Reddish Soils formed in Limestone Area of the Ryukyu Islands
Part I Minor Element Contents

Hatsuo Taira*, Yasushi Kitano** and Kiyoshi Kaneshima*

Abstract

The minor elements such as Mn, Co, Ni, Zn, Cu, Cd and Pb with some major chemical components such as Fe₂O₃, Al₂O₃, CaO, MgO and SiO₂ have been determined in reddish soils collected from the limestone area of the Ryukyu Islands. The manganese is concentrated in reddish soils which in-hold the manganese nodules and display the exponential increase toward the surface of the reddish soil. The manganese dioxide as well as the clay minerals and iron oxides in reddish soils show the important role for the concentration of minor elements. The manganese dioxide can be precipitated out in each strata in the reddish soils heterogeneously depending upon the conditions of oxidation-reduction states and the supply of the manganese.

I. Introduction

Corals and barrier of coral reef are well developed on the shorelines around the islands. There are different types of limestones and a full variety of carbonate materials formed on different ages. These carbonates, which might have been weathered and/or transformed from corals and shells, are observed anywhere on the islands. And they include crystalline and hard types of carbonates in certain areas of the islands. Reddish soils which were partially considered to be formed from Riukiu Limestone, and manganese nodules are often observed in these reddish soils. It does not always follow, however, that reddish soils store the manganese nodules. The interesting fact obtained from the field observation is that a layer of limestone is always observed underneath the reddish soil which in-holds the terrestrial ferromanganese nodules. This may imply that certain reddish soils are significantly associated with limestone and may concern with the formation of the manganese nodules.

The authors have worked for the mineral and chemical compositions of the reddish soils in relation of the study of the concentration mechanism of the manganese dioxide. The present report shows the distribution of minor elements in reddish soils to discuss the interelemental correlations and geochemical migrations of the minor elements in the reddish soils.

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II. Observation and experimental

Twenty samples of reddish soils were collected from Okinawa and Ishigaki Islands which include 5 samples with manganese nodules found, 8 samples with manganese clod found and 7 lateritic samples without any of manganese nodules or clod found. The lateritic reddish soils were collected from the areas in which is considered to have no connection with Ryukyu Limestone. The sampling locations are shown in Fig. 1.

![Fig. 1 Locations of reddish soil samples](image)

In the relatively thick layer of the reddish soils, the following two cases have been observed. The manganese dioxide rich layer exists discontinuously only at a definite depth in some particular areas or mostly the manganese dioxide content of the soil increases continuously towards the surface without a clear manganese dioxide rich layer. For example, the higher concentration of MnO₂ toward the surface is observed as given in Table 1 in the reddish soil of about 2 m thick accumulated on the Yomitan type of limestone.

For the chemical analysis, the reddish soils are totally ground in porcelain mortar to pass a 100 mesh sieve. Two and a half grams of each sample are subjected to decompose to solution with hydrochloric and nitric acids with the addition of a small portions of hydrogen peroxide, and the solution is almost dried up. Then it is redissolved in diluted hydrochloric acid solution to filter off the residue. The final solution of the filtrate placed in 250ml graduated flask is made up to be 1 N
Table 1  Vertical profile of manganese and iron contents in reddish soil collected from Yomitan Limestone area

<table>
<thead>
<tr>
<th>Depth from Surface(m)</th>
<th>MnO₂ (%)</th>
<th>Fe₂O₃ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.33</td>
<td>3.34</td>
</tr>
<tr>
<td>0.5</td>
<td>0.23</td>
<td>4.30</td>
</tr>
<tr>
<td>1.0</td>
<td>0.07</td>
<td>5.37</td>
</tr>
<tr>
<td>1.5</td>
<td>0.04</td>
<td>6.14</td>
</tr>
<tr>
<td>2.0*</td>
<td>0.01</td>
<td>0.06</td>
</tr>
</tbody>
</table>

*: Limestone boundary

hydrochloric acid solution.

Cobalt, Ni, Zn, Cu, Cd and Pb are determined by the atomic absorption spectrophotometry of Hitachi 207 type with the use of acetylen gas plus air as fuel. The calibration curves for their determination are made in the way of standard addition technique. The major components are determined by the following methods: SiO₂ by gravimetry, Fe₂O₃, Al₂O₃, CaO and MgO by titration method with EDTA.

III. Results and Discussion

III-1 Major components of reddish soils

It has been observed that there are three types of reddish soils in Ryukyu Islands: 1) with manganese nodules, 2) without manganese nodules but with manganese clod, 3) without both manganese nodules and clod. The average chemical compositions with minimum and maximum values are listed in Table 2, and the average contents for the three types of the reddish soils are listed separately in Table 3.

The reddish soils with manganese nodules found vary the SiO₂ content in 60 to 70% with higher content of minor elements than that in the other two types of the reddish soils. The reddish soils with manganese clod contain SiO₂ in 70 to 80% and Fe₂O₃ + Al₂O₃ in 10 to 20%. The lateritic soils without manganese nodules and

Table 2  Average chemical compositions with minimum and maximum values in reddish soils

<table>
<thead>
<tr>
<th>Major components(%)</th>
<th>Minor elements (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>MnO₂</td>
</tr>
<tr>
<td>Min. 61.9</td>
<td>0.004</td>
</tr>
<tr>
<td>Max. 90.5</td>
<td>0.55</td>
</tr>
<tr>
<td>Ave. 75.6</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Table 3  Average contents of chemical components in three types of reddish soils

<table>
<thead>
<tr>
<th>Type of reddish soil</th>
<th>No. of samples</th>
<th>SiO₂</th>
<th>MnO₂</th>
<th>Fe₂O₃</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Mn</th>
<th>Cu</th>
<th>Ni</th>
<th>Zn</th>
<th>Cd</th>
<th>Co</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn-nodule found</td>
<td>5</td>
<td>64.4</td>
<td>0.21</td>
<td>9.5</td>
<td>9.0</td>
<td>0.96</td>
<td>0.47</td>
<td>1350</td>
<td>91</td>
<td>38</td>
<td>115</td>
<td>2.8</td>
<td>27</td>
<td>45</td>
</tr>
<tr>
<td>Mn-clod found</td>
<td>8</td>
<td>76.2</td>
<td>0.06</td>
<td>8.1</td>
<td>6.8</td>
<td>0.26</td>
<td>0.31</td>
<td>400</td>
<td>50</td>
<td>25</td>
<td>63</td>
<td>1.9</td>
<td>18</td>
<td>35</td>
</tr>
<tr>
<td>Latteritic</td>
<td>7</td>
<td>86.3</td>
<td>0.03</td>
<td>4.6</td>
<td>2.9</td>
<td>0.10</td>
<td>0.34</td>
<td>190</td>
<td>30</td>
<td>15</td>
<td>38</td>
<td>1.2</td>
<td>9</td>
<td>14</td>
</tr>
</tbody>
</table>

Clod contain more than 80% of SiO₂ and less than 10% of Fe₂O₃ + Al₂O₃ contents. The former two types of reddish soils which are considered to have an immediate connection with the Riukiu Limestone from the field observations show a relatively high amount of manganese. The lateritic soils, however, seem to have no connection with Riukiu Limestone and generally contain only a small amount of manganese and conglomeratic quartz. Tokuyama and Kitano discussed on the origin of the lateritic soils that they are formed by the weathering of silicate rocks. One of the X-ray diffraction patterns of these soils is shown in Fig. 2 which indicates a clear

![Latteritic Soil](image)

Fig. 2  X-ray diffraction pattern of reddish soils. Q is denoted to the quartz. None of significant peaks other than quartz are observed. Following conditions were set for X-ray powder analysis with the use of Geigerflex GF-DL of Rigaku-Denki: target; Cu, filter; Ni, tubes; 35 KV, 15 mA, full range; 400 cps, time const.; 2 sec., scan sp.; 2°/min., slits; div.; 1°, scatt.; 1°, Rec.; 0.15mm.
presence of quartz. This may imply that the silicate rocks are significantly associated with the formation of some types of reddish soils. Although the presence of illite and kaolinite is observed in some reddish soils, the same pattern as shown in Fig. 2 is obtained for many soil samples. And particularly, the presence of quartz in large amount for reddish soils which are not contain the manganese nodules may support the idea of Tokuyama and Kitano about the formation of the reddish soil.

The \( \text{Fe}_2\text{O}_3 \) content indicates the positive correlation with \( \text{Al}_2\text{O}_3 \) content in reddish soil as seen from Fig. 3 for 20 analyzed samples. The mineralogical states of iron, aluminum and silicate are very difficult to be identified from the X-ray diffraction patterns since none of the X-ray mineral peaks other than quartz are observed as given in Fig. 2. In order to study the mineralogy more in reddish soils from the chemical standpoint, the authors have tried a leaching of powdered samples with various solutions such as acetic acid, acetic acid plus hydroxylamine solution or hydrochloric plus nitric acids. The results should suggest that aluminum is mostly present as clay form with certain portions of silicate and iron. The other portion of iron is present as oxide and the major portion of silicate is as quartz.

![Graph showing correlation between \( \text{Fe}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) contents in reddish soils.](image)

**Fig. 3** Correlation between \( \text{Fe}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) contents in reddish soils.

Empty circles express reddish soils with manganese nodules found.
Other solid circles are those of without manganese nodules found.
This leaching procedure might be called chemical attack treatment which was developed by Chester et al. \cite{Chester1, Chester2, Chester3} to know the partitions of minor elements in marine sediments. The procedure and results of the chemical attack treatment in detail will be reported in another paper.

As will be pointed out in the next section in detail, the positive correlations are obtained between the contents of minor elements and Fe$_2$O$_3$ + Al$_2$O$_3$. This may indicate both Fe$_2$O$_3$ and Al$_2$O$_3$, in other words clay minerals, may act an important role on the concentration of minor elements in the reddish soils. With the increase of Fe$_2$O$_3$, however, the manganese contents also increase as seen from Fig. 4. The rate of the increase is much higher for the manganese content than that for the Fe$_2$O$_3$ content giving the exponential change in the manganese content with respect to the leanear changes of Fe$_2$O$_3$ and other major components of the soil. This is probably due to the fact that the manganese dioxide is strongly cohesive whereas the iron oxide and others are relatively dispersive in the soil.

![Graph](image-url)

**Fig. 4** Relationship between Fe$_2$O$_3$ and Mn contents in reddish soils. Empty circles; reddish soils which contained manganese nodules. Solid circles; reddish soils which did not contain manganese nodules.
III-2 Correlation between minor elements and Fe$_3$O$_3$+Al$_2$O$_3$ contents

The contents of all analyzed chemical components except MgO in the reddish soils show the negative correlations against SiO$_2$ content and the positive distribution with Fe$_3$O$_3$+Al$_2$O$_3$ contents.

The distribution patterns of some elements such as Zn, Cd and Pb with respect to that of Fe$_3$O$_3$+Al$_2$O$_3$ are shown in Fig. 5. It is apparent from the figure that with increasing Fe$_3$O$_3$+Al$_2$O$_3$ content the concentrations of minor elements increase. Since the reddish soil is considered to be formed under oxidative conditions,

![Fig. 5 Relationship between some minor elements and Fe$_3$O$_3$+Al$_2$O$_3$ contents in reddish soils.](image)

various types of oxide minerals of iron and manganese may be formed and the minor elements are concentrated depending upon the geochemical behavior of the elements through the processes of formation and weathering. The minor heavy metal contents in the soils not containing the manganese nodules show a clear positive linear correlation with the Fe$_3$O$_3$+Al$_2$O$_3$ content rather than that in soils of the high manganese. And, to know the partition of these minor elements in the reddish soils, the chemical attack treatment has been applied to the samples. The results indicate that practically all of Cu, Ni, Cd and Co, and 70% of Zn and 50% of Pb are accompanied with clay fraction in the soils. These might support the consideration that clay minerals and iron oxides may play the important role for the concentration of the minor elements in the reddish soil.
III-3 Correlation between minor elements and manganese dioxide contents

As it has already been pointed out, the manganese content increases with increasing iron content. The relationship between MnO₂ content and some minor element contents are shown in Fig. 6. This means that the minor element contents of the reddish soil are also affected by the manganese dioxide content to a certain extent. The positive correlations on the plots do not necessarily mean that the manganese dioxide is the main host component to concentrate the minor elements in any soil, since the minor element contents also increase with increasing iron and aluminum contents.

![Figure 6: Relationship between some minor elements and MnO₂ contents in reddish soils.]

III-4 Concentration of manganese dioxide

In the consideration of the mechanism of the distribution and migration of elements in limestone areas, two processes have to be taken into account. One is the simple concentration of the elements, for example the concentration may occur in the processes of weathering of carbonate materials, and the other is from the point of geochemical behaviors of elements when the chemical forms of elements are transformed to the oxides.

If the total iron in the reddish soil is assumed to be originated from the diagenesis of the limestone \(^1, 5\) the manganese content may be enough to form the manganese nodules. However, this should be discussed exactly because the amount of limestone to be dissolved must be too large to form the present amount of the reddish soils.

In the consideration of the concentration mechanism of manganese, the
following discussions may be applicable. The ferrous ions will be more easily oxidized than Mn$^{2+}$ ions, to form ferric hydroxide and/or oxide of Fe$_2$O$_3$.nH$_2$O at relatively high temperature. Along with the formation of ferric hydroxide, Mn$^{2+}$ ions will be oxidized to form insoluble MnO$_2$.nH$_2$O form. Since pH value for Mn$^{2+}$ ions to form MnO$_2$.nH$_2$O is much higher than that for Fe$^{2+}$ ions to form Fe(OH)$_3$ or Fe$_2$O$_3$.nH$_2$O the environmental conditions may allow the existence of the state Mn$^{2+}$ ions for a relatively long period of time. The manganese is then supplied continuously to form manganese dioxide whereas iron is easily precipitated out as hydroxides. The existence of free Mn$^{2+}$ ions may cause the migration toward the surface to form manganese dioxide whereas iron is easily precipitated out as hydroxides. The existence of free Mn$^{2+}$ ions may cause the migration toward the surface to form manganese dioxide in the processes of weathering. This phenomenon may particularly be accelerated in evaporation processes after raining. The distribution of MnO$_2$ may largely be affected by the oxidative condition in the soil causing either the continuous increase of MnO$_2$ contents toward the surface or MnO$_2$ rich band at certain depth from the surface. These phenomena can be observed at many places on Ryukyu Islands.

In contrast, the iron content may decrease toward the surface since the ferrous ions may be easily oxidized to form hydroxides or oxide forms before migrating up toward the surface. The vertical profile of manganese and iron contents for the reddish soil collected from Yomitan Limestone area is given in Table 1.

Although many possible mechanism for the concentration of MnO$_2$ with Fe$_2$O$_3$ have been proposed by many workers, many problems remain unsolved. The authors will discuss the possible mechanisms including the sources of manganese in another paper where partition studies of minor elements for the reddish soils and manganese nodules will be shown.

IV Acknowledgment

The authors are grateful to Mr. Shigeru Ooide of Water Research Institute at Nagoya University for his kind assistance to take X-ray diffractogram of reddish soils.

V References

2) R. Chester and M. J. Hughes, A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. Chem. Geol. 2, 249-262 (1967)
