NOTE

Ammonia volatilization and high $^{15}\text{N}/^{14}\text{N}$ ratio in a penguin rookery in Antarctica

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Ammonium fractions from a soil of a penguin rookery in Antarctica and from water of a pond in the rookery exhibit the highest $^{15}\text{N}/^{14}\text{N}$ ratios among biogenic nitrogen so far observed. Though soils of seabird rookeries appear, in general, to have high nitrogen isotope ratios, the still higher ratios make the penguin rookery stand out from other seabird rookeries. The observation suggests that ammonia volatilization is a cause of the ^{15}N enrichment in the soil ammonium and that the Antarctic climate is particularly effective on ^{15}N enrichment for ammonium remained in the soil and water.

INTRODUCTION

Seabird rookeries in Antarctica are a doubly unique, natural environment from the viewpoint of nitrogen cycling. Seabirds deposit there large quantities of nitrogenous substances of oceanic origin that fertilize the rookeries. The cold climate of Antarctica slows biological nitrogen metabolism in the soil. We now show that the nitrogen isotope ratios of soils from seabird rookeries are far higher than any other natural, biogenic nitrogen reported to date, and indicate that none but the unique environment is responsible for the extremely high ratio.

The large flux of organic nitrogen essential for the development of flora and fauna in a seabird rookery must be significant in determining its ecological feature. Indeed, the amount of nitrogen deposited to a seabird rookery in the form of excreta alone exceeds for some cases in terms of unit area that of fertilizer applied to a cultivated field in the most fertilizer-intensive agriculture (Mizutani, 1984). And a characteristic, heavy plant growth is observed there (Ishizuka *et al.*, 1985). This is especially apparent in polar regions, where a plant community around a rookery forms a luxuriant, closed community in contrast with surrounding barrens (Summerhayes and Elton, 1923;

Matsuda, 1964).

Since nitrogen in avian excreta is mostly in the form of uric acid (often as high as 70–90%) that cannot be directly utilized by higher plants, bacterial transformation of uric acid must come first to start the nitrogen cycle in a peculiar ecosystem where the activity of large animals is situated at the beginning of nutrient flow.

One of characteristic features of soils of seabird rookeries is their high nitrogen isotope ratio. For instance, an earlier work by one of us found from a rookery soil and an algal felt of the same location as the present study, the highest ratios so far reported for unfractionated biogenic matters in nature (Wada *et al.*, 1981). And our work on rookery soils of a wide variety of their nitrogen content (4.4%–0.02% of dry soil) agrees with the observation (Mizutani *et al.*, 1986). As the distribution of $^{15}\text{N}/^{14}\text{N}$ reflects sources and metabolism of nitrogen in a biogeochemical system (Wada, 1980), a study of the nitrogen isotope composition of various nitrogenous substances from a rookery should help to understand its nitrogen cycle.

SAMPLES AND EXPERIMENTAL PROCEDURES

Surface soils (0–5 cm), pond water, and

bottom mud were collected from an Adelie Penguin (*Pygoscelis adeliae*) rookery (77° 12'S, 166° 28'E) in Cape Bird, Ross Island, Antarctica, and kept frozen until they were ready for chemical analyses. The pond was located near the center of the rookery. Fresh droppings were collected soon after their deposition onto the soil surface, kept frozen, and later vacuum-dried. Samples were obtained on January 6, 1981 (Nakaya *et al.*, 1982), about a few days before the formation of crèche* (Aoyanagi, 1981).

All the samples except the excreta were subjected to the measurement of their nitrogen content and to the mass analysis without drying. Their water content was separately obtained by drying a portion of them. Procedures for isotopic analysis were described elsewhere (Kreitler, 1975; Wada and Hattori, 1976). Nitrogen isotopic composition is expressed as the per mil deviation from atmospheric nitrogen as follows.

$$\delta^{15}\text{N (per mil)} = \left[\frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}}}{(^{15}\text{N}/^{14}\text{N})_{\text{air}}} - 1 \right] \times 1000$$

Organic nitrogen was determined by Kjeldahl digestion (Wada *et al.*, 1975). Soil ammonium was extracted by the method given elsewhere (Mizutani *et al.*, 1985), and its amount was measured by a phenol-hypochlorite method (Solorzano, 1969). The chromatographic isolation of uric acid and its mass analysis were done according to the method described elsewhere (Mizutani *et al.*, 1985; Mizutani and Wada, 1985). After the isolation, uric acid content of a fraction was obtained spectroscopically, and its purity in the fraction was checked by comparing the content with organic nitrogen content of the fraction.

RESULTS AND DISCUSSION

Nitrogen content and $\delta^{15}\text{N}$ of these samples gave a variety of figures (Table 1). Among them, the high values of 47.7 per mil and 49.6 per mil for $\text{NH}_4^+\text{-N}$ in the pond water and the rookery soil would be most noteworthy: They are the highest $\delta^{15}\text{N}$ values for a fractionated nitrogen so far found from natural, biogenic samples.

Table 1. Nitrogen content and $\delta^{15}\text{N}$ in samples from a penguin rookery in Cape Bird, Ross Island, Antarctica.

Sample	Water content (% wet weight)	Nitrogen content (mgN/g dry sample)			$\delta^{15}\text{N}$ (per mil)		
		Kjeldahl-N ^a	$\text{NH}_4^+\text{-N}$	Uric acid-N	Kjeldahl-N ^a	$\text{NH}_4^+\text{-N}$	Uric acid-N
Soil near the edge of glacier	3.1	0.039	0.0040	n.d.	—	—	—
Soil in between glacier and rookery ^b	0.27	0.11	0.034	n.d.	12.2	16.8	—
Dried excreta	n.d.	126.8	—	60.3	7.4	—	6.2
Bottom mud	22.4	20.4	7.2	0.28	33.7	39.4	7.5
Rookery soil near the pond	1.3	28.5	5.7	0.085	32.1	49.6	8.3
Pond water	97.1	135.5	110.2	n.d.	43.1	47.7	—

A short, horizontal bar indicates that the size of the sample was not sufficient to perform an accurate measurement, and n.d. stands for "not detected." The chromatographic isolation procedure was done twice to obtain the acid from the rookery soil, while each of the other two uric acid fractions was prepared after only one isolation procedure.

a: Sum of organic nitrogen and ammonium nitrogen.

b: The location is about a few hundred meters away from an approximate periphery of the rookery, and penguins and skuas (*Catharacta maccormicki*) are sighted to come nearby casually.

* Chicks of some species of *Sphenisci* (penguins) form during a certain period of their growth (in the case of the Adelie Penguin, age from 3 weeks to 8 weeks after hatching) a large gathering of their own, which can be compared to a public nursery for infants while their mothers are at work or in hospital, etc. Hence, the gathering is called a crèche.

Fig. 1. Distribution of $\delta^{15}\text{N}$ for various natural substances of biogeochemical interest with special reference to those from seabird rookeries.

For the definition of $\delta^{15}\text{N}$, see the text. Ranges for most samples are shown by black bars. Symbols of various kinds stand for the ratios obtained for samples from seabird rookeries. Circles are for samples from the Adelie Penguin rookery in Cape Bird, Ross Island, Antarctica: black ones for Kjeldahl-N and white ones for $\text{NH}_4^+\text{-N}$; black triangles are for Kjeldahl-N from Black-tailed Gull (*Larus crassirostris*) rookeries in Japan; and a black square for Kjeldahl-N from a Short-tailed Albatross (*Diomedea albatrus*) rookery in Torishima (alias: Ponafidin Island), Izu Islands, Japan, which is the only island known to date as a rookery of the albatross (Hasegawa, 1984). Among $\delta^{15}\text{N}$ for gull and albatross rookery samples, only highest values are shown. All the penguin rookery data but the one for aquatic plants are of the present study. A number of published results as well as our unpublished data are used to draw the figure.

The previous record was 34.7 per mil for nitrate-N of a surface soil from recharge and discharge areas at a university farm in Canada (Karamanos and Rennie, 1980). Since the nitrogen found in the samples from the rookery must have come mostly from droppings and organic remains of penguins, the isotope ratio of the incoming nitrogen and the fractionations of nitrogen isotopes during their transformation to ammonium found in the soil must contribute to the high $\delta^{15}\text{N}$ values.

Figure 1 shows the distribution of nitrogen isotope ratios for various natural substances; bars cover ranges for samples normally encountered and individual symbols represent the ratios found from seabird rookeries. Because of an enrichment of ^{15}N along a food chain (Miyake and Wada, 1967; DeNiro and Epstein, 1981), the isotope ratios for animals are gene-

rally higher than those for plants. It is seen in Figure 1 as the shift toward higher ratio of the bars for animals from those for plants. The enrichment continues within the animal kingdom (Schoeniger and DeNiro, 1984; Minagawa and Wada, 1984), and the extent of the bars for animals includes this phenomenon.

As seabirds feed mostly on fish and squid, they are at the top end of an oceanic food chain. Therefore, the ^{15}N content of seabirds is one of the highest among aquatic animals. Primary feathers of two gull species (*Larus crassirostris* and *Larus schistisagus*), one albatross species (*Diomedea albatrus*), and one cormorant species (*Pharacrocorax carbo*) gave an average nitrogen isotope ratio of 14.4 per mil (altogether 17 analyses) (Mizutani *et al.*, 1986). It is near the upper end of the range of the ratio for aquatic animals.

A rather low value of 6.2 per mil for uric acid-nitrogen in the penguin excreta (Table 1) may appear contradictory to the above argument. However, the low value results partly from a material balance of nitrogen isotopes: Because of the enrichment of ^{15}N in animal body, the nitrogen in excreta must, in turn, be depleted in ^{15}N . Another cause for the low value is the relatively low isotope ratio for nitrogen in their diet (Mizutani and Wada, in preparation). In fact, the $\delta^{15}\text{N}$ values for various organs (including feathers) of Adelie penguins yielded an average of 10.5 per mil with the standard deviation of 1.4 per mil (12 analyses) (Mizutani *et al.*, 1986). This is considerably lower than those for feathers of other seabirds.

Owing to the enrichment along the food chain before the penguin, however, even this low value is still markedly higher as the $\delta^{15}\text{N}$ value for incoming nitrogen to an ecosystem than that for common sources of the incoming nitrogens. Usually, nitrogen enters into a terrestrial ecosystem in the form of nitrate and ammonium in precipitation and by *in situ* nitrogen fixation. These incoming nitrogen normally have an isotope ratio of near or less than zero per mil (Wada *et al.*, 1984). Therefore, the nitrogen in excreta and other organic remains that enter the rookery has an exceptionally high $\delta^{15}\text{N}$ value.

The high $\delta^{15}\text{N}$ value of incoming nitrogenous substances to the rookery, however, still falls far short of the isotope ratio of the ammonium-nitrogen found in the rookery. The discrepancy must be understood in terms of the isotope fractionations during the transformation of the nitrogen.

It has been shown that the isotope fractionation during the soil microbial transformation to ammonia of uric acid that must account for the majority of the incoming nitrogen is no more than 5 per mil (Mizutani *et al.*, 1985). Hence, it cannot explain the extent of ^{15}N enrichment in ammonium in the rookery soil and water.

The surface water of the pond was deep green probably because of the presence of cyanobacteria, and the water had a pH value of 8.3. Kreitler (1975) reported an apparent frac-

tionation factor of 1.038 for NH_3 volatilization from barnyard and feedlot soils. And our study on soils from a black-tailed gull rookery at Kabushima, Hachinohe, Japan, gave a similar result (Mizutani *et al.*, 1985). The microbial decomposition of uric acid together with the photosynthetic activity of cyanobacteria must have locally raised the pH, and a large fractionation associated with ammonia volatilization must have occurred.

A laboratory experiment by Lindeboom (1984) demonstrated that the nitrification of ammonia and the subsequent denitrification were relatively unimportant processes in a Macaroni Penguin (*Eudyptes chrysolophus*) rookery and a King Penguin (*Aptenodytes patagonicus*) rookery in Marion Island (46°54'S, 37°44'E), and the volatilization of ammonia, instead, was suggested to be the most important process for its loss from the rookeries.

Since more than 80% of the Kjeldahl nitrogen in the pond water comprises ammonium, the isotope ratio of the Kjeldahl nitrogen is also high. The value of 43.1 per mil observed for the Kjeldahl nitrogen of the pond water is the highest so far reported for an unfractionated nitrogenous matters in nature, the previous record being 30.7 per mil for an algal felt and 28.6 per mil for a surface soil (Wada *et al.*, 1981), both of which were collected from the same penguin rookery as the one for the present study.

In a clear contrast with these high nitrogen isotope ratios in the penguin rookery, the $\delta^{15}\text{N}$ value for uric acid (6.2 per mil) found from the penguin excreta was about 3 per mil lower than that reported for the acid in excreta of black-tailed gulls (9.1 per mil) (Mizutani *et al.*, 1985). This may be due to the fact that the penguins at Cape Bird feed on mostly krill, while the gulls live on primarily sardine and anchovy (Mizutani and Wada, in preparation).

In spite of the higher $\delta^{15}\text{N}$ value for incoming nitrogenous substances, rookery soils of the gulls did not give isotope ratios as high as those from the penguin rookery and the pond water (Fig. 1). This may be because the climate of

Antarctica retards the decomposition of uric acid and the nitrification of the resultant ammonium, and, thus, allows a longer period of time for the ammonia to evaporate.

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