Biodegradation and demethylation of C_{28} sterols in marine phytoplankton

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Introduction

Diatoms, which appeared on the Earth in the late Cretaceous, are now the major primary producers in the ocean. They inhabit various environments irrespective of saline water or fresh water. Diatoms often form siliceous sediments, which are the useful samples for understanding of biochemical evolution of diatom. Steroidal compounds are especially abundant in siliceous sedimentary rocks. Among various steroidal compounds, 24-norcholestane (C_{26}) and 27-nor-24-methylcholestane (C_{27}) are known as characteristic steroidal hydrocarbons in siliceous sediments (Suzuki *et al.*, 1993). Their precursory sterols with the same carbon skeletons, however, have not been detected yet in cultured diatoms. Artificial biodegradation of bacillariophyceae (diatoms) and haptophyceae are carried out in the present study to clarify the origin of unique steroidal carbon skeletons often found in siliceous sediments and sedimentary rocks.

Result and Discussion

Sterol anaysis for cultured diatoms (*Chaetoceros didymus*, *Chaetoceros sociale*, *Cosinodiscus marginatus*, *Cosinodiscus* sp., *Rhyzosolenia setigera*, *Skeletonema* sp., and *Thalassiosira* sp.), cultured haptophyceae (*Emiliania Huxleyi* and *Gephyrocapsa oceanica*), and Diatom (*Cosinodiscus marginatus*) rich natural samples collected at Tomakomai bay, Hokkaido showed that they do not contain 24-norcholesterol (24-norcholesta-5,22E-dien-3β-ol) and 27-nor-24-methylchole- sterol (27-nor-methylcholesta-5,22E-dien-3β-ol). Some of selected diatoms and haptophyceae were kept in the isothermal oven at 3, 10, or 15°C for 3 to 90 days with and without natural sea water. Compositional change of sterols in each alterartion experiment was examined.

24-Norcholesterol and 27-nor-24-methylcholesterol were selectively detected in the sample that was kept at 3°C with natural sea water, and contained 24-methylcholesta-5,24(E)-dien-3β-ol (brassicasterol: C_{28}) and/or 24-methylcholesta-5,24(28)-dien-3β-ol (C_{28}). Bacterial demethylation of 24-methylcholesterols at low temperature in the Ocean was strongly suggested for the formation of 24-norcholesterol and 27-nor-24-methylcholesterol. Effective demethylation of brassicasterol to form 24-Norcholesterol and 27-nor-24-methylcholesterol seems to be related to the configuration at C-24.

Reference

Suzuki. N., Sampei. Y., and Koga.O. (1993) Geochim. Cosmochim. Acta 57, 4539-4545.

Compositional variations of altered igneous rocks in epithermal system: A useful geochemical prospecting indicator of gold-silver mineralization

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Chemical compositions of hydrothrmally altered andesite which hosts the Hishikari gold-silver vein-type deposits, southern Kyushu, Japan were analyzed and summarized. It was found that ($CaO + Na_2O$) content inversely correlates with K_2O content. The variations in these contents can be explained in terms of the superimposed hydrothermal alterations; Potassic, advanced argillic and calcium alterations cause these variations. The altered rocks in the high gold-grade mining area (Main), low gold-grade mining area (Yamada), and gold-absent area (Masaki) are characterized by intermediate K_2O content and variable CaO content, high K_2O content, and low K_2O content and low CaO content, respectively. The K_2O, Na_2O and CaO contents data, oxygen isotopic compositions and solubility of gold due to thio complex suggest that gold deposition was caused by two fluids (acidic groundwater and neutral hydrothermal solution) mixing. This model can explain the gold content variations in ores in the Hishikari district and compositional variations of hydrothermally altered rocks are useful for the exploration of epitheermal gold-silver deposits.