Selective chemical leaching of cadmium, copper manganese and iron in marine sediments

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(Received March 11, 1980: Accepted June 10, 1980)

The selective chemical leaching of cadmium, copper, manganese and iron from various minerals has been examined in the laboratory experiment. And the selective leaching technique has been applied to marine sediments to elucidate the role of clay minerals as a scavenger chiefly for cadmium in the sea. The obtained results show that clay minerals assume some significant role for the removal of cadmium from seawater.

INTRODUCTION

The amount of cadmium discharged to seawater through atmospheric precipitation and river water is larger than the amount of cadmium removed from seawater as carbonates and ferromanganese oxides of marine sediments (KITANO, 1978; KITANO et al., 1978a, b, c; KITANO, 1980).

In a series of studies to search for scavengers of cadmium in seawater, the present authors previously investigated the distribution of cadmium between solution and calcium carbonate, calcium phosphate and manganese oxide (KITANO et al., 1978a, b, c; KITANO and FUJIYOSHI, 1979a, b). However, these materials were not expected to be good scavengers for cadmium in seawater from the experimental results. The present report shows chiefly the partitioning of cadmium into organic and mineral fractions in marine sediments by using a selective chemical leaching technique to elucidate the role of clay minerals as scavengers for cadmium.

EXPERIMENTAL

Samples Samples used in the present study are as follows: calcite from Kiura mining district in Kyushu, Japan; montmorillonite from Matsuida in Gunma Prefecture, Japan; kaolinite from Ideki-cho in Kagoshima Prefecture, Japan; chlorite from Wanibuchi mining district in Shimane Prefecture, Japan; humic acid (commercial reagent). Table 1 gives the description of ferromanganese nodules and pelagic sediments, which were given by N. TAKEMATSU at Institute of Physical and Chemical Research, Japan (TAKEMATSU, 1978, 1979).

All samples were air-dried and ground in an agate mortar. Analyzed values were given on the basis of dry weight.

Chemical leaching experiment Figure 1 shows the flow chart of chemical leaching procedure established for the present study (CHESTER and HUGHES, 1967; PRESLEY et al., 1972; GUPTA and CHEN, 1975; AGEMIAN and CHAU, 1976; DEURER et al., 1978; FARAH and PICKERING, 1978; KITANO and SAKATA, 1978; TAKEMATSU, 1978; SKEI and PAUS, 1979; KITANO, et al., 1980). The partitioning of copper, manganese and iron as a control has also been determined. It may lead us to understanding the role of real clay minerals as scavengers for cadmium.
The exchangeable fraction is to be separated into solution by filtering through a 0.45μ millipore filter. The filtrate was adjusted to a suitable volume at pH 2 for trace metal analyses. Heavy metals in the filtrate were determined. This is designated as 1M CH₃COONH₄ soluble fraction.

(2) The residue from ammonium acetate treatment was washed with distilled water, and was digested in 1M acetic acid (40ml) for 1 hour. The suspension was centrifuged and then filtered through a 0.45μ millipore filter. The extract is designated as 1M CH₃COOH soluble fraction, and is regarded mostly as carbonate fraction. Heavy metals in the solution were determined.

(3) The residue from acetic acid treatment was washed with distilled water, and then leached with 10ml of 30% H₂O₂ solution (pH 2) at 35°C for 3 hours. Heavy metals in the filtrate were determined. The filtrate is designated as sulfide and organic fractions. Parts of iron and manganese oxide may also be dissolved in this solution.

(4) The washed residue from H₂O₂ treatment was digested with 0.04M hydroxylamine hydrochloride in 25% acetic acid solution (40ml) at 100°C for 3 hours. The suspension was then cooled to room temperature, and the extract was separated as described earlier. This is designated as 0.04M NH₂OH·HCl soluble fraction, and is regarded as iron and manganese oxide fraction. Heavy metals in the filtrate were determined.

(5) The washed residue from the previous treatment was transferred to a teflon beaker (100 ml). And it was digested in a mixed solution of nitric acid (6ml), hydrofluoric acid (4ml) and perchloric acid (3ml) at about 175°C. After the solution had been almost dried up, dilute nitric acid was added to it. Heavy metals in the solution were determined. This fraction is designated as silicate lattice fraction.

All of the determinations of Cd, Cu, Mn, Fe and Ca were performed by using a Perkin Elmer 503 atomic absorption spectrometer.

The above results* are shown in the figures. Carbon dioxide in “carbonate fraction” of the sediment sample was determined as follows: Carbon dioxide was quantitatively released from the carbonate fraction by adding acetic or sulfuric acid to the powdered sample in the nitrogen atmosphere. The released carbon dioxide was introduced into a definite amount of 0.1M Ba(OH)₂ standard solution, and the remaining amount of Ba(OH)₂ was then titrated with standard HCl solution by using bromphenol

* On the other hand, the dried original sample (1g) was digested directly in each solution (1M ammonium acetate, 1M acetic acid, 30% H₂O₂ solution, 0.04M hydroxylamine hydrochloride in 25% acetic acid, or the mixed solution of nitric, hydrofluoric and perchloric acids). And heavy metals leached were determined. These direct leaching treatments with individual chemical solution showed the same results as those of the successive leaching treatment. Therefore, these results are not shown in this paper.
blue indicator.

Powder X-ray diffraction analysis was carried out with a Rigaku Denki X-ray diffractometer.

**EXPERIMENTAL RESULTS ON CHEMICAL LEACHING**

**Montmorillonite** Figure 2 shows the result of chemical leaching from montmorillonite sample. The figure shows the amounts of heavy metals leached.

The results show the following facts: A large amount of cadmium in montmorillonite is contained in silicate lattice fraction, and a small amount of cadmium is dissolved into 30% H₂O₂ solution.

Copper in montmorillonite is distributed in three fractions, such as 30% H₂O₂ soluble, 0.04M NH₃·HCl soluble and silicate lattice fractions. The amount of copper in silicate lattice fraction is the largest of the three.

A similar leaching pattern of manganese is obtained as that of copper in montmorillonite. Almost all iron in montmorillonite exists in silicate lattice fraction. Iron is tightly bounded within the lattice of montmorillonite.

**Kaolinite** Figure 3 shows the result of chemical leaching from kaolinite sample. Most cadmium in kaolinite exists in silicate lattice fraction. In contrast to cadmium, copper in kaolinite exists mostly in 1M CH₃COONH₄ soluble (mostly exchangeable) and 1M CH₃COOH soluble (carbonate) fractions. Manganese in kaolinite is more mobile than copper. The total manganese content is as small as about 0.7 ppm. And all manganese in kaolinite is in 1M CH₃COONH₄ soluble (mostly exchangeable) fraction. These behaviors of copper and manganese may have resulted from the fact that divalent ions such as Cu(II) and Mn(II) are difficult to be captured in the lattice of kaolinite. Almost all iron in kaolinite exists in silicate lattice fraction like cadmium.

**Chlorite** Figure 4 shows the result of chemical leaching from chlorite sample. The total amount of cadmium in chlorite is larger than those in montmorillonite and also kaolinite. Cadmium in chlorite is contained predominantly in silicate lattice fraction. The cadmium content of chlorite should depend on the lattice structure of chlorite and also on the chemical environment for its formation. Now, it is not decided which factor is more responsible for the cadmium content of chlorite sample. As the cadmium content of chlorite, the total copper content of chlorite is larger than those of montmorillonite and kaolinite. And about 50% of copper is contained in H₂O₂ soluble

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**Fig. 2.** Amounts of cadmium, copper, manganese and iron leached in each process of leaching treatment from montmorillonite. Ordinate represents the metal contents of each fraction on the basis of dry weight. Number on the right side of the figure represents the each process of leaching treatment.

**Fig. 3.** Amounts of cadmium, copper, manganese and iron leached from kaolinite in selective leaching treatment. Notation is the same as that in Fig. 2.
fraction. In contrast to manganese in kaolinite, most manganese in chlorite exists in silicate lattice fraction. The iron content of chlorite is exceedingly higher than those of montmorillonite and kaolinite. A leaching pattern of iron in chlorite similar to that of manganese is observed. That is, most iron in chlorite exists in silicate lattice fraction.

Calcite It has been said that trace amounts of heavy metals are contained not always in the lattice of carbonates but in coexisting clay and/or ferro-manganese oxide. The chemical leaching of heavy metals was examined for the composite sediment sample of montmorillonite, kaolinite, chlorite, carbonate, humic acid and ferro-manganese oxide. The result is shown later. Therefore, the chemical leaching from carbonate sample to be used is examined here.

Figure 5 shows the result of chemical leaching from calcite sample. All metals (Cd, Cu, Mn, Fe) examined in this study are dissolved completely in 1M acetic acid solution.

Humic acid Since most marine sediments contain organic materials, the chemical leaching of heavy metals from humic acid was examined. Figure 6 shows that all cadmium in humic acid sample is contained in 30% H2O2 soluble fraction. About 50 to 60% of copper and iron in humic acid sample were not leached into 30% H2O2 solution. In contrast to copper and iron, manganese is rather mobile and is easily dissolved in 1M ammonium acetate solution.

Ferro-manganese nodule The chemical leaching technique was applied to eleven samples of marine ferro-manganese nodules (see Table 1). The results are shown in Figs. 7-1, 7-2, 7-3 and 7-4. The total amount and the leaching pattern of cadmium are completely different for each ferro-manganese nodule sample (Fig. 7-1). It may be caused by the difference in the
Table 1. Description of samples

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Location</th>
<th>Depth (m)</th>
<th>Note on sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deep-sea manganese nodules</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>44°30'</td>
<td>N</td>
<td>1280</td>
</tr>
<tr>
<td></td>
<td>170°25'</td>
<td>E</td>
<td>flat nodule without a core</td>
</tr>
<tr>
<td>b</td>
<td>9°16.7'</td>
<td>N</td>
<td>5940</td>
</tr>
<tr>
<td></td>
<td>179°19.6'</td>
<td>W</td>
<td>containing some clay materials</td>
</tr>
<tr>
<td>c</td>
<td>17°16.9'</td>
<td>N</td>
<td>4400</td>
</tr>
<tr>
<td></td>
<td>176°18.2'</td>
<td>W</td>
<td>coated on a core of hard materials</td>
</tr>
<tr>
<td>d</td>
<td>19°5'</td>
<td>N</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>121°</td>
<td>E</td>
<td>clay core</td>
</tr>
<tr>
<td>Baltic Sea manganese nodules</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>64°53'</td>
<td>N</td>
<td>74</td>
</tr>
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<td></td>
<td>22°48'</td>
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<td>spherical concretion</td>
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<td>f</td>
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<td>280</td>
</tr>
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<td></td>
<td>19°09'</td>
<td>E</td>
<td>discoidal concretion</td>
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<tr>
<td>g</td>
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<td>19°48'</td>
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</tr>
<tr>
<td>h</td>
<td>64°42'</td>
<td>N</td>
<td>74</td>
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<tr>
<td></td>
<td>23°05'</td>
<td>E</td>
<td>spherical concretion</td>
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<tr>
<td>Gulf of Finland manganese nodules</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>i</td>
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<td></td>
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<tr>
<td>Strait of Georgia manganese nodules</td>
<td></td>
<td></td>
<td>flat concretion with a pebble at the center</td>
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<tr>
<td>j</td>
<td>—</td>
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<tr>
<td>Jervis Inlet manganese nodules</td>
<td></td>
<td></td>
<td>ring shaped concretion around a pebble</td>
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<tr>
<td>k</td>
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<tr>
<td>Sediments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>N</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>128°53.4'</td>
<td>E</td>
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<tr>
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<td>N</td>
<td>6080</td>
</tr>
<tr>
<td></td>
<td>170°13.2'</td>
<td>E</td>
<td>Dark brown clay</td>
</tr>
<tr>
<td>n</td>
<td>10°04.5'</td>
<td>S</td>
<td>5260</td>
</tr>
<tr>
<td></td>
<td>169°49.0'</td>
<td>E</td>
<td>Red clay</td>
</tr>
<tr>
<td>o</td>
<td>0°37.0'</td>
<td>N</td>
<td>3010</td>
</tr>
<tr>
<td></td>
<td>149°19.5'</td>
<td>E</td>
<td>Calcareous ooze</td>
</tr>
<tr>
<td>p</td>
<td>28°52.3'</td>
<td>S</td>
<td>3210</td>
</tr>
<tr>
<td></td>
<td>168°28.7'</td>
<td>E</td>
<td>Calcareous ooze</td>
</tr>
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</table>

chemical environment in which manganese nodules were formed. A large amount of cadmium is dissolved into 30% H₂O₂ solution, which may be partly derived from ferro-manganese oxide fraction of the nodule. A part of cadmium in deep sea ferro-manganese nodule is leached into 1M acetic acid solution. In order to examine whether or not cadmium leached into acetic acid solution is derived from carbonate fraction, the amount of carbon dioxide released with 1M acetic acid treatment was determined with the procedure mentioned earlier in the chemical leaching procedure. The result shows that 1M acetic acid-soluble fraction did not contain any carbon dioxide. Thus, it is concluded that ferro-manganese nodules contain cadmium in rather unstable and mobile forms to be leached easily without carbonate.

The partitioning of copper, manganese and iron in these ferro-manganese nodule samples were already reported by Takematsu (1979, 1980). According to his result, near-shore manganese nodules were rather unstable than deep-sea ones, and contained much impurities such as silicate minerals and iron oxides. And he assumed that a large amount of copper would exist in sorbing sites of manganese dioxide phase in ferro-manganese nodules.

Figure 7-2 obtained in the present experiment shows the following distinct difference in the copper content between deep-sea and near-shore manganese nodules, that is, deep-sea
manganese nodules contain a larger amount of copper than near-shore nodules. This may be explained as follows: Deep-sea manganese nodule generally contains a large amount of todorokite, whereas near-shore nodule contains a large amount of birnessite (CRONAN, 1969; GLASBY, 1972). A large amount of copper is concentrated in todorokite rather than in birnessite, and the copper content of ferro-manganese nodule is controlled mostly by the amount of todorokite in the nodule (BARNES, 1967).

Some of manganese and iron in ferro-manganese nodules are contained in 30% H$_2$O$_2$ soluble fraction like cadmium.

Composite sediment sample The present authors examined chemical leaching of heavy metals from a mixture of materials. The composite sediment sample examined in the present experiment has the following composition (wt %): montmorillonite 23%, kaolinite 35%, chlorite 20%, ferro-manganese nodule 3%, humic acid 6% and calcite 13%. Figure 8 shows that the observed results for the composite sample agreed well with those calculated from the experimental results obtained earlier on each material.

Marine sediments The samples used in the present study are manganese nodule samples, greenish silt (150m deep), brown clay (6,080m deep), red clay (5,260m deep) and two calcareous ooze samples (about 3,000m). The description of these samples is listed in Table 1. The successive chemical leaching treatment was carried out for those marine sediments. The partitioning of cadmium, copper, manganese and iron in ferro-manganese nodules was described earlier (see Figs. 7-1, 7-2, 7-3 and 7-4). Then, the experimental results are shown in Fig. 9 for greenish silt, brown clay, red clay and calcareous ooze.

From the figure, the following are seen: Greenish silt — About 40% of cadmium is contained in 1M CH$_3$COOH soluble fraction. Carbon dioxide released from this fraction by adding acetic or sulfuric acid was determined to be $5.2 \times 10^{-2}$ mol/kg. The amount of calcium dissolved into 1M acetic acid solution was
measured to be about 6 times larger than the amount of carbon dioxide. It is clear that carbonate is dissolved by this treatment. But it must be considered from the following fact that cadmium does not come from carbonate fraction: About 5g of CaCO₃ is contained in 1kg of this silt sample. Marine calcium carbonate generally contains 0.1 to 0.2ppm of cadmium. Therefore, only about 0.5 to 1.0×10⁻²mg of cadmium is contained in carbonate fraction of 1kg of this silt sample. This value is too small to be detected. Thus, it is said

that cadmium dissolved into 1M acetic acid solution is not derived from carbonate fraction but from fractions to be dissolved easily in 1M acetic acid solution. About 60% of cadmium is contained in silicate lattice fraction.

The copper and manganese contents of greenish silt are rather small as compared with those of other sediment samples.

Most iron exists in silicate lattice fraction of the greenish silt sediment.

Brown clay — Most cadmium and iron in the pelagic brown clay exist in silicate lattice fraction. Copper in the brown clay is distributed in 1M CH₃COOH soluble (carbonate), 30% H₂O₂ soluble (organic and ferro-manganese oxide),

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Fig. 7-3. Amount of manganese leached from ferro-manganese nodules in selective leaching treatment.

Fig. 7-4. Amount of iron leached from ferro-manganese nodules in selective leaching treatment.

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Fig. 8. Amounts of cadmium, copper, manganese and iron leached from a composite sediment sample in selective leaching treatment. The composite sediment sample has the following composition (wt %): montmorillonite 23%, kaolinite 35%, chlorite 20%, ferro-manganese nodule 3%, humic acid 6% and calcite 13%. Notation is the same as those in Table 1 and Fig. 2.

Fig. 9. Amounts of cadmium, copper, manganese and iron leached from marine sediments in selective leaching treatment. Notation is the same as those in Table 1 and Fig. 2.
0.04 M NH$_2$OH·HCl soluble (ferro-manganese oxide) and silicate lattice fractions. Most manganese is easily dissolved into 30% H$_2$O$_2$ solution. Manganese contained in 30% H$_2$O$_2$ soluble fraction may derived mostly from ferro-manganese oxide fraction of the brown clay.

Red clay — The contribution of silicate lattice fraction is important for both cadmium and iron contents of red clay as of brown clay. Copper is distributed in four fractions such as 1 M CH$_3$COOH soluble, 30% H$_2$O$_2$ soluble, 0.04 M NH$_2$OH·HCl soluble and silicate lattice fractions. And manganese is mostly dissolved into 30% H$_2$O$_2$ solution.

It is seen that the amount of cadmium in silicate lattice fraction of marine sediments (greenish silt, brown clay and red clay) seems to be larger than that of clay minerals formed in land area. It might be suggested that clay lattice assumes some significant role as a scavenger for cadmium from seawater. As shown in Fig. 9, cadmium in pelagic clay minerals such as brown clay and red clay is not dissolved into 1 M ammonium acetate solution. It indicates that the cadmium content of exchangeable sites in clay minerals is negligible. It might be considered that clay itself assumes some significant role as a scavenger for cadmium from seawater.

Calcereous ooze — 50 to 60% of cadmium exists in 1 M CH$_3$COOH soluble fraction. Even if these ooze samples contain of carbonate, the cadmium content of carbonate lattice is expected to be 0 ppm (see Fig. 5). The amount of cadmium dissolved from 1 gm carbonate is negligibly small as compared with that contained in 1 M CH$_3$COOH soluble fraction of these ooze samples. This indicates that cadmium in 1 M CH$_3$COOH soluble fraction should have been derived mostly from the other fraction such as ferro-manganese oxide fraction. As seen from Fig. 7-1, some cadmium is dissolved into 1 M acetic acid solution from ferro-manganese nodule samples. This fact also leads us to consider that cadmium in 1 M CH$_3$COOH soluble fraction in ooze samples is ascribed to the dissolution of ferro-manganese oxide fraction of the sediment.

The rest of cadmium is mostly contained in silicate lattice fraction. The leaching pattern of copper is rather complex. That is, copper is contained in all fractions: 1 M CH$_3$COONH$_4$ soluble (mostly exchangeable), 1 M CH$_3$COOH soluble, 30% H$_2$O$_2$ soluble, 0.04 M NH$_2$OH·HCl soluble and silicate lattice fractions. In both ooze samples almost all manganese is dissolved into 30% H$_2$O$_2$ solution. About 50% of iron exists in silicate lattice fraction in both ooze samples. Manganese and iron are not contained in 1 M CH$_3$COOH soluble fraction significantly. It should be noted that heavy metals are not always contained in 1 M CH$_3$COOH soluble fraction even in calcereous ooze, that is, about 50% of heavy metals at most and very often only quite small portions of heavy metals are contained in 1 M CH$_3$COOH soluble fraction, in other words, carbonate fraction.

**SUMMARY**

1. Chemical leaching technique is very effective to clarify the partitioning of heavy metals into 1 M CH$_3$COONH$_4$ soluble (mostly exchangeable), 1 M CH$_3$COOH soluble (carbonate and/or ferro-manganese oxide), 30% H$_2$O$_2$ soluble (organic and ferro-manganese oxide), 0.04 M NH$_2$OH·HCl soluble (ferro-manganese oxide) and silicate lattice fractions. The leaching patterns of heavy metals in clay minerals have some correlation with their lattice structures as well as the environment in which they were formed. For example, most cadmium exists in silicate lattice fraction in the pelagic clay sediments, whereas 1 M CH$_3$COOH soluble fraction is important for the partitioning of cadmium in near-shore clay sediments. Clay minerals assume some significant role as a scavenger for cadmium from seawater.

2. Ferro-manganese nodules, even pelagic ones, contain rather mobile fractions, and heavy metals such as copper and cadmium are easily dissolved into 1 M acetic acid or 30% H$_2$O$_2$ solution. Cadmium and copper dissolved into acetic acid solution are not derived from carbonate, and they are rather mobile to be leached into
1 M acetic acid solution.

The copper content of ferro-manganese nodule is strongly dependent on the environment in which it was formed that is, deep-sea manganese nodule contains a large amount of copper than near-shore nodule.

3. In calcareous ooze, about 50% of cadmium is contained in 1 M CH₃COOH soluble fraction. However, cadmium contained in CH₃COOH soluble fraction may be derived from ferro-manganese oxide fraction rather than carbonate fraction of the sediment. Copper is distributed in various fractions, most manganese exists in 30% H₂O₂ soluble fraction, and iron is contained mostly in silicate lattice fraction and also in 30% H₂O₂ soluble and 0.04 M NH₄OH-HCl soluble fractions. Iron and manganese in calcareous oozes are not contained in 1 M CH₃COOH soluble fraction significantly.

Acknowledgement—The authors wish to thank Dr. NOBURU TAKEMATSU at Institute of Physical and Chemical Research (Japan) for giving valuable samples and helpful suggestion. This study was supported by a grant from the Ministry of Education.

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