

Iron isotopic signature of red blood cell samples from shark and seal : new tracer for biological cycle of Fe in marine

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Among the essential metal elements, Fe is one of the most important essential elements for all organisms because its flexible redox activity contributes to a cell respiration, photosynthesis, nitrogen fixation, and hemoglobin enhances the efficiency of oxygen transport in blood. Recent Fe isotope studies have revealed that the $^{56}\text{Fe}/^{54}\text{Fe}$ and $^{57}\text{Fe}/^{54}\text{Fe}$ isotope ratios for the terrestrial plants or animals were systematically decreased with increasing the nominal trophic level (about 1‰/amu per trophic level). The systematical decrease in the $^{56}\text{Fe}/^{54}\text{Fe}$ isotope ratio can be attributed to the preferential absorption of lighter Fe isotopes from nutrients or dietary foods [1, 2]. However, the same is not true on the marine organisms. Despite the quite limited number of Fe isotope data, there were no significant difference in the reported $^{56}\text{Fe}/^{54}\text{Fe}$ ratio data between the marine organisms (phytoplankton, shrimp and tuna samples [3]) and the seawater samples [4], suggesting very small change in the $^{56}\text{Fe}/^{54}\text{Fe}$ ratio against the trophic level. This is contrasting to the $^{56}\text{Fe}/^{54}\text{Fe}$ ratio for the terrestrial plants or animals. To investigate the possible correlation in the $^{56}\text{Fe}/^{54}\text{Fe}$ isotope ratio and the trophic level for the marine organisms, the $^{56}\text{Fe}/^{54}\text{Fe}$ ratio for marine organism with high-trophic level is highly desired. In this study, we have measured the $^{56}\text{Fe}/^{54}\text{Fe}$ and $^{57}\text{Fe}/^{54}\text{Fe}$ ratios for red blood cell (RBC) samples from the high-trophic level animals of various ages (15 shark and 13 seal samples of various ages). After the series of chemical procedures, including sample decomposition, chemical purification, and the adjustments of the Fe valence, the $^{56}\text{Fe}/^{54}\text{Fe}$ and $^{57}\text{Fe}/^{54}\text{Fe}$ isotopic ratios were obtained by a multiple-collector ICP-mass spectrometry (MC-ICPMS). The resulting $^{56}\text{Fe}/^{54}\text{Fe}$ ratio for shark and seal samples were ranging from -1.11‰ to -2.56‰ and -0.70‰ to -1.26‰, respectively. For shark samples, there were no significant differences in the measured $^{56}\text{Fe}/^{54}\text{Fe}$ ratio between the male and female samples. This is contrasting with the $^{56}\text{Fe}/^{54}\text{Fe}$ ratio for the terrestrial animals, including human RBC samples. For the seal samples, no correlation in the resulting $^{56}\text{Fe}/^{54}\text{Fe}$ ratio and both the age and body length was found. More importantly, the resulting $^{56}\text{Fe}/^{54}\text{Fe}$ ratios for the shark and seal samples were significantly higher than those for the high-trophic level terrestrial animals. We will discuss the difference in the correlation of the $^{56}\text{Fe}/^{54}\text{Fe}$ ratio with trophic level between the terrestrial and marine organisms.

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Keywords: stable isotope geochemistry, iron isotopes, red blood cell, marine environment, biocycle of Fe, essential element

Processes of stromatolite formation examined from the modern analogs

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Stromatolites, macroscopically laminated domal, columnar and lentic shaped sediments, are an abundant sedimentary facies in Precambrian carbonates. Despite of 100-yr-long study history of taxonomy, paleontology, and sedimentology for understanding early biosphere and ocean chemistry, the detailed formation processes have not been well defined because the initial structures and chemical features were obscured due to recrystallization, deformation, and scarcity of microfossils. After the discovery of the modern stromatolite at restricted marine settings such as Bahamas and Western Australia (e.g. Logan, 1961), the detailed processes for the stromatolite formation have revealed, for example, growth by trapping and binding of detrital particles in the surface cyanobacterial mat, and lamina formation by cyanobacterial phototactic behavior and intermittent sediment supply. These processes were often adopted for interpreting the genesis of ancient stromatolites, however, its applicability is doubtful because the fabrics consisting of in situ precipitated carbonate minerals is different from the modern ones. Therefore, it is necessary to seek and investigate other modern analogs having similar fabrics to ancient stromatolites.

Travertines, carbonate precipitates from hot spring, have common fabrics to the ancient stromatolites in terms of sub-mm order lamination and scarcity of detrital particles. Travertines are inorganically precipitated by mechanical degassing of carbon dioxide from the water enriched with DIC and calcium ion. Previous studies mainly focusing on calcite travertines have indicated that cyanobacterial daily biofilm formation overcoming the inorganic mineral precipitation formed daily lamination (Takashima and Kano, 2008). However, aragonite is another component of travertine and was the primary mineral of some ancient stromatolites (Grotzinger, 1989). Here, I study aragonite travertines to understand the geomicrobiological processes forming laminated textures.

Aragonite travertines consist of radially expanded needle crystals, which is different from calcite fabrics called as dendrite consisting of tree-like aggregation of rhombic crystals. Sequences of sampling through day and night showed the lamination in the aragonite travertines was also formed daily cycle. There are two types of processes forming lamina formation in aragonite travertines; one is cyanobacterial direct role for daily lamination by their daily migration, another is cyanobacterial indirect role by daily production of organic materials (Okumura et al., 2011). It was also observed rapid decomposition of microbes in the travertine, which prevent preservation of microfossils in the sediment. The textural features of the aragonite travertines such as radially expanded needle crystals and scarcity of microfossils are common in some Precambrian stromatolites.

Despite of differences in water chemistry, hydrological setting, and mineralogy, geomicrobiological processes in the daily-laminated travertines show one detailed microbial behavior for interpreting the Precambrian stromatolites. If the relationship between stromatolite texture and microbial processes is clearly confirmed by geomicrobiological studies for modern analogs, it leads new possible interpretation for the stromatolite microbiology and the early biosphere.

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Keywords: stromatolite, travertine, modern analogs, cyanobacteria, lamination

Millennial-scale effect of microbes on soil organic matter buried by volcanic ash

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Soil is considered to be the major carbon (C) reservoir accounting for about 70% of terrestrial C. Turnover time of C accumulated in soil often exceeds thousands years, thus much concerns have recently been directed to the mechanism of long-term sequestration and preservation of organic matter in soil. Microbes are the major contributor for changing the characteristics of preserved organic matter and influencing its stability. However, because soil typically comprise a mixture of old and young organic residues, it is difficult to analyze long-term effect of microbes on soil organic matter. Buried soil allows us to study the long-term changes in soil organic matter, because supply of young organic matter is limited. Thus, in this study, we analyzed hydrolyzable amino acids (AA) and amino sugars (AS) in soils buried for hundreds to thousands years in order to clarify the long-term effect of microorganisms on soil organic matter. Buried soils were sampled in Tomakomai, Memuro, and Abashiri in Hokkaido Island. Carbon content in buried soil ranged from 1.12 to 8.06%, unrelated to the soil age or the type of volcanic ash, suggesting strong influences other than time and parent material. The positive correlation between yield of AA and AS suggests a strong influence of microorganisms on chemical changes in organic matter in buried soils. Ratio of GlcN/GalN was lower in older soils, suggesting grater progress of diagenesis in soils buried for a longer period. This was supported by the lower yield of AA and AS in older soils. These observations suggest that soil organic matter sequestered for hundreds to thousands years is influenced partly by microorganisms, and is diagenetically altered to more uncharacterizable compounds.

Keywords: Soil organic matter, Carbon sequestration, Buried soil, Microbial contribution, Diagenetic alteration

Nature of organo-mineral interaction in volcanic-ash soil. Par II. Particle size and aggregate hierarchy

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Soil organic matter (SOM) is the largest carbon pool of terrestrial ecosystem. Stabilization of SOM is largely controlled by interaction of organic matter (OM) and soil minerals. Volcanic-ash soils are characterized by a high SOM content and consist mainly of short-range-order minerals such as allophane, imogolite and ferrihydrite. Allophane/imogolite are unique nanoclays of hollow spherule/tube structures with the diameter of <5 nm and have extensive, variable-charge surfaces. Due to the dominance of these nanoclays, SOM stabilization process in volcanic soils may differ drastically from that in non-volcanic soils consisting of well-crystalline minerals. Particle-size fractionation is an effective approach to distinguish different types of organo-mineral associate. These nanoclays form stable micro-aggregates and are difficult to disperse, which makes the effectiveness of this approach obscure. Here we hypothesized that, with an appropriate dispersion technique, major portions of SOM is stabilized in finer size fractions (<2 micro-m) as sub-micron aggregates of short-range-order minerals with microbially-processed organic matter in volcanic-ash soils. To test this, we chose a typical allophanic Andisol in Japan and characterize each particle-size fraction by selective-dissolution, isotopic (N-15, C-13, C-14), and spectroscopic techniques. Results showed that: (i) total organic carbon and nitrogen were mainly stabilized in finer size fractions (<2 micro-m), (ii) <0.2 micro-m and 0.2-2micro-m sized fractions largely consist of the association between OM and short-range-order minerals, (iii) the decline of C:N ration and enrichment of N-15 towards finer fraction indicate that the OM in finer-sized aggregates appeared to be more strongly altered by soil microbial activity. Based on these results, we attempt to provide a speculative synthesis on the progression in organo-mineral associations and the development of aggregate hierarchy in the volcanic-ash soil.

Keywords: soil organic matter, organo-mineral associate, particle size fraction, allophanic soil, carbon stabilization

Isotopic study on atmospheric nitrate discharge from forested watersheds

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Clarifying the source of discharged nitrate is important to discuss the influence of increasing nitrogen deposition on forest ecosystem, because in the forested ecosystem where discharged nitrate derived from atmospheric nitrate, increasing atmospheric nitrate deposition is difficult to accumulate into the forest ecosystem and influence on nitrogen saturation might be small. However, increasing atmospheric nitrate may directly increase the amounts of discharged nitrate from such forest ecosystems. On the other hand, in the forested ecosystem where discharged nitrate derives from nitrified nitrate, increase of nitrate deposition should not immediately increase nitrate discharge from watershed because atmospheric nitrate is taken up by nitrogen cycle in such forest ecosystems at least one time. However, atmospheric nitrate should easily accumulate in such forest ecosystem.

In this study, we conducted the observation of several storm events and quantitatively clarify the source of nitrate discharged from forest ecosystems at storm events.

Keywords: isotope, nitrogen, forest, biogeochemistry

Effects of clear-cutting on nitrate dynamics in a forested watershed using the triple oxygen isotopes as tracers

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Temporal variations in the triple oxygen isotopic compositions of nitrate in stream water were investigated to understand the effect of clear-cutting on trees (January to March, 2003) and subsequent stripcutting of understory dwarf bamboo (*Sasa senanensis*) (October 2003) on biogeochemical processes of forested watershed in northern Japan. In accordance with the significant increase in stream nitrate concentration up to 15 micromols L⁻¹ in spring 2004, probably in response to the *Sasa*-cutting (Fukuzawa et al., 2006), we found significant increase in the ¹⁷O anomalies. The maximum anomaly (+14 permil) suggest that the direct drainage of atmospheric nitrate occupied more than 50% of total nitrate being exported from the forested watershed during spring 2004. Similar increases in both concentrations and the ¹⁷O anomalies were found in spring 2005 as well. On the other hand, we found little anomalies in the other seasons, irrespective to increases in stream nitrate concentration. That is to say, most portion of the increased nitrate, being exported from the forested watershed during the seasons other than spring, was remineralized nitrate: those preserved in the forested ecosystem as either organic-N or ammonium and then been converted to nitrate. The annual export flux of atmospheric and remineralized nitrate from the forest ecosystem increased to more than 20-times and 4-times, respectively, from those prior to the *Sasa*-cutting. These results suggest that *Sasa* is important not only for preventing nitrogen leaching from soil, but also for enhancing biological consumption of atmospheric nitrate before being exported from forest ecosystem, especially when significant quantities of atmospheric nitrate were added to forest floor through the spring thaw.

Keywords: forest ecosystem, nitrogen leaching, triple oxygen isotopic compositions, nitrate, clear-cutting of trees, *Sasa*

The response of litter dynamics of Sasa and trees to the long-term atmospheric nitrogen deposition in forest ecosystem

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Nitrogen is fundamental nutrient for plants and microbes in forest ecosystem. However, it has been concerned that increased nitrogen deposition cause a change of the internal cycling between soil and plant system such as enhancement of litter decomposition by increase nitrogen content in the litter and nitrogen leaching from soil to stream water. It has been known that responses of the forest ecosystem to nitrogen deposition vary with an amount of the nitrogen entering into the forest ecosystem, the period and comprised main plant species. In forest ecosystem of northern Hokkaido, Sasa dwarf bamboo on the forest floor is an important component of vegetation, in addition to the overstory tree. It has been reported that Sasa has a role reducing a change of short-term soil nitrogen increment after the forest management due to the nutrient absorption by Sasa. However, the influence the change of long-term soil nitrogen environment on Sasa litterfall and litter decomposition is not understood. This aim of this study is to clarify the influence the long-term nitrogen addition to soil on the litter dynamics of Sasa and tree in the forest ecosystem.

Nitrogen additional experiment was conducted on Nakagawa experimental forest of Hokkaido University in northern Hokkaido. The study area is a cool-temperate climate. Predominant tree species are birch (*Betula ermanii*), acer (*Acer mono*), oak (*Quercus crispula*) and fir (*Abies sachalinensis*). The forest floor is covered with understory vegetation, Sasa (*Sasa senanensis*) having high density and tall structure. Study sites were established in flat ridge of the experimental watershed (1.43 ha) and the adjacent control watershed (1.06 ha), respectively. Nitrogen of 5 g N m⁻² year⁻¹ (particulate form of NH₄NO₃) has been added to the whole watershed at the snowmelt season from 2002. We investigated above-ground standing stock of Sasa and litterfall of Sasa and trees in each watershed. The litter decomposition experiment of Sasa and trees using litter samples collected from both watersheds conducted on the control watershed to avoid the directly effect of the nitrogen addition. Stream water was collected in the outlet of each watershed to analyze the nitrogen export from each watershed.

The nitrogen amount of above-ground of Sasa and litterfall of trees were significantly higher in treatment site than in control site. The nitrate concentration in stream water was not significantly different between the watersheds before and 1-year after the first nitrogen addition, but tended to increase in the treatment watershed from three years after the initial addition. These results suggested that the nitrogen absorption of Sasa and trees and the nitrogen leaching from soil to stream increased by long-term nitrogen addition. The litter decomposition rate of tree leaf was faster in treatment watershed than that in the control watershed. The nitrogen content in initial litter increased in tree leaf, suggesting that the increased nitrogen content in initial litter influenced on enhancement of litter decomposition of tree leaf. On the other hand, those of Sasa leaf and culm litter were not significantly different between the watersheds. These results suggested that Sasa litter have some degree of the resilience capacity to maintain the nitrogen dynamics of the soil-vegetation system through the stable nitrogen concentration of litter against the atmospheric nitrogen deposition.

Keywords: Biogeochemistry, Understory vegetation, Nitrogen cycling, Litterfall, Litter decomposition, Litter-bag method

Atmospheric mercury accumulation by carbonized trunk

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In March 1945, Tokyo was bombed by B29, and most of all plants of Tokyo was fired. At that time, *Ginkgo biloba* was also fired. The fired trunk *G.biloba* was carbonized.

Mercury that in the bark evaporates to the atmosphere when it is fired, and we expect mercury(Hg⁰)contains in the carbonized *G.biloba* trunk because biochar has ability of get the environmental pollutants.

In this study, We collected the carbonized tree trunk and contain of mercury in the carbonized tree trunk was analyzed by thermal decomposition amalgamation.

Keywords: Mercury, Carbonized trunk, Mercury accumulation