmospheric CH₄ between northern and southern high latitudes was estimated to be almost three times as much as we have measured for the pre-industrial/pre-agricultural era. From this fact it was suggested that a large amount of CH₄ was being released into the atmosphere from anthropogenic CH₄ was being released into the atmosphere from anthropogenic CH₄ sources especially in the northern hemisphere and/or OH radicals have decreased more rapidly in the northern hemisphere, perhaps due to an increase of the atmospheric CO concentration by fossil fuel combustion.

Chapter 6 .

We analyzed ice core drilled at H 15, Antarctica, where the annual accumulation was estimated to be about 250 kgm⁻². In this chapter, the variations of the atmospheric CO₂, CH₄ and N₂O concentrations and $\delta^{13}\text{C}$ during the last 250 years are discussed using the results from this ice core with the age resolution of about 30 years.

The CO₂, CH₄ and N₂O concentrations increased and values of $\delta^{13}\text{C}$ decreased significantly during the last 250 years due to human activities. However, the growth rates of their concentrations were somewhat fluctuated, reflecting changes in their anthropogenic sources as well as in their natural sources and sinks.

The pre-industrial/pre-agricultural levels of the N₂O concentration obtained from H 15 core as well as Mizuho core ranged from 265 to 275 ppbv, which are apparently lower than about 285 ppbv from previous studies.

The results derived from the CO₂ concentration and $\delta^{13}\text{C}$ variations of H 15 core and box-diffusion model suggested that the increase of the atmospheric CO₂ concentration should be ascribed mainly to deforestation during the period from the 18th century to the mid-20th century and to fossil fuel combustion after that.

論文審査の結果の要旨

温室効果気体の増加原因を定量的に理解し、将来の濃度を予測するためには、過去におけるこれらの気体の変動の実態を知ることが不可欠である。また、得られる知見は温室効果気体の変動と気候変化の関係を明らかにする上でも有益な情報となる。本論文においては、南極みずほ、南やまと、H 15、及びグリーンランド site J の各コアから抽出した空気を分析することによって、過去における CO_2 、 CH_4 、 N_2O の濃度と CO_2 の $\delta^{13}\text{C}$ の変動を明らかにし、その原因について考察している。結果をまとめると以下の通りである。

1. 南極みずほコアより得られた CO_2 、 CH_4 、 N_2O の濃度は9000年前から300年前にかけてほぼ一定の値で推移しており、それぞれの平均値は 280.9 ± 4.6 ppmv、 729 ± 20 ppbv、 265 ± 8 ppbv である。
2. 南極南やまとコアを分析することによって得られた CO_2 、 CH_4 、 N_2O の濃度はそれぞれ、200~240 ppmv、400~600 ppbv、210~260 ppbv の間を推移しており、みずほコアより得られた後氷期の濃度に比べて著しく低く、南やまとコアが氷期のものであることが明らかとなった。
3. 氷期中の CO_2 の変動は $\delta^{13}\text{C}$ と逆位相で対応しており、当時の大気中 CO_2 濃度の変動は植物（特に海水中の）との CO_2 交換に支配されていたと考えられる。
4. グリーンランド site J コアから求めた産業革命以前の半球高緯度での CH_4 濃度は 756 ± 10 ppbv であり、みずほコアから得られた同時期の南半球高緯度の濃度に比べて約 54 ± 20 ppbv 程高い。このことから、南北両半球における陸地面積の違いを反映して、 CH_4 の自然的発生源が北半球で強かったと言える。
5. また、現在の南北両半球高緯度での CH_4 濃度の差が150 ppbvであることを考慮すると、北半球における CH_4 の人為的発生源が時間の経過と共に強まったこと、または、化石燃料の消費による CO の放出などによって CH_4 の消滅源である大気中の OH ラジカルが特に北半球で減少したことが示唆されており。
6. 南極 H 15 コアを分析することによって得られた CO_2 、 CH_4 、 N_2O の濃度は、18世紀中頃より急激に増加し、 CO_2 の $\delta^{13}\text{C}$ はそれに応じて減少を示した。また、それぞれの濃度変動には、人為起源による放出量の年代毎の違いを反映して細かな変化が見られた。
7. H 15 コアから得られた CO_2 濃度の変動をボックスディフュージョンモデルを用いて解析した結果は、19世紀には森林破壊によって大量の CO_2 が生物圏から放出されており、その後、化石燃料消費が濃度増加の主因となっていることを強く示唆している。

以上の知見は関連分野の科学の進展に寄与するところ大であり、本論文は、博士（理学）の学位論文として合格と認める。