434 © 1983 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 56, 434—438 (1983) [Vol. 56, No. 2

Mineralogical Characterization of the Reference Material of "Pond Sediment"

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(Received January 13, 1982)

The identification of rock-forming and clay minerals contained in the reference material of "Pond Sediment" (Reference Material NIES No. 2 from the National Institute for Environmental Studies, Japan) has been made with X-ray diffraction method. It was found that the sediment contained α-quartz and feldspars as the principal components along with small quantity of pyroxenes, amphiboles, and some clay minerals. The sediment sample was treated chemically for extraction, and also separated with density and with grain sizes. Elemental compositions of such extracted or separated fractions of the sediment were determined by inductively coupled argon plasma emission and atomic absorption spectrometry. The identified minerals and the elemental distributions in the separated fractions helped to characterize the pond sediment.

In recent years, much attention has been paid to environmental and biological reference materials because of the importance of pollution control. Recently NBS issued a standard reference material of "River Sediment."¹⁾ We have also prepared independently a reference material of "Pond Sediment,"²⁾ which was collected from the Sanshiro-ike (Pond at the University of Tokyo), and issued as Reference Material No. 2 from the National Institute for Environmental Studies, Japan. The Sanshiro-ike pond sediment consists basically of volcanic ash called Kanto loam, atmospheric dust, and organic matters originating from plants, animals, and microorganisms. There have been no significant flows of freshwater, and industrial or sewage waste into the pond. Therefore, the composition of the sediment sample should mainly reflect air pollution from a big city environment (*i.e.*, imports of pollutants arisen from traffic and industrial discharges into the air). Goldberg reported that the history of the environmental pollution in Tokyo was recorded in the Palace Moat Sediment.³⁾

The procedure for preparing reference materials, homogeneity test, and its elemental composition have been reported in the previous communication.²⁾ In order to understand the significance of the "Pond Sediment," it may be further desirable to investigate the elemental distributions in a variety of partial extractions of the sedimant. Hence, in this study, extraction tests and mineralogical characterization of the "Pond Sediment" have been performed, and the origins and the chemical forms of elements are described.

Experimental

Chemicals. All the chemicals used were of analytical reagent grade. Standard solutions were prepared by dissolving pure metals, metallic oxides and their salts in acidic or deionized distilled water. Final acidity of each working standard solution was adjusted at 1 M ($1\ M = 1\ mol\ dm^{-3}$) with nitric acid and/or hydrochloric acid. In addition, standard rock sample JB-1 (basalt) from the Geological Survey of Japan⁴⁾ was also analysed to examine the accuracy and precision of the analytical method for elemental compositions.

Instruments. X-Ray diffraction measurements were performed using an X-ray diffractometer, Model JEOL-GO-S. The diffraction patterns were measured in the range of the diffraction angle (2θ) from 4° to 70°. An inductively coupled plasma (ICP) emission spectrophotometer (Model Jarrell-Ash Plasma AtomComp Mark II), and an atomic absorption spectrophotometer (Model Shimadzu AA-640-13) was used for the determination of the elemental distributions in separated fractions. Total carbon and nitrogen were determined using a C. H. N. Coder (Model Yanagimoto MT-2).

Separation of the Sediment for Mineral Identification. The "Pond Sediment" was separated into 4 groups, *i.e.*, organic matters and carbonates, iron oxides, primary and secondary minerals, and heavy and light minerals. The separation procedure which is a modified method of those reported in the literature,⁵,⁶⁾ is summarized as follows:

(1) Organic Matter and Carbonates: Ten ml of 30% H_2O_2 was added to 5 g of the sediment sample, and the mixture was heated until the vigorous reaction was over. After cooling, 50 ml of 0.2 M HCl was added with stirring for 1 h at room temperature. Then, the suspension was filtered by means of suction with a No. 5C filter paper (Toyo Co., Ltd.). The filtrate was diluted to 100 ml with water (F-1).

(2) Iron Oxides: The air-dried residue of (1) was suspended in 50 ml of 0.3 M sodium citrate solution, and 5 g of sodium dithionite was added into suspension. The suspension was heated at 80 °C with occasional agitation for about 30 min, and then filtered by means of suction with a No. 5C filter paper. The filtrate was diluted to 100 ml (F-2).

(3) Primary and Secondary Minerals: The residue of (2) was transferred into water. Then, the secondary minerals (diameters less than 20 μm) was separated from the primary minerals (diameters larger than 20 μm) by the elutriation as follows: After stirring the suspension vigorously, the mixture was allowed to stand for 4 min and 48 s. Then the supernatant down to 10 cm depth was removed with a siphon. This siphoning was repeated several times. In this procedure, the particles of diameter larger than 20 μm remain in the lower part of the solution, which was difined as the primary minerals. Most of these particles may be classified as fine sand, and consist mainly of the primary minerals. The siphoned materials, which is the mixture of silt and clay, consists mainly of secondary minerals.

(4) Heavy and Light Minerals: The air-dried primary minerals of (3) was treated with heavy organic liquids such as dibromomethane ($d=2.5$), tribromomethane ($d=2.9$), and diiodomethane ($d=3.3$) for further separation. Each fraction of heavy organic liquids was separated by centrifugation, and each separated sample was washed well with acetone, and then

dried under an IR lamp.

In addition to the above treatments, magnetic minerals were separated independently using a magnet, although they were found in very small quantities. In order to determine the elemental distributions, the sample was boiled with 12 M HCl.[6] The residue in 12 M HCl solution was dried at 500 °C to examine on the primary minerals.

Elemental Analysis of Separated Fractions. Each separated fraction was treated for elemental analysis according to the following procedure, which was modified from the one reported by Yoshida.[7] The sample was digested with a mixture of 10 ml concd HNO_3 and 10 ml concd $HClO_4$ for 30 min on a hot plate at 200 °C. After cooling, 20 ml of HF was added and the mixture was kept standing at room temperature for 30 min. Then it was evaporated until fuming, and 5 ml HNO_3 and 5 ml $HClO_4$ were again added, and the mixture was heated. After dissolution the mixture was heated to incipient dryness. The residue was dissolved with 10 ml of 6 M HCl and then diluted to 100 ml with water.

Results and Discussion

The amount of each separated fraction in weight % is shown in Table 1. Organic matter, oxides, and minerals were approximately 20, 15, and 60%, respectively. Fine sand (>20 μm), silt (2—20 μm), and clay (<2 μm), separated by the siphoning procedure, were found to be 20, 30, and 10%, respectively.

Mineral Composition. Minerals identified by the X-ray diffraction are summarized in Tables 2 and 3. For identification the ASTM (American Society for Testing Materials) cards were used.

Table 2 shows good agreement between the densities of separated primary minerals and their reported values.[8] These results are substantiated by the data of the elemental analyses mentioned later. It can then be stated that this "Pond Sediment" contains quartz and feldspars as the principal components, together with a small quantity of pyroxenes, amphiboles, micas, and iron ores.

Besides these rock-forming minerals, the sediment contains montmorillonite, halloysite, vermiculite, and many other clay minerals, as shown in Table 3. Since the separation of clay minerals was difficult and their X-ray peaks were not sharp, the identification of secondary minerals was not so easy. However, a few clay minerals could be identified, and these are summarized in Table 3. In addition to the above clay minerals, the sediment contains likely gibbsite and hematite, because much Al and Fe were found in the extractable fractions of the "Pond Sediment." However, X-ray peaks of these minerals were not identified because of the interferences of other large peaks. Further separation of the secondary minerals were tried based on sinking velocity using mixtures of bromoform and acetone as heavy liquids. Separation of secondary minerals could not, however, be made because of co-adsorption of fine particles.

It is known that allophane is present in high concentration in the Tachikawa loam in the upper stratum of the Kanto loam.[8] Although the "Pond Sediment" may contain such a non-crystalline clay mineral, allophane could not be identified by X-ray diffraction.

TABLE 1. AMOUNT OF EACH FRACTION SEPARATED WITH VARIOUS TREATMENTS

Fraction	Amount weight %
H_2O_2–HCl soluble (organic matter and carbonates, F-1)	20
Citrate–dithionite soluble 15 (free iron oxides, F-2)	15
Minerals	60
Primary minerals (ϕ>20 μm)	20
Magnet	<1
H-1(d>3.3)	1
H-2(3.3>d>2.9)	2
H-3(2.9>d>2.5)	13
H-4(2.5>d)	4
Secondary minerals (ϕ<20 μm)	40
Silt	30
Clay	10

TABLE 2. IDENTIFICATION OF ROCK-FORMING MINERALS IN THE PRIMARY MINERALS OF THE "POND SEDIMENT"

Fraction No.	Identified minerals (density[a])
Magnet	magnetite (5.174)
H-1 (d>3.3)	hypersthene (3.37), augite (3.34), ilmenite ? (4.2)
H-2 (3.3>d>2.9)	hornblende (3.2)
H-3 (2.9>d>2.5)	α-quartz (2.65), feldspars: orthoclase (2.57) albite (2 61) anorthite (2.76) etc.
H-4 (2.5>d)	α-quartz (2.65), feldspars, clay minerals
R.M.[b]	hypersthene (3.37), α-quartz (2.65), feldspars, muscovite (2.76—3.0)

a) Cited from Ref. 8. b) Residual minerals after hot HCl treatment.

TABLE 3. IDENTIFICATION OF CLAY MINERALS IN THE SECONDARY MINERALS OF THE "POND SEDIMENT"[a]

Mineral	Treatment		
	None[b]	H_2O_2[c]	$Na_2S_2O_4$[d]
Montmorillonite	+	(+)	(+)
Chlorite	+	+	+
Vermiculite	(+)	(+)	−
Illite	+	(+)	(+)
Halloysite	+	+	(+)
Metahalloysite	(+)	−	+

a) Symbols: + positive, (+) not conclusive, − not identified. b) Separated by the siphoning method without any chemical treatment. c) Separated by the siphoning method after H_2O_2 treatment. d) Separated by the siphoning method after H_2O_2 and $Na_2S_2O_4$ treatments.

Elemental Compositions of Fractions Separated with Density. The elemental compositions concerned with major constituents in primary minerals are shown in Fig. 1 for each fraction separated with heavy liquids. The separated fractions are represented as H-1 (d>3.3), H-2 (3.3>d>2.9), H-3 (2.9>d>2.5), and H-4 (d<2.5).

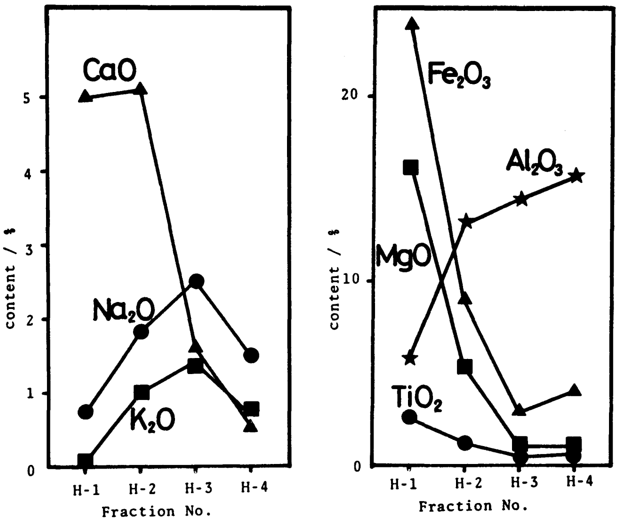

Fig. 1. Elemental compositions of primary minerals in the "Pond Sediment" separated with heavy liquids. Fraction No. H-1: $d>3.3$, H-2: $3.3>d>2.9$, H-3: $2.9>d>2.5$, H-4: $d>2.5$.

Fraction H-1 contains Ca, Mg, and Fe as the principal constituents. This result may be related to the fact that pyroxenes have Ca, Mg, and Fe end-members of the solid solution [(Ca, Mg, Fe)$_2$Si$_2$O$_6$].[10] As can be seen in Fig. 1, the contents of Fe, Mg and Ca are high, while that of Al is less. These elemental compositions also suggest that fraction H-1 contains much hypersthene [(Mg, Fe)SiO$_3$] and a little augite [Ca(Mg, Fe, Al)(Si, Al)O$_6$].[10] In addition Fe and Ti are richer in fraction H-1 than in other fractions. This may indicate that magnetite [Fe_3O_4] and ilmenite [$FeTiO_3$] are contained in fraction H-1,[11] although they could not be identified clearly. Consequently, the large contents of Fe, Ca, Mg, and Ti in fraction H-1 may be interpreted by the existence of minerals such as pyroxenes, hypersthene, and augite as well as magnetite and ilmenite.

Fraction H-2 ($3.3>d>2.9$) contains much Al, Ca, Mg, and Fe (see Fig. 1). Since the densities of amphiboles are in the range from 2.9 to 3.3, it is likely that fraction H-2 mainly contains amphiboles. In many cases, hornblende [Ca$_2$Na$_{0-1}$(Mg, Fe, Al)$_5$[(Al, Si)$_4$O$_{11}$]$_2$][10] can be identified by X-ray diffraction. The elemental composition of fraction H-2 supports the presence of hornblende, and it likely consists of hornblende as the principal component, as well as of small quantities of other amphiboles.

As can be seen in Fig. 1 the contents of Na and K were largest in fraction H-3 ($2.9>d>2.5$), although Na, K, and Ca were contained at almost equal levels in this fraction. Fraction H-3 appears to contain much feldspar in a mixture of solid solutions which consist of three end-members such as $NaAlSi_3O_8$, $KAlSi_3O_8$, and $CaAlSi_2O_8$.[10]

There were more clay minerals in fraction H-4 ($d<2.5$), although the elemental composition was almost similar to fraction H-3. Fraction H-4 contains clay minerals, quartz, and feldspars which are not separated by the siphoning treatment and/or by heavy liquid separation because of co-adsorption and fineness of the materials.

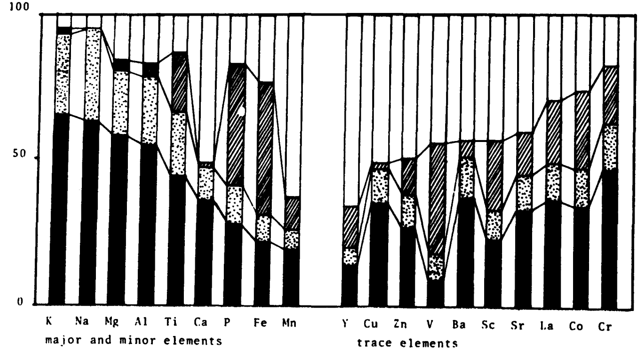

Fig. 2. Distributions of major, minor, and trace elements in the fractions separated with various treatments.
□: "H_2O_2" treatment, ▨: "$Na_2S_2O_4$" treatment, ░: secondary minerals, ■: primary minerals.

Distribution of Major, Minor, and Trace Elements in the Fractions. The distribution of major, minor and trace elements in each separated fraction was determined, and the calculated percentage of each element is illustrated in Fig. 2. The separated fractions of "H_2O_2" and "$Na_2S_2O_4$" in Fig. 2 correspond to solutions F-1 and F-2, respectively, as described previously in the separation procedure. The "primary" and "secondary" in Fig. 2 indicate primary and secondary minerals, respectively, which were separated and digested with HNO_3, $HClO_4$, and HF, as described previously. From these results, it is evident that Fe, P, and Ti are mostly leached with the dithionite-citrate treatment. This suggests that these elements may be present mainly in the chemical form of easily reducible oxides. It is known that hydrous iron oxides have great scavenging efficiency, and so many trace elements may be caught by the concretion or coatings around the second particles.

The fraction treated with hydrogen peroxide and hydrochloric acid contains much Mn and Ca. Calcium may be in the form of carbonate minerals such as dolomite or in the form of exchangeable cations. Manganese is considered to be in two modes: the one is related to the organic matter which is decomposed by hydrogen peroxide, and the other is hydrous manganese oxides which are decomposed by the mixture of hydrogen peroxide and hydrochloric acid. Na, K, Mg, and Al exist mostly in primary and secondary minerals, and more than half of them appear in the fractions containing the rock-forming minerals.

Most of trace elements were leached in the fraction treated with hydrogen peroxide–hydrochloric acid. Therefore, they may be present as species adsorbed on the minerals or as the constituents in the organic matter.

Variation of Major and Minor Components in Minerals. Figure 3 shows the variations of elemental compositions in primary minerals with and without various chemical treatments. The amount of Fe and Al decrease after each treatment step, suggesting that various oxides and organic matter exist as coatings around mineral particles which were separated only by the siphoning method. Therefore, the primary fractions after the hydrogen peroxide–hydrochloric acid and dithionite–citrate treat-

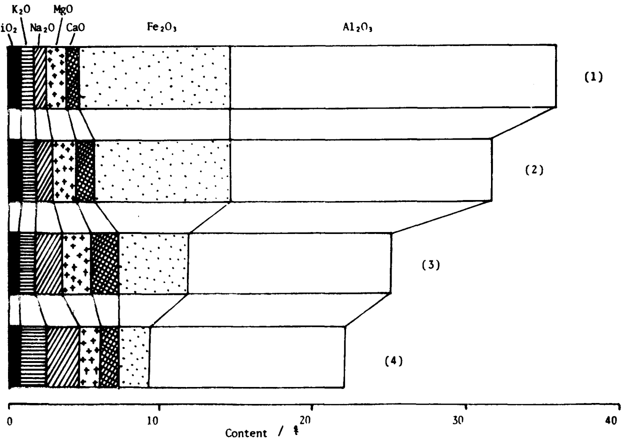

Fig. 3. Major and minor constituents of primary minerals in the "Pond Sediment" with and without various chemical treatments.
(1): Original sample, (2): primary minerals without chemical treatment, (3): primary minerals with H_2O_2 and $Na_2S_2O_4$ treatments, (4): residual minerals with hot HCl treatment.

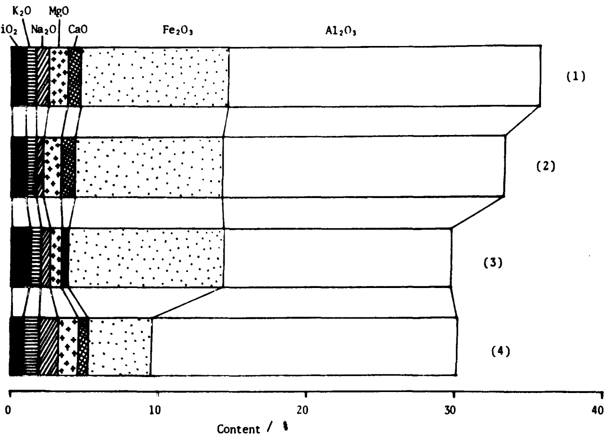

Fig. 4. Major and minor constituents of secondary minerals in the "Pond Sediment" with and without various chemical treatments.
(1): Original sample, (2): secondary minerals without chemical treatment, (3): secondary minerals with H_2O_2 treatment, (4): secondary minerals with H_2O_2 and $Na_2S_2O_4$ treatments.

Table 4. The contents of carbon, nitrogen, and phosphorus in the "Pond Sediment"

Element	Content/%
C	5.5
N	0.27
P	0.12

Ignition loss was 15.5%.

ments contain only rock-forming minerals.

The variation of major and minor components in secondary minerals are also shown in Fig. 4. Without the dithionite–citrate treatment the content (%) of most elements slightly decreased. This decrease may be caused by the loss of the principal elements of rock-forming minerals. In the last bar which corresponds to the dithionite–citrate treatment Fe decreases significantly, and the percentages of other elements increase slightly. Most of the removed Fe is considered to be iron oxides and some clay minerals (*e.g.*, goethite) which are easily degradable.

The elemental composition of secondary minerals treated with dithionite–citrate is almost identical to that of primary minerals with the same treatment, which their X-ray diffraction patterns showed some differences.

Evaluation of Non-metallic Elements. The analytical results of carbon and nitrogen are summarized in Table 4 along with the content of phosphorus. The results show that the "Pond Sediment" contains much carbon. Most of carbon exists as organic matter, and the remainder appears to be carbonate minerals such as dolomite [$(Ca, Mg)CO_3$] and calcite [$CaCO_3$].[10] The content of Ca in the hydrogen peroxide–hydrochloric acid soluble fraction is large, suggesting the presence of calcite in the "Pond Sediment." Carbonate minerals, however, were not positively identified probably because all the carbonate minerals were degraded by the chemical treatments using acids.

Half of phosphorus content occurs in the mineral fractions, but the phosphorus-rich minerals like apatite were not identified by the X-ray diffraction method, and the petrographic microscopic method is required for positive identification.

The content of nitrogen in the "Pond Sediment" (2700 $\mu g\ g^{-1}$) is close to the average value of the general soils, which contain nitrogen in the range of 200—5000 $\mu g\ g^{-1}$.[11]

Conclusion

It has been found that the principal components of the pond sediment are quartz and feldspars. Other identified minerals present at lower levels were pyroxenes, amphiboles, and clays. Olivines were not found in the sample. These results indicate that this sediment has not undergone extensive weathering because of the existence of many rock-forming minerals along with quartz. The results obtained by the extraction with citrate–dithionite suggest a scavenging action of trace metals by iron oxides.

Besides the identification of minerals the fractionation including chemical extraction has been found to be useful for environmental and geochemical characterization of sediments, because some elements are partitioned into specific fractions separated with appropriate chemicals.

The authors thank Dr. T. Yamanaka in the Department of Mineralogy, Faculty of Science, The University of Tokyo, for his assistance and discussion in mineral identifications. They also thank Dr. K. Okamoto in the National Institute for Environmental Studies for providing the sediment samples and carrying out the determination of carbon and nitrogen by a C. H. N. Corder. One of the authors (J.C.V.L.) expresses his sincere thanks to the Japan Society for Promotion of Science for supporting the fellowship to stay in the University of Tokyo as the visiting professor (1981).

This research has been supported by Grant-in-Aid for Environmental Science No. 56030019 from the Ministry of Education, Science and Culture.

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