AMMONIUM AND INSOLUBLE NITROGEN IN PRECAMBRIAN ROCKS FROM THE GAWLER CRATON, AUSTRALIA: INFERENCE OF LIFE ACTIVITY

YUUKO ITIHARA* and YOSHIKI TAINOSHO**

Abstract Ammonium content of biotite and carbonate-carbon, organic carbon, soluble nitrogen and insoluble nitrogen contents of rocks from the Gawler Craton, Australia, were determined to infer the life activity at the Archaean and the early Proterozoic. NH₄⁺ content of biotite is 21-46 ppm in the granitic rocks intruded in middle and early Proterozoic time (Charleston Gr.: 1500-1450 Ma, Middle Camp Gr.: 1700 Ma, Donington Gr.: 1850 Ma), and 103-117 ppm in the Hutchison Schists (2100-1850 Ma), and 8-33 ppm in the Carnot Gneisses (about 2600 Ma). Insoluble N content of rocks (sum of NH₂⁺-N in mineral structure and organic N in kerogen) is 33-62 ppm in the Hutchison Schists and 3-8 ppm in the Carnot Gneisses. Carbonate-C, organic C, soluble N were detected in the Hutchison Schists and the Carnot Gneisses, but the quantities are negligible or small (0-0.01%, 0.02-0.08%, and 0-9 ppm, respectively) and there is no significant difference of the contents between the Hutchison Schists and the Carnot Gneisses. The analytical results lead to the following conclusions: There was some biologic activity in the depositional environments of the original sediments of the Hutchison Schists and organic matter accumulated in the sediments, while for the Carnot Gneisses the existence of organisms in the depositional environments of the original sediments is difficult to infer from the low insoluble N contents of the rocks and also from the low NH₄⁺ contents of their biotites, but it does not necessarily mean no life in the environments because NH₄⁺ might be removed from the rocks during metamorphism.

Introduction

ITIHARA and SUWA (1985) proposed ammonium in biotite for a possible chemical fossil inferring biologic activity in Precambrian time. This proposal is based on the fact that biotite in metamorphosed pelitic rocks contains a large amount of ammonium ion which was inherited from organic matter of the original sedimentary rocks (ITIHARA & HONMA, 1979). From this viewpoint, geochemical studies on nitrogen have been carried out for Precambrian rocks from various areas; Finland (ITIHARA & SUWA, 1985), Kenya (ITIHARA et al., 1986), South Africa and Swaziland (ITIHARA & SUWA, 1987), and Canada (ITIHARA & AHARA, 1987). These studies indicate predominant biologic activity in Proterozoic time and rather less activity in Archaean time. The purpose of this study is to obtain geochemical data of nitrogen for early Proterozoic and Archaean rocks in Australia. Samples were collected from Precambrian rocks of the Gawler Craton in Eyre Peninsula, and ammonium contents of biotites and carbonate-carbon, organic carbon, soluble nitrogen and insoluble nitrogen contents of rocks were determined.

Geological setting of samples

Geology of Eyre Peninsula, which is the southern part of the Gawler Craton, has been described by PARKER et al. (1985). Fig. 1 shows tectonic sketch of Eyre Peninsula (PARKER et al., 1985) and the locations of rocks used in this study. Table 1 summarizes geological evolution of Eyre Peninsula in Precambrian time. According to PARKER et al. (1985, 1986), the Gawler Craton consists of Archaean to early Proterozoic gneisses, granites

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* Fujishiro-dai 2-5-11, Suita, 565 Japan.
** Department of Geology, Faculty of Education, Kobe University, Kobe, 657 Japan.
and metasediments, and middle Proterozoic sediments, volcanics, and granitoids.

The oldest rocks in Eyre Peninsula are the Sleaford Complex (about 2700–2100 Ma). Sample Nos. 8 to 14 are from the Carnot Gneisses which are Archaean rocks in the Sleaford Complex. These gneisses have been highly metamorphosed during the Sleafordian Orogeny (2500–2300 Ma) and the Kimban Orogeny (1850–1580 Ma), which are major tectonic events recognized in the southern Gawler Craton. Garnetiferous quartzofeldspathic gneiss is the dominant lithology in the Carnot Gneisses.

The Sleaford Complex is unconformably overlain by the Hutchison Group, which is a mixed clastic and chemical sedimentary sequence consisting of a basal quartzite unit, interlayered clastic carbonate and iron formation facies, and an upper psammopelitic unit. Sample Nos. 5 to 7 are from mica schists in the Hutchison Group. The schists consist of fine-grained biotite, muscovite, quartz and feldspar.

The Hutchison Group was deformed and metamorphosed during the Kimban Orogeny, and granitoids were emplaced during and after the Kimban Orogeny. Granitoids intruded during the Kimban Orogeny belong to the Lincoln Complex, a series of granitic, migmatic, gneissic and volcanic rocks. Sample No. 3 is from the Donington Granitoid and No. 4 is from a paragneiss in the Lincoln Complex. The Donington Granitoid (1850 Ma) was emplaced during the first tectonic event of the Kimban Orogeny. The Donington Granitoid is comprised of various granitoids ranging from quartz gabbro-norite, through hypersthene granite to late-stage leucogranite. The Middle Camp Granite of the Lincoln Complex was emplaced during the second tectonic event of the Kimban Orogeny and folded by the third tectonic event (PARKER et al., 1985). This granite is foliated biotite
Table 1. Geological evolution of Eyre Peninsula in Precambrian time (after Parker et al., 1985). Paragneiss in Lincoln Complex was added by authors.

**CRATONIZATION**

- Hiltaba Suite Granites
- Gawler Range Volcanics and Corunna Conglomerate sedimentation

**PROTERozoIC**

- Moody and Carpa Granites
- Middle Camp Granite

**KIMBAN OROGENY**

- McGregor Volcanics and Moonable Fm sedimentation
- Myola Volcanics
- Donington Granitoid and paragneiss

**LINCOn COMPLEX**

- HUTCHISON GROUP SEDIMENTATION

<table>
<thead>
<tr>
<th>AGE (million years)</th>
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<tbody>
<tr>
<td>2500</td>
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<td>2000</td>
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<td>1500</td>
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</tbody>
</table>

**SLEAFORD COMPLEX**

- Gilloth Granite
- Kiana and Whidbey Granites
- Gneiss-Waddeikeye Rocks
- Gneiss-Warramboo
- Carnot Gneiss (minimum age)

**ARCAHAEN**

- Miltalie Gneiss (Plug Range)

- SLEAFORD OROGENY

<table>
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<th>AGE (million years)</th>
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<td>2500</td>
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The youngest of the granitoids in the Gawler Craton is represented by the Charleston Granite of the Hiltabe Suite, which is a massive, homogeneous, porphyritic granite intruded at 1500–1450 Ma after the Kimban Orogeny. Sample No. 1 is from the Charleston Granite.

**Experimental methods**

Biotites were separated by standard procedures. The biotite samples are more than 95% pure. Ammonium contents of the biotites were measured by the same method described by Itihara and Honma (1979), except that indophenol reagent was used instead of Nessler's reagent in the colorimetric estimation of ammonium ion. Powdered whole rock samples were obtained from a few pieces of each rock which was cleaned with HCl-HF solution and rinsed with methanol-benzene. Organic carbon, carbonate-carbon, soluble nitrogen and insoluble nitrogen contents of the powdered rocks were measured by the procedure described by Itihara et al. (1986), except that indophenol reagent was used in the colorimetric estimation of
Table 2. NH$_4^+$ contents of biotites in Precambrian rocks of the Gawler Craton, Australia.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>NH$_4^+$ (ppm)</th>
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</thead>
<tbody>
<tr>
<td>1 Charleston Granite, Hiltaba Suite (1500-1450 Ma)</td>
<td>24</td>
</tr>
<tr>
<td>2 Middle Camp Granite (1700 Ma)</td>
<td>46</td>
</tr>
<tr>
<td>3 Donington Granitoid (1850 Ma)</td>
<td>Lincoln Complex</td>
</tr>
<tr>
<td>4 Paragneiss (2100-1850 Ma)</td>
<td></td>
</tr>
<tr>
<td>5 Schist</td>
<td></td>
</tr>
<tr>
<td>6 Schist</td>
<td>Hutchison Group (2100-1850 Ma)</td>
</tr>
<tr>
<td>7 Schist</td>
<td></td>
</tr>
<tr>
<td>8 Carnot Gneiss</td>
<td></td>
</tr>
<tr>
<td>9 Carnot Gneiss</td>
<td></td>
</tr>
<tr>
<td>10 Carnot Gneiss</td>
<td></td>
</tr>
<tr>
<td>11 Carnot Gneiss</td>
<td>Sleaford Complex (2600 Ma)</td>
</tr>
<tr>
<td>12 Carnot Gneiss</td>
<td></td>
</tr>
<tr>
<td>13 Carnot Gneiss</td>
<td></td>
</tr>
<tr>
<td>14 Carnot Gneiss</td>
<td></td>
</tr>
</tbody>
</table>

the nitrogen contents, instead of Nessler’s reagent.

**Results and discussion**

1. **Ammonium content of biotites**

Table 2 shows NH$_4^+$ contents of biotites. Biotite in the Chareston Granite (No. 1) contains 24 ppm of NH$_4^+$, and biotites in the Middle Camp Granite, the Donington Granitoid and a gneiss, which are of the Lincoln Complex (Nos. 2-4), contain 21-46 ppm of NH$_4^+$. The level of these contents is similar to contents obtained from biotites in I-type granitic rocks of the Lachlan Fold Belt, Australia (Cambrian-Devonian) (Range: 2-60 ppm, average: 30 ppm, number of analyses: 11, TAISHO & ITIHARA, 1988). Sample No. 3 is from a hypersthene granite gneiss, possibly highly metamorphosed granite, and No. 4 is from a paragneiss which is located at a distance of about 30 m from the hypersthene granite gneiss body. The origin of the paragneiss is supposed to be the Hutchison metasediments. NH$_4^+$ content of biotite is 39 ppm in the paragneiss and is 21 ppm in the hypersthene granite gneiss.

Biotites in schists of the Hutchison Group (Nos. 5 to 7) contain 103-117 ppm NH$_4^+$. The contents are a few times higher than those of biotites from the Charleston Granite and the Lincoln Complex. The contents are about the same as that of biotite in a schist in the Cooma district of the Lachlan Fold Belt (113 ppm, TAISHO & ITIHARA, 1988). The previous studies showed that biotites in igneous rocks contain relatively low NH$_4^+$ (tens of ppm), while biotites in metamorphosed pelitic rocks contain considerably high NH$_4^+$ (hundreds of ppm) (ITIHARA & HONMA, 1979, 1983; ITIHARA & SUWA, 1985). The origin of NH$_4^+$ in the latter is mostly organic N in the original pelitic rocks. Taking the data in consideration, the relatively high NH$_4^+$ contents of the biotites from the Hutchison Schists suggest that there was biologic activity in the depositional environments of the original sediments, and that organic residue formed from the organisms accumulated in the sediments.

NH$_4^+$ contents of biotites in the Carnot Gneiss (Nos. 8 to 14) of the Archaean Sleaford Complex range from 8 to 33 ppm. The contents are comparable to those of biotites in the Chareston Granite and the Lincoln Complex (Nos. 1 to 4). According
Table 3. Carbonate-C, organic C, soluble N and insoluble N contents of Precambrian rocks in the Gawler Craton.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Carbonate-C (%)</th>
<th>Organic C (%)</th>
<th>Soluble N (ppm)</th>
<th>Insoluble N (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hutchison Schist 5</td>
<td>nd</td>
<td>0.03</td>
<td>nd</td>
<td>62</td>
</tr>
<tr>
<td>6</td>
<td>0.01</td>
<td>0.04</td>
<td>nd</td>
<td>33</td>
</tr>
<tr>
<td>7</td>
<td>nd</td>
<td>0.08</td>
<td>9</td>
<td>42</td>
</tr>
<tr>
<td>Carnot Gneiss 9</td>
<td>0.01</td>
<td>0.05</td>
<td>nd</td>
<td>8</td>
</tr>
<tr>
<td>11</td>
<td>0.01</td>
<td>0.02</td>
<td>nd</td>
<td>3</td>
</tr>
</tbody>
</table>

to PARKER et al. (1985), the evolution of the Gawler Craton can be traced back to at least 2700 Ma, and the oldest Carnot Gneiss of the region probably were formed from sedimentary rocks deposited on the margin of a much older craton. Actually the rocks of sample Nos. 8–10 is sedimentary rocks in origin on reference to the occurrence and garnet-rich (up to 25%) lithofacies (layered garnetiferous quartzofeldspathic gneiss). If there was high life activity in the depositional environments of the sedimentary rocks, relatively high NH₄⁺ contents are expected in biotites of the gneisses. Nevertheless, they show extremely low NH₄⁺ contents.

The Carnot Gneiss was highly metamorphosed to a prograde granulite facies at about 2400 Ma, and pressure-temperature estimates for the metamorphism are 800–900°C at a total pressure of 7–9 Kb (FUNNING et al., 1979). Sample No. 10 is obtained from a rock which contains granulite. This sample shows especially low NH₄⁺ content, 8 ppm. The low content is probably due to the liberation of NH₄⁺ from the rock during granulite facies metamorphism. Experimental studies show that NH₄⁺ in mica is not affected by heating below 400°C (VEDDER, 1965; YAMAMOTO & NAKAHIRA, 1966) but it is removed considerably from mica structure above 500°C (HIGASHI, 1978). In fact, this heat effect on NH₄⁺ in mica structure has been recognized in the Cooma district of the Lachlan Fold Belt, for example a NH₄⁺ content of biotite decreases from 113 ppm in a schist through 88 ppm in a gneiss to 43-51 ppm in migmatites (TAIONO & ITHARA, 1988). Similarly, in a series of the Svecokarelian metapelites, Finland, biotite in the garnet-cordierite-sillimanite zone have 57 ppm NH₄⁺, while biotite in the mica schist zone, the K-feldspar-sillimanite zone, and the K-feldspar-cordierite zone have hundreds of ppm NH₄⁺ (ITHARA & SUWA, 1985). The low NH₄⁺ contents observed in the Carnot Gneisses seem to indicate liberation of NH₄⁺ from mica structure during high temperature metamorphism. However, relatively high NH₄⁺ content (over 100 ppm) has not yet been obtained from biotites in Archaean rocks. The highest value among the biotites in Archaean rocks is 80 ppm from a gneiss in Swaziland (3500 Ma) (ITHARA & SUWA, 1987). As pointed out in the study on nitrogen in the rocks of the Onverwacht Group, South Africa (about 3500 Ma) (ITHARA et al., 1988), less biologic activity in Archaean time should be also considered as one of the reason for the low NH₄⁺ contents of biotites in the Carnot Gneisses.

2. Carbon and nitrogen contents of rocks

Table 3 shows carbonate-C, organic C, soluble N and insoluble N contents of the rocks from the Proterozoic Hutchison Schists (Nos. 5 to 7) and the Archaean Carnot Gneisses (Nos. 9 and 11). These rocks contain a negligible amount of carbonate-C (0.01%>) and a small amount of organic C (0.02–0.08%). Significant differences of carbonate-C contents and of organic C contents, however, are not recognized between the Hutchison Schists and the Carnot Gneisses. Soluble N,
which is considered to be ammonium-N originated from recent contaminants, is not detected in all of the tested samples except for No. 7 (9 ppm).

Insoluble N is detected in all of the samples tested. There is a considerable difference of the contents between the Hutchison Schists (33-62 ppm) and the Carnot Gneisses (3-8 ppm). In sediments, insoluble N consists of ammonium-N in silicate minerals and organic N in kerogen. In metamorphosed sedimentary rocks, most of the insoluble N is ammonium-N in the lattice structure of silicate minerals, because nitrogen in organic matter (kerogen) was mostly decomposed to NH$_4^+$ during diagenesis and metamorphism. The NH$_4^+$ is inherited largely by K-bearing minerals which crystallizes in an early stage of metamorphism because of the similar ionic radius of NH$_4^+$ to K$^+$ and the same electric charge (Ithihara & Honma, 1979). If this process is accepted, higher insoluble N contents in the Hutchison Schists indicate a presence of biologic activity in the depositional environments of the original sediments of the schists. Since the age of sedimentation is considered to be 2100-1850 Ma for the Hutchison Group (Parker et al., 1985), this conclusion is in accordance with an important event in Precambrian time, a great increase of plant biomass (mainly algal) at 2400-2200 Ma (Salop, 1983). In fact, 1886 ppm of insoluble N (981 ppm is in silicate minerals and the rest is in kerogen) together with 5.7% of organic C has been recognized in an organic mudstone of the Whitewater Group, Canada (1800 Ma) (Ithihara & Aihara, 1987). On the other hand, insoluble N content of the Archaean Carnot Gneisses are extremely low (3, 8 ppm). The values are similar to those of the sedimentary rocks in the Huronian Supergroup, Canada (2500-2200 Ma), in which insoluble N is 10 ppm in a mudstone and 0-7 ppm in sandstone, tillite and banded calcareous rock (Ithihara & Aihara, 1987). These low insoluble N contents do not possibly suggest a presence of the biologic activity in the depositional environments of the rocks. As for the Carnot Gneisses, however, the low insoluble N contents in the gneisses do not necessarily mean an absence of life in the depositional environments of the original sedimentary rocks. The low insoluble N contents could be the result of the liberation of nitrogen from the rocks during metamorphism. Thus, the conclusion drawn from the insoluble N contents of rocks is in accordance with that drawn from the ammonium contents of their biotites.

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References


AMMONIUM IN AUSTRALIAN PRECAMBRIAN ROCKS


* In Japanese with English abstract

(要 旨)


オーストラリアの Gawler 橋状地の岩石について, 黒雲母のアンモニウム含有量と, 全岩の炭酸塩炭素・有機炭素・可溶性塩素・不溶性塩素の含有量を測定した。黒雲母のアンモニウム含有量は、花崗岩質岩石(18.5-14.5 億)で 21-46 ppm, Hutchison 片岩(21-18.5 億)で 103-117 ppm, Carnot 片麻岩(約 26 億)で 8-33 ppm である。全岩の不溶性塩素(NH₄⁺ 態 N と Org. N からなる)含有量は、Hutchison 片岩で 33-62 ppm, Carnot 片麻岩で 3-8 ppm である。炭酸塩炭素・有機炭素・可溶性塩素は、測定した Hutchison 片岩と Carnot 片麻岩の一部に少量検出されたが、両者間に、含有量に関する有意の差は認められない。分析結果から次の結論が得られる。Hutchison 片岩の原岩が堆積した環境には生物活動があり、その生物から生じた有機物が蓄積した。Carnot 片麻岩に関しては、変成作用によるアンモニウムの逸脱が考えられるので、原岩が堆積した環境に生物活動があったかどうかは明らかにできない。