

The distribution and diagenesis of monosaccharides in skeletal carbonates and carbonate sediments

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Abstract: Monosaccharides in Recent skeletal carbonates, Recent carbonate sediments and Pleistocene limestones were analyzed by high performance liquid chromatography.

The total monosaccharides in the Recent skeletal carbonates range from 0.042 to 17.4 mg/g, and fluctuate extremely among different species of organisms and different specimens. The highest amounts were found in a calcareous algal skeleton and the lowest in a molluscan shell. The total monosaccharides in the various carbonates show a tendency to decrease with increasing age.

In the Recent carbonates, monosaccharide compositions vary widely due to the influence of organic source materials. However, in the Pleistocene limestones monosaccharide compositions are generally even because the characteristics of the source materials have been lost during diagenesis after the deposition.

INTRODUCTION

Monosaccharides, building blocks of structural and storage polysaccharides in plants and animals, are the most abundant organic compounds, and probably present at the same level as amino acids in geological samples (DEGENS and MOPPER, 1979).

Geochemical studies of carbohydrates in various environments have been performed by several workers (DEGENS *et al.*, 1964; ROGERS, 1965; SWAIN and BRATT, 1971; HANDA and MIZUNO, 1973). Recently, SAKUGAWA and HANDA (1985) have isolated the dissolved and particulate polysaccharides in Mikawa Bay and examined their chemical characteristics. KLOK *et al.*, (1984 a, 1984 b), and COWIE

and HEDGES (1984) have conducted geochemical studies of carbohydrates in the Recent marine sediments. Therefore, the distribution and diagenesis of carbohydrates in Recent muddy sediments have been clarified by the above workers. However, the distribution of carbohydrates in carbonates is scarcely known, except for their occurrence in carbonate sediments (BÖHM *et al.*, 1980).

The aims of the present investigation are the following; (1) to indicate distribution and chemical characteristics of monosaccharide compositions in various carbonates, and (2) to clarify the fate of individual monosaccharides with passing of geological time.

SAMPLES

The localities and related data concerning samples are shown in Tables 1-4.

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Table 1 Analyzed samples of Recent skeletal carbonates.

| | Sample No. | Species | Locality |
|--------------|------------|--------------------------|--------------------------------|
| Molluscs | 1 | <i>Glycymeris</i> sp. | Nakaumi, Shimane Pref. |
| | 2 | <i>Anadara</i> sp. | Nakaumi, Shimane Pref. |
| | 3 | <i>Serpulorbis</i> sp. | Kii Peninsula, Mie Pref. |
| | 4 | <i>Dosinia</i> sp. | Nakaumi, Shimane Pref. |
| Alga | 1 | <i>Penicillus</i> sp. | Unknown |
| Coral | 1 | <i>Acropora</i> sp. | Wake Island, USA. |
| | 2 | <i>Dendrophyllia</i> sp. | Kii Peninsula, Mie Pref. |
| | 3 | <i>Fungia</i> sp. | Okinawa Island, Okinawa Pref. |
| | 4 | <i>Melithaea</i> sp. | Ishigaki Island, Okinawa Pref. |
| Bryozoa | 1 | Unknown | East China Sea |
| Foraminifera | 1 | <i>Baculogypsina</i> sp. | Ishigaki Island, Okinawa Pref. |
| | | <i>Sphaerulata</i> sp. | |

Table 2 Analyzed samples of Recent marine carbonate sediments recovered by dredging.

| Sample No. | Locality | Depth | |
|-----------------------------|------------------------|---------|-----------------------------------------|
| (Calcareous ooze) 73-105 | 11°43.6' N 163°44.3' E | 2000 m | dredged, planktonic foraminiferal ooze |
| 73-108 | 11°58.8' N 164°45.9' E | 1320 m | " |
| 73-116 | 13°57.8' N 164°06.2' E | 2030 m | " |
| (Shell sand) 73-349 | 32°03.3' N 129°21.8' E | 69 m | dredged, very coarse grained shell-sand |
| 73-407 | 33°14.1' N 129.02.2' E | 70-78 m | " |
| 73-417 | 34°03.5' N 129°17.8' E | 97 m | " |

Table 3 Analyzed samples from the Holocene Numa coral bed in Tateyama, Chiba Prefecture.

| Sample No. | Age | Locality | Species |
|------------|---------|-----------------------|--------------------------|
| Nu-1 | 6,600 y | Tateyama, Chiba Pref. | <i>Dendrophyllia</i> sp. |
| Nu-2 | 6,600 y | Tateyama, Chiba Pref. | <i>Acropora</i> sp. |
| Nu-3 | 6,600 y | Tateyama, Chiba Pref. | <i>Favites</i> sp. |
| Nu-4 | 6,600 y | Tateyama, Chiba Pref. | <i>Favia speciosa</i> |
| Nu-5 | 6,600 y | Tateyama, Chiba Pref. | <i>Cyphastrea</i> sp. |

Recent skeletal carbonates

The samples were mainly collected from the beaches and floors of the sea and lakes.

Molluscan shells, no. 2 *Anadara* and

no. 4 *Dosinia*, were collected from muddy sediments obtained with a piston corer from brackish lake Nakaumi. The no. 2 was taken at 2.6 m from the top of the core and the no. 4, at 5.3 m.

Table 4 Analyzed samples from the Pleistocene Ryukyu Group and Holocene raised coral reef in Kikai Island, Kagoshima Prefecture.

| Sample No. | Locality | Age |
|--------------------------------------------------------------------|---------------------------------------|-----------------|
| (Raised coral reef) Ki-1, Ki-2, Ki-15, Ki-41 (Wan Formation) | Kikai Island, Kagoshima Prefecture | 5,000—6,500 y |
| Ki-5, Ki-40 (Hyakunodai Formation) | " " | 55,000—70,000 y |
| Ki-39, Ki-42, Ki-43, Ki-45, Ki-46, Ki-47, Ki-51 | " " | >200,000 y |

The ^{14}C age on a shell of *Dosinia* taken at 4.4 m of the core was $2,940 \pm 80$ yBP.

Recent calcareous ooze

The Recent calcareous oozes are composed of testes of planktonic foraminifera, which were dredged from deep sea floor in the North Pacific.

Recent shell sands

Three samples of Recent shell-sands composed of coarse-grained shell fragments were collected from the Goto-Nada Sea and the Tsushima Strait with a cylinder-type dredge. The samples no. 73-407 and no. 73-417 contained more than 70% CaCO_3 .

According to INOUE (1975), the shell-sands consist of more than 50% molluscan shell debris, 20% echinoids and bryozoa, 15-20% quartz and rock fragments. OHSHIMA *et al.*, (1975) suggested that the shell-sands nos. 73-407 and 417 were Pleistocene in age.

Corals from Holocene Numa coral bed

The corals were collected from the Holocene Numa coral bed near Tateyama City, Chiba Prefecture. The bed have been dated at 6,600 yBP by the ^{14}C method.

Pleistocene and Holocene limestones from Kikai Island

In Kikai Island, Kagoshima Prefecture, the Pliocene Somachi Formation, Pleistocene Ryukyu Group and Holocene deposits are exposed. The Ryukyu Group consists of the Hyakunodai Formation, Wan Formation and Lower terrace deposits in descending order (NAKAGAWA, 1969). The Hyakunodai and Wan Formations are composed of limestones formed of coral, foraminifera, molluscs, calcareous algae and other calcareous organic remains and are well consolidated but poorly cemented, while the limestones in the Hyakunodai Formation are frequently recrystallized.

According to KONISHI (1967), the $^{230}\text{Th}/^{234}\text{U}$, $^{231}\text{Pa}/^{235}\text{U}$ ages of the limestones from the Hyakunodai Formation, Wan Formation and the raised coral reefs are >200,000 y, 55,000-70,000 y and 5,000-6,500 y respectively.

The concentration of individual amino acids in the samples from Kikai Island dealt in this work, were determined by the writer in a previous work (TERASHIMA and TANAKA, 1976). The results were as follows: In spite of a variety of carbonate samples from different environments and accumulations, the amino acids composition of the carbonates showed a similar tendency throughout

all samples, namely, (1) aspartic acid was the most prominent constituent, contributing more than 30% to the total, (2) non-protein amino acids were present in low concentrations, ranging from trace to 2% of the total.

ANALYTICAL METHODS

Sample preparation

As the first preparation, the Recent skeletal carbonates were washed by ultrasonic cleaner and rinsed with cold distilled water. The carbonate sediments were washed with distilled water.

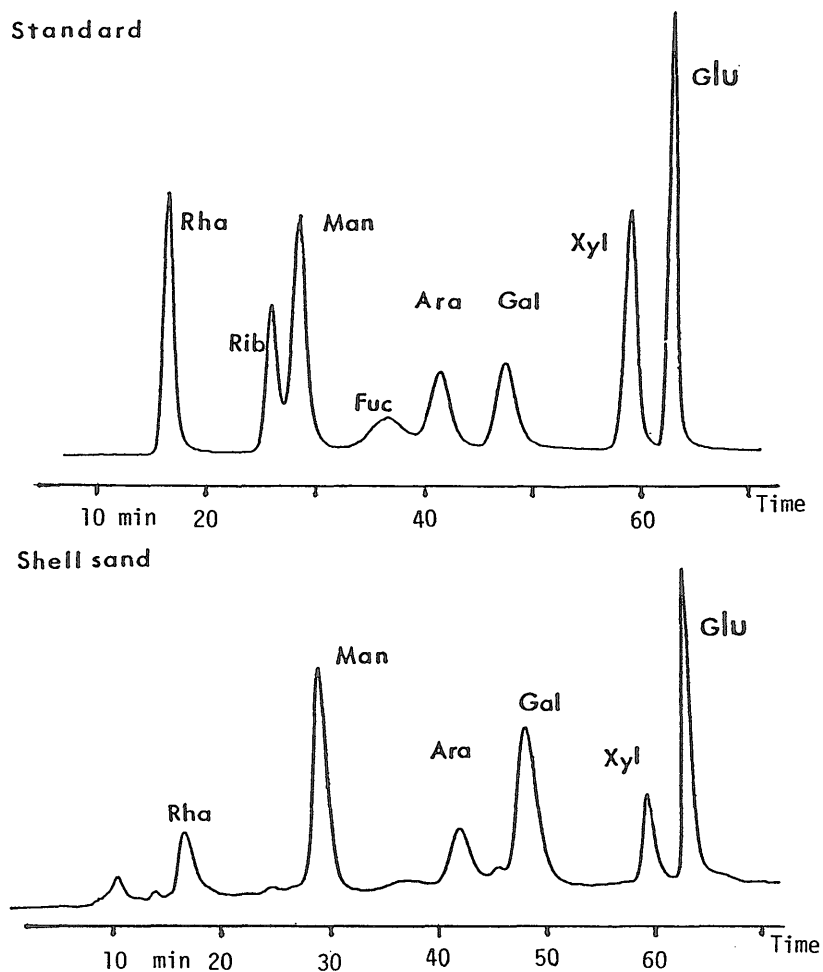


Fig. 1 HPLC Chromatograms of monosaccharides.

Rha: Rhamnose, Fuc: Fucose, Rib: Ribose, Ara: Arabinose, Xyl: Xylose, Man: Mannose, Gal: Galactose, Glu: Glucose.

Analytical condition; Column: LC Column ISA-07/S 2504 (anion exchange resin), Mobile phase: Step gradient 0.15-0.40 M boric acid (pH 8.0-9.0), Column temp.: 65°C, Flow rate: 0.6 ml/min, Detector: Fluorescence detector, Reaction reagent: 5% monoethanolamine + 4% boric acid, Reaction temp.: 150°C.

The distribution and diagenesis of monosaccharides in carbonates (M. Terashima)

Table 5 Monosaccharide compositions of the Recent skeletal carbonates.

| Sample No. (weight %) | Molluscs | | | | Alga | Coral | | | | Bryozoa | Forami- nifera |
|--------------------------|----------|-------|-------|-------|------|-------|-------|-------|------|---------|-------------------|
| | 1 | 2 | 3 | 4 | | 1 | 2 | 3 | 4 | | |
| Rhamnose | — | — | — | — | 1 | 2 | 6 | — | 2 | 9 | 6 |
| Fucose | — | — | — | — | — | 40 | 20 | 29 | — | — | 5 |
| Ribose | — | — | — | — | 1 | 2 | — | — | 5 | — | — |
| Arabinose | 34 | 37 | 48 | 50 | 11 | 12 | 13 | 17 | 8 | 16 | 9 |
| Xylose | 26 | 15 | — | 9 | 11 | 3 | 2 | 13 | 3 | 12 | 6 |
| Mannose | — | — | — | 15 | 2 | 9 | 8 | — | 3 | 15 | 14 |
| Galactose | — | — | — | — | 18 | 19 | 26 | 22 | 23 | 17 | 27 |
| Glucose | 40 | 48 | 52 | 26 | 56 | 12 | 25 | 19 | 56 | 31 | 33 |
| Total (mg/g) | 0.067 | 0.072 | 0.138 | 0.042 | 17.4 | 1.53 | 0.461 | 0.128 | 1.60 | 0.480 | 0.439 |

Table 6 Monosaccharide compositions of the Recent carbonate sediments.

| Sample No. (weight %) | Calcareous ooze | | | Shell sand | | |
|---------------------------|-----------------|--------|--------|------------|--------|--------|
| | 73—105 | 73—108 | 73—116 | 73—349 | 73—407 | 73—417 |
| Rhamnose | 10 | 4 | 4 | 14 | — | 10 |
| Fucose | 4 | — | — | — | — | — |
| Ribose | 4 | 3 | — | — | — | — |
| Arabinose | 11 | 15 | 22 | 17 | 55 | 23 |
| Xylose | 5 | 14 | 16 | 14 | 10 | 22 |
| Mannose | 21 | 15 | 14 | 16 | — | — |
| Galactose | 31 | 27 | 22 | 20 | 11 | 10 |
| Glucose | 14 | 22 | 22 | 19 | 24 | 35 |
| Total ($\mu\text{g/g}$) | 168 | 92.8 | 75.2 | 144 | 39 | 37 |

Table 7 Monosaccharide compositions of corals from the Holocene Numa coral bed in Tateyama, Chiba Prefecture.

| Sample No. (weight %) | Sample No. | | | | |
|---------------------------|------------|------|------|------|------|
| | Nu-1 | Nu-2 | Nu-3 | Nu-4 | Nu-5 |
| Rhamnose | — | — | — | 4 | — |
| Fucose | — | — | 36 | 47 | 6 |
| Ribose | — | — | — | 2 | — |
| Arabinose | 46 | 62 | 8 | 12 | 33 |
| Xylose | 25 | + | 4 | 1 | 19 |
| Mannose | — | 12 | 14 | 6 | — |
| Galactose | — | 18 | 25 | 22 | 24 |
| Glucose | 29 | 8 | 13 | 3 | 18 |
| Total ($\mu\text{g/g}$) | 120 | 237 | 163 | 294 | 58.9 |

Table 8 Monosaccharide compositions of the limestones from the Pleistocene Ryukyu Group and Holocene raised coral reef in Kikai Island, Kagoshima Prefecture.

| Sample No. (weight %) | Raised coral reef | | | | Wan Formation | | Hyakunodai Formation | | | | | | |
|---------------------------|-------------------|------|-------|-------|------------------|-------|----------------------|-------|-------|-------|-------|-------|-------|
| | Ki-1 | Ki-2 | Ki-15 | Ki-41 | Ki-5 | Ki-40 | Ki-39 | Ki-42 | Ki-43 | Ki-45 | Ki-46 | Ki-47 | Ki-51 |
| Rhamnose | 5 | — | 6 | 9 | 11 | 17 | 13 | 13 | 12 | 11 | 13 | 11 | 12 |
| Fucose | — | 49 | 4 | — | — | — | — | — | — | — | — | — | — |
| Ribose | — | — | 2 | — | — | — | — | — | — | — | — | — | — |
| Arabinose | 66 | 17 | 11 | 11 | 10 | 12 | 18 | 14 | 14 | 14 | 11 | 18 | 13 |
| Xylose | 3 | 4 | 8 | 6 | 16 | 10 | 11 | 13 | 12 | 10 | 6 | 18 | 7 |
| Mannose | 5 | 6 | 12 | 13 | 17 | 17 | 16 | 17 | 18 | 15 | 18 | 15 | 14 |
| Galactose | 17 | 19 | 27 | 23 | 21 | 24 | 21 | 20 | 19 | 21 | 21 | 21 | 24 |
| Glucose | 4 | 5 | 30 | 37 | 24 | 20 | 21 | 23 | 25 | 29 | 31 | 17 | 30 |
| Total ($\mu\text{g/g}$) | 184 | 79.9 | 134 | 52.0 | 19 | 29 | 32 | 33 | 32 | 45 | 42 | 34 | 40 |

The carbonate fragmental samples were dried at 70°C for 5 hours and ground by hand tools to 100 mesh powder.

The weathered surfaces of rock samples were cut and the fresh parts were quickly washed with 3 N HCl, rinsed with cold distilled water and dried at 70°C for 5 hours. They were crushed by a jaw crusher and ground using a ball mill, to 100 mesh powder. The powdered samples were dried at 60°C for 3 to 5 hours.

Extraction and isolation of monosaccharides

One to five (1-5) grams of the powdered samples were placed in an ampule and 3 N HCl was added. The mixture was hydrolyzed in a heating block at 110°C for 6 hours. The hydrolysate was vacuum evaporated at 50°C to remove the acid and desalted by passing through a set of three columns (the upper and the lower of which were filled with Dowex 50 W and the middle with duolite A-4, according to DEGENS *et al.*, 1963). The elute was vacuum evaporated at 50°C.

High performance liquid, chromatograph (HPLC) of monosaccharides

The dried samples containing monosaccharides were dissolved in a sample solvent (0.15 M H₃BO₃) to form borate complex. Monosaccharides were analyzed on a SHIMADZU LC-3 A high performance liquid chromatograph. The chromatograms and analytical conditions of monosaccharides by HPLC are shown in Fig. 1.

RESULTS

The respective analytical results are presented in Tables 5-8.

Recent skeletal carbonates

The total monosaccharides in the Recent skeletal carbonates ranged from 0.042 to 17.4 mg/g and varied widely among the different species of organisms and individual samples. Total monosaccharide concentrations were the lowest in the molluscs ranging from 42 to 138 $\mu\text{g/g}$. This range of concentration was the same level for bivalves' shells previously reported by BÖHM *et al.*, (1980). However, the monosaccharide compositions of the molluscs in this

study were different from the bivalves'. According to BÖHM *et al.*, (1980), mannose was the most prominent constituent in bivalves. In this study the sample no. 4, *Dosinia*, was the only sample in which mannose was determined, and the main constituents of monosaccharides in the bivalves were glucose, arabinose and xylose.

The total monosaccharides in the Recent corals ranged from 0.128 to 1.60 mg/g and varied considerably. The concentration in the samples no. 1 and no. 4 were higher than those in the others.

In terms of weight percentage (%) monosaccharides in the corals were 12-56% in glucose and 19-26% galactose. Fucose of 20-40% was the most or the second most abundant constituent in the corals except for coral no. 4 in which fucose was not detected.

The total monosaccharides of 17.4 mg/g in calcareous alga, *Penicillus*, was approximately 20-200 times as much as in corals and molluscs, was the highest of all samples.

Recent calcareous sediments

The total monosaccharides in the calcareous ooze ranged from 75.2 to 168 $\mu\text{g/g}$ and were lower than those of the Recent skeletal carbonates. Several kinds of monosaccharides were found in the calcareous ooze. The most abundant constituent was galactose (22-31%), followed by mannose (14-21%) and arabinose (11-22%). Fucose and ribose were found to be either very low (3-4%) or not detected.

The total monosaccharides in the shell-sands ranged from 37-144 $\mu\text{g/g}$ (mean 73 $\mu\text{g/g}$) and were lower than those of the calcareous ooze (mean 112 $\mu\text{g/g}$).

The monosaccharide composition var-

ied remarkably in the shell-sands. Fucose and ribose were generally not detected. The monosaccharide compositions of the samples nos. 73-407 and 73-417 inclined toward a few monosaccharides, namely, glucose, arabinose, galactose, xylose.

Corals from Holocene Numa coral bed

The total monosaccharides in the corals from the Numa coral bed ranged 58.9-294 $\mu\text{g/g}$ and fluctuated extremely. Their monosaccharide composition also varied remarkably, and then the samples can be divided into the following two groups; (1) the samples Nu-3 and Nu-4 are rich in fucose, 36% and 47% respectively. (2) the samples Nu-1, Nu-2 and Nu-5 are rich in arabinose 46%, 62% and 33% respectively, in which fucose is present only in traces. Glucose in organisms and sediments is generally the most abundant monosaccharide. However, the lower weight percentage glucose levels were found in Nu-2 (8%) and Nu-4 (3%). The samples Nu-1 and Recent coral no. 2 are *Dendrophyllia*, Nu-2 and Recent coral no. 1 are *Acropora*. Among them the monosaccharide compositions were not similar in spite of belonging to the same species.

Pleistocene and Holocene limestone from Kikai Island

The total monosaccharides in the limestones from the Hyakunodai and Wan Formations of the Pleistocene Ryukyu Group were 32-45 $\mu\text{g/g}$ and 19-29 $\mu\text{g/g}$ respectively. In general the total monosaccharides show a decreasing trend with the passing of geological time.

The monosaccharide compositions of Ki-1 and Ki-2 from the Holocene raised coral reef were different from the others, namely, arabinose of 66% in the

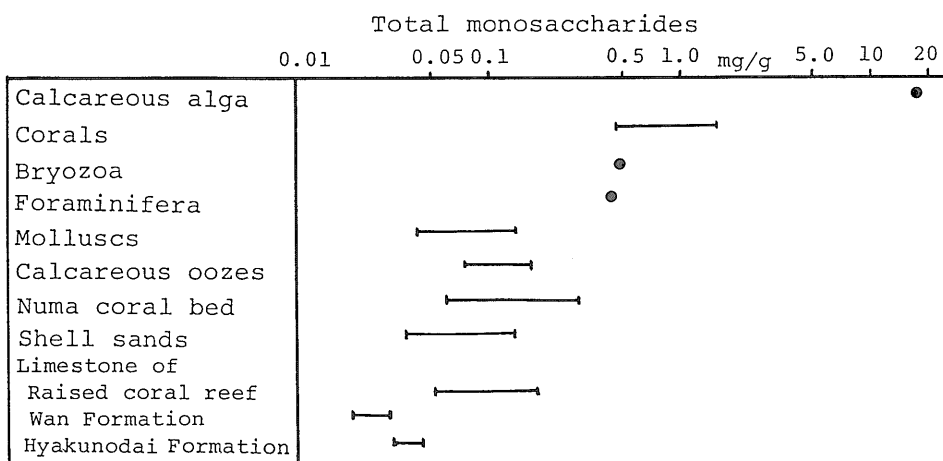


Fig. 2 Total monosaccharides in various carbonates.

Ki-1 and fucose of 49% in the Ki-2 were the single most abundant constituents in each sample and the others were minor or trace, especially with extremely low concentrations of glucose. Ribose was found in the only one sample, Ki-15 in 2%. Fucose was detected only from the Ki-2 in 49% and the Ki-5 in 4%.

DISCUSSION

Distribution of total monosaccharides in various carbonates.

The total monosaccharides in the various carbonates are shown in Fig. 2.

The total monosaccharides in the Recent skeletal carbonates varied extremely among the different species of organisms and specimens. On the whole, molluscs showed the lowest monosaccharide values, and calcareous alga the highest. The highest values in the calcareous alga is believed to be due to the fact that *Penicillus* belongs to the calcareous green algae, and that its cell wall is composed of structural polysaccharides.

The total monosaccharides in the corals also fluctuated widely. Coral is

subject to contamination by other organisms, due to its being extremely porous structure. Reef corals, in particular, have often been contaminated by symbiotic algae and/or microboring organisms, although it can be seen that the concentration of organic matter within the coral skeleton is originally low (BÖHM *et al.*, 1980).

The total monosaccharides in the Recent carbonate sediments are generally lower than those in the Recent skeletal carbonates which are their source materials.

The Recent calcareous oozes are deep sea sediments dredged from deep sea floor as mentioned before. Organic materials in the deep sea sediments seem to have been efficiently preserved under reducing environments. On the other hand the bottom water on the deep sea floor is not saturated with calcium carbonates. Therefore, it is conceivable that small calcareous tests such as of calcareous plankton are not always preserved efficiently on the deep sea floor.

The total monosaccharides in the shell-sands were still lower than in the

calcareous oozes. One of the main reasons for this is that these sediments are Pleistocene in age. Therefore, a large portion of original amounts seems to have been lost by weathering and/or diagenetic alteration. Another reason is probably due to the low concentration of monosaccharides in the source materials of shell-sands of which, as mentioned before, molluscs is the prominent component (50%).

The average value of the total monosaccharides in the corals from the Numa coral bed is 195 $\mu\text{g/g}$ and is one sixth in the Recent corals. On the other hand, according to previous work by the writers (TERASHIMA and TANAKA, 1976),

the average total amino acids (430 $\mu\text{g/g}$) in the corals from the Numa coral bed is no less abundant than that in the Recent corals (412 $\mu\text{g/g}$). Monosaccharides contained within the coral skeleton are thought to be originally low. Moreover, the total monosaccharides in corals decrease sharply with increasing age.

In general, the total monosaccharides in the limestones from Kikai Island show a decreasing trend with passing of geological time. The concentration and composition of monosaccharides in the limestones from the Hyakunodai and Wan Formation of the Pleistocene Ryukyu Group do not show so much

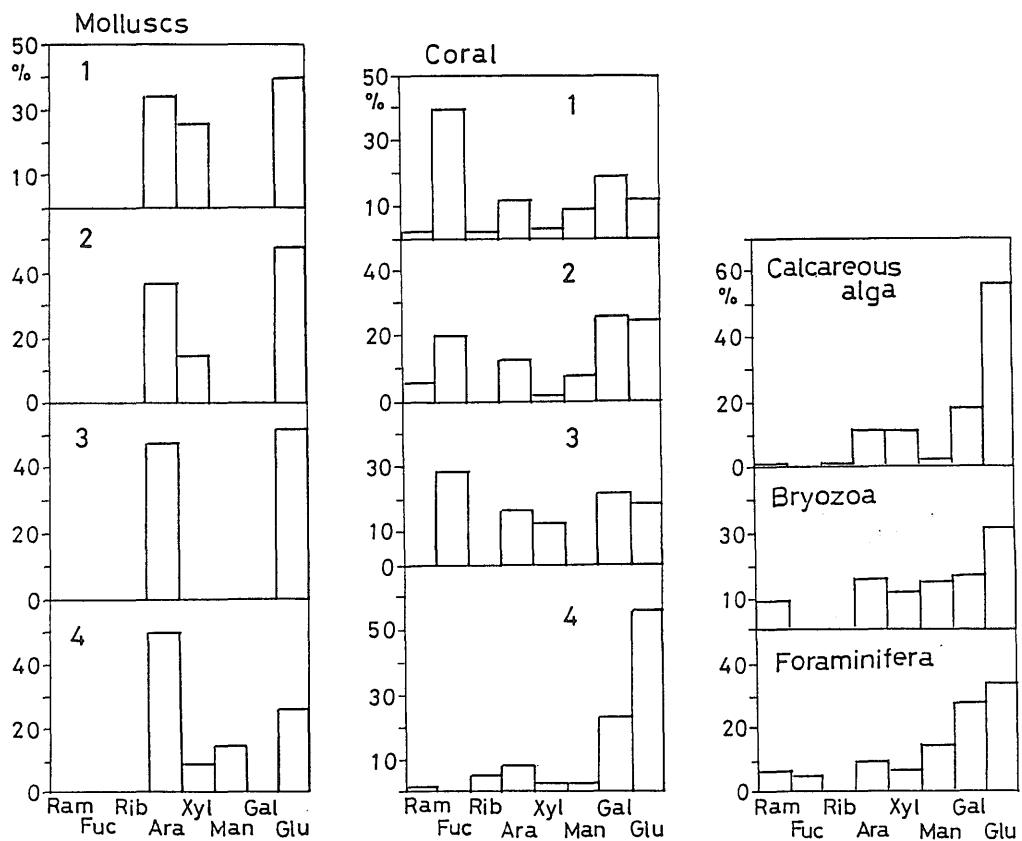


Fig. 3 Diagrams representing the relative concentrations of monosaccharides in the Recent skeletal carbonates.

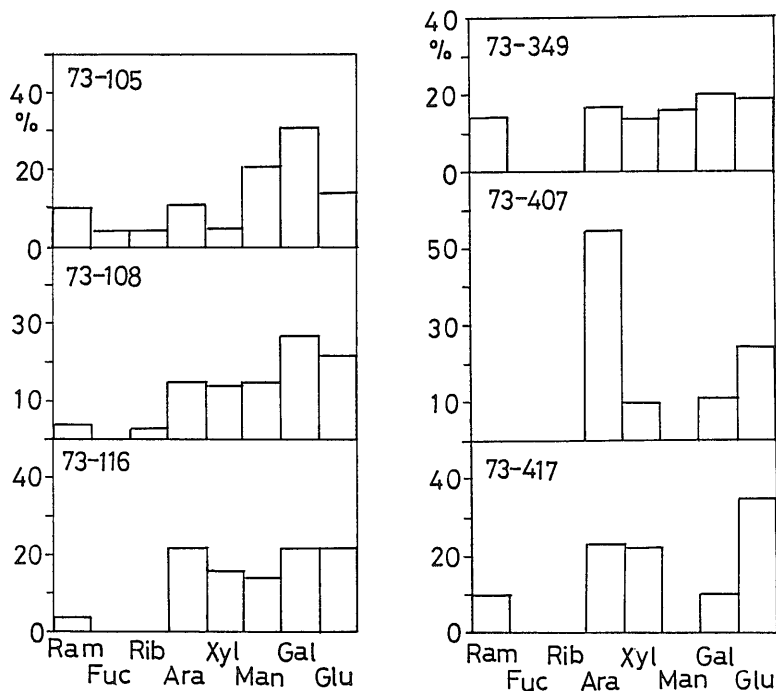


Fig. 4 Diagrams representing the relative concentrations of monosaccharides in the Recent carbonate sediments.

variation except for some samples. Metastable materials contaminated the coral skeletons in association with symbiotic algae and microboring organisms are believed to be lost by the present after the deposition of the Wan Formation (55,000 y). Then, the distributional patterns of monosaccharides in the samples from the Ryukyu Group have come to resemble one another.

Chemical characteristics of monosaccharide compositions in carbonate materials

There is little geochemical information on the occurrence and composition of monosaccharides in the various carbonates (fossils and carbonate rocks).

Histograms of monosaccharides in the various carbonates are shown in Figs.

3-6.

The monosaccharide compositions vary extremely in the various carbonate materials. In spite of their variety, however, characteristic distributional patterns are observed in each group of the carbonate samples.

Recent skeletal carbonate

Molluscan shell contains a few kinds of monosaccharides in which glucose and arabinose are the main constituents and xylose is secondary.

Among all of samples calcareous alga *Penicillus* was the only plant analysed in this study and glucose was the most abundant constituent in it. Plant cell walls are generally formed of structural polysaccharides which are often composed of xylan (xylose), galactan (gala-

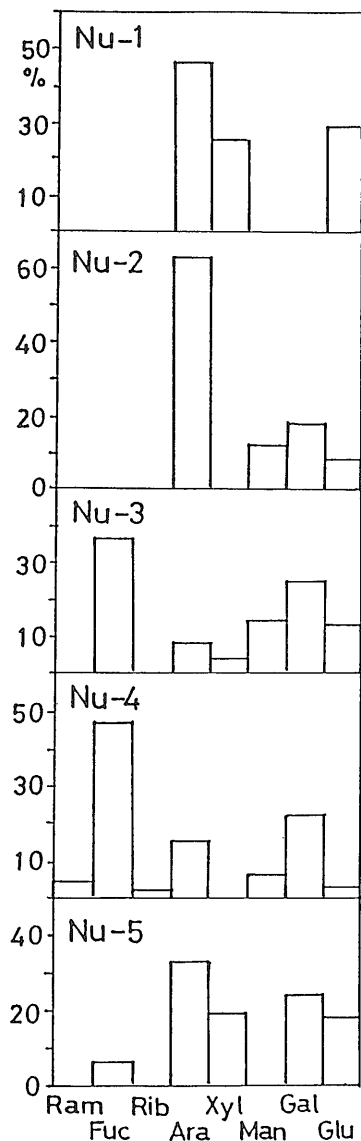


Fig. 5 Diagrams representing the relative concentrations of monosaccharides in corals from the Holocene Numa coral bed in Tateyama, Chiba Prefecture.

ctose) and mannan (mannose) without glucose in other kinds of algae (EGAMI, 1971). Therefore, more analytical data on algae is required.

Fucose was the highest monosaccharide in most Recent corals except for

the sample no. 4. According to BÖHM *et al.*, (1980), fucose may be used as a bio-indicator of corals in modern age. However, the monosaccharide composition of the sample no. 4, one of the Recent corals, was different from the others', namely, in the Recent coral no. 4, glucose was the single most prominent constituent, comprising of about 56% of the total, with no fucose.

Fucose is present in brown algae as a component of fucan. Corals are divided into hematypic coral where *Zooxanthella* is present as symbiotic algae and ahematypic coral where it is not. *Zooxanthella* plays an important role in calcification of corals (YAMASATO, 1975). Therefore, high fucose levels in the Recent corals may be due to symbiotic algae or epiphytes.

Recent carbonate sediments

Monosaccharide composition of calcareous oozes is represented by polysaccharides in the tests of planktonic foraminifera. As shown in Fig. 4, monosaccharide compositions of the oozes are fluctuated somewhat and it seems to be due to dissolution during passing through a long water column.

Shell-sands are composed of many kinds of fossil remains. Shell-sand 73-349 is composed of a mixture of various fossil fragments and contains many kinds of monosaccharides. On the other hand, the monosaccharide compositions of nos. 73-407 and 73-417 incline toward a few monosaccharides as shown in Fig. 4. Their distributional patterns are resemble to those of molluscs nos. 1, 2 and 4.

Corals from Holocene Numa coral bed

Monosaccharide compositions of corals show a wide variation, especially in the samples from the Holocene Numa

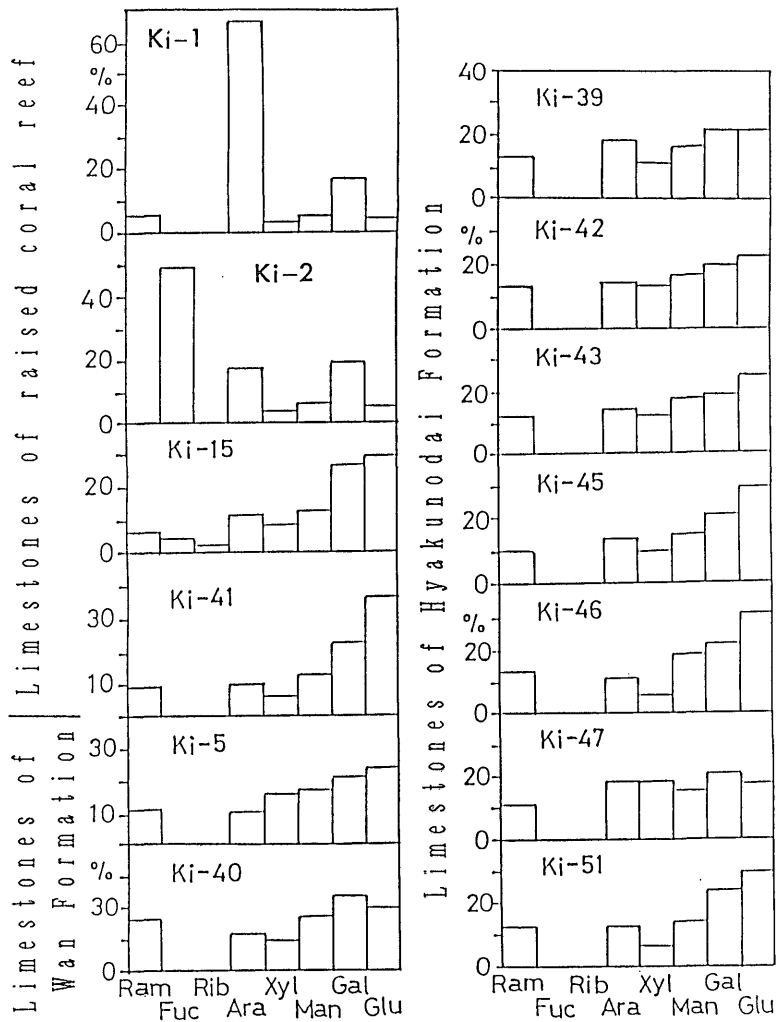


Fig. 6 Diagrams representing the relative concentrations of monosaccharides in the limestones from the Pleistocene Ryukyu Group and Holocene raised coral reef in Kikai Island, Kagoshima Prefecture.

coral bed. Such a large variation is believed to be due to the morphological and ecological characteristics of corals. Namely, corals are subject to contamination by other organisms such as symbiotic algae, epiphytes and boring organisms.

As mentioned before, fucose is generally the most prominent constituent and gives rise to large variations in the

monosaccharide compositions of Recent corals. However, the highest concentration of fucose was found in the only two samples from the Numa coral bed.

Monosaccharides contained in the symbiotic algae, epiphytes and boring organisms are believed to be lost more rapidly during diagenesis than those in the coral skeleton.

Pleistocene and Holocene limestones from Kikai Island

The Pleistocene Ryukyu Group in Kikai Island contains many kinds of fossil remains including reef corals. Seven monosaccharides were found in the samples from the Group. Ribose is missing in all of them except Ki-15, and fucose is also missing but two samples.

The distributional patterns of monosaccharide compositions in the limestones from the Hyakunodai and Wan Formations of the Ryukyu Group are different from those of the samples Ki-1 and Ki-2 from the Holocene raised coral reef. The monosaccharide compositions of Ki-1 and Ki-2 resemble those of corals from the Holocene Numa coral bed. The distributional patterns of monosaccharide composition in the limestones from the Hyakunodai and Wan Formations are similar in each other. Although, mannose and rhamnose were minor constituents in Recent corals, they are present in considerable amounts in most samples from the Ryukyu Group.

HANDA and MIZUNO (1973) have conducted a geochemical study of carbohydrates in the lake sediments of Lake Suwa. They suggested that the stability of monosaccharides of sedimentary carbohydrate against microbiological attack were ordered as follows; glucose, galactose, fucose > mannose > ribose, rhamnose, and arabinose. However, fucose, one of the most stable constituents, appears to be rapidly lost in our samples, and rhamnose and arabinose, metastable constituents, appears to remain in the limestones of the Ryukyu group in Kikai Island.

Consequently, the preservation of individual monosaccharides seems to depend on their occurrence, that is, whether they are present in the coral skeleton or

attached to the outside of it.

CONCLUSIONS

Individual monosaccharides in Recent skeletal carbonates, Recent carbonate sediments and Pleistocene limestone were analyzed by high performance liquid chromatography. The distributional patterns of monosaccharides in the various carbonates were shown. Moreover, the sources, chemical characteristics and diagenesis of monosaccharides in the carbonates were discussed. The results are summarized as follows.

1) The total monosaccharides in the Recent skeletal carbonate ranged from 0.042 to 17.4 mg/g, and fluctuated extremely among different species of organisms and different specimens. The highest amount was found in the calcareous alga and the lowest in the molluscs. Recent corals generally showed higher levels of monosaccharides caused by contamination by other organisms.

2) monosaccharide compositions fluctuated among different species and different specimens.

3) Fucose was the most abundant constituent in some of the Recent corals. However, it was not detected in a coral from the Pleistocene Ryukyu Group. It can be seen that the high fucose levels in some of the Recent corals are due to contamination by symbiotic and/or epiphytic algae.

4) Monosaccharides in the Recent skeletal carbonates have gradually been lost during diagenesis. The distributional pattern of individual monosaccharides in the carbonates of the Ryukyu Group also shows the similar trend.

In spite of the variation of individual monosaccharides in the various carbo-

nates, a few types of distributional patterns could be recognized, and in general the total monosaccharides showed a decreasing trend with increasing age.

If more data on monosaccharides in the various carbonates investigated, the monosaccharide compositions may be useful for the clarification of origins and diagenesis of carbonate sediments and rocks consisting of various skeletal materials.

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現世生物遺骸炭酸塩及び炭酸塩堆積物における単糖類の分布と続成作用

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要 旨

現世生物遺骸炭酸塩、現世炭酸塩堆積物、更新世石灰岩中に含まれる単糖類含有量を高速液体クロマトグラフィーにより求めた。

現世の生物遺骸炭酸塩中の総単糖類含有量は、0.042-17.4 mg/g の間にあり、種や試料の違いにより非常に広い範囲を示す。その含有量は石灰藻において最も高く、二枚貝において最も低い。現世さんごは一般に共生藻類などの影響により高い含有量を示す。

更新世の石灰岩中の総単糖類含有量は19-45 $\mu\text{g/g}$ の範囲を示す。すなわち、現世炭酸塩物質中の単糖類の含有量は非常にばらつくが、地質時代が古くなるに従って急激に減少する傾向を示す。

現世の生物遺骸炭酸塩中の単糖類の組成は、種や試料の違いにより大きく変動するが、根源物質の組成を反映する様なタイプに分けられる。しかし、続成作用により根源物質の影響は次第に失われて、更新世の石灰岩中の単糖類の組成は互いに類似したものになっている。

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