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Environmental mineralogy on fine grained minerals and particles in acid rains at the Niigata district

by

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abstract

Acid rain contains small solid particles, which may suggest the origin of the pollution of acid rain or polluted air. Fine mineral grains and solid particles in the acid rains which were collected at the Niigata district have been examined from the standpoint of mineralogy using TEM-AEM method. Large amounts of fine grained minerals or materials in acid rains were found and identified. They were classified as artificial and natural types , and into soluble and insoluble types in water. Examples of the most characteristic type are mullite and Al Si spherules. Mullite and " sulphate" may suggest their pollution origin. Some another soluble sulphates , such as thenardite and aphthitalite, may also correspond to strong acidity and/or polluted rain.

Key words : acid rain , small solid particles, TEM, AEM, mullite, Niigata, environmental mineralogy

Introduction

Among various environmental problems, air pollution is one of the global environmental problems on the Earth. Dust particles in air are removed by rain fall. Acid rain is becoming important problem also in Japan.

Acid rain has been studiesd in detail mainly from the standpoint of analytical chemistry on solution. Acid rain contains solid particles although their quantities are very small and their contribution to acidity may be small. Such solid particles may , however, strongly suggest the origin of the pollution of acid rain or polluted air.

Although some studies on aerosol dust particles have been carried out (Fyfe, 1985; Tazaki *et al.*,

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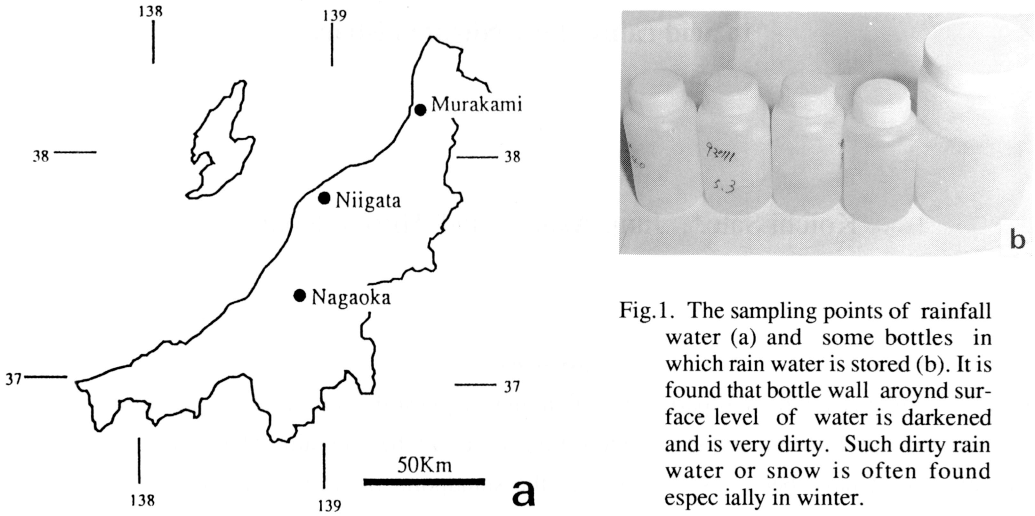


Fig.1. The sampling points of rainfall water (a) and some bottles in which rain water is stored (b). It is found that bottle wall aroynd surface level of water is darkened and is very dirty. Such dirty rain water or snow is often found espec ially in winter.

1989; Tazaki *et al.*, 1992a; Tazaki *et a*l., 1992 b; Watanabe *et al.,* 1992), almost no systematic studies on such solid particles in acid rain have been reported especially from mineralogical viewpoint using TEM-AEM . Mineralogy on such fine particles may suggest some important informations on their source of acidity and polluted air.

The analytical method fitting for these fine particles is TEM-AEM. TEM with analytical apparatus (AEM) is most suitable for perfect characterization of fine solid particles by analyzing structures and compositions of such small grains.

The purposes of this paper are to describe identified various fine mineral grains contained in acid rain collected in the Niigata district and to consider characters and origins of the acid rain in the Niigata district preliminarily.

Specimens and Experimental

Rain water was collected at the housetop of the Faculty of Science, Niigata University using receptacle of 20 cm in diameter and polyethylene bags which were collected or disposed in the every morning. The Polyethylene bags were exchanged day by day even when no rainfall day.

Some another rain water specimens collected at Nagaoka City were supplyed from Mr. Sadao Abe of Nagaoka Agricultural high school, Niigata Prefecture. Some rainfalls were also collected at Murakami in Niigata Prefecture. The sampling points above mentioned are shown in Fig.1.

These rainfall water was then treated as follows; pH of the rain water was measured and then the

Table 1 List of specimens collected at the housetop of Faculty of Science, Niigata University.
pH values of rain waters collected April 1992 to January 1993 and weather are contained.

			Wind velocity*		Wind direction*				Wind velocity*		Wind direction*
Date	Precipitation*	pH	Avg	Max		Date	Precipitation*	pH	Avg	Max	
1992/4/2	7.5	4.5	2.6	5.9	SW	1992/10/26	7	5.7	5.5	11.9	W
1992/4/5	6	5	2.8	5.1	SSE	1992/10/30	10.5	4.2	3.8	8.9	W
1992/4/7	3.5	4.2	3.3	7	N	1992/10/31	19	5.2	5.4	10.3	WSW
1992/4/9	8	3.7	3.3	7.7	WSW	1992/11/1	12	5.7	5.3	8.7	NW
1992/4/10	5.5	4.8	4	8.1	SE	1992/11/4	10	5.1	3.4	10.7	W
1992/4/11	3	4.1	7.7	14.8	WSW	1992/11/6	2	4.7	1.8	5.3	N
1992/4/12	7	4.8	3.7	11.9	WSW	1992/11/9	11.5	4.9	3.5	4.9	SE
1992/4/16	7.5	4.6	5	10.1	W	1992/11/10	31.5	4.8	3.5	10	W
1992/4/19	17	4.6	3.4	7	SW	1992/11/13	1	4.5	2.1	3.9	NE
1992/4/22	11.5	4.8	4.4	10.3	WSW	1992/11/14	0.5	4	2.7	7.4	WSW
1992/4/24	7	5.3	4.4	12.6	WNW	1992/11/16	7.5	4.9	5.3	11.4	WSW
1992/4/30	36	6.7	4.9	10.3	NE	1992/11/20	18	5.8	3.9	11.3	N
1992/5/7	13	5	3.7	5.9	SE	1992/11/23	2	4.2	4.8	13.1	WSW
1992/5/14	18.5	4.7	4.6	7.8	WSW	1992/12/4	8	5.2	2.8	5.6	W
1992/5/15	4.5	4.3	3.8	6.9	NNE	1992/12/7	0	5.6	3.9	5.7	S
1992/5/16	4	6.7	3.7	6.9	W	1992/12/8	15.5	6.3	4.7	10.5	W
1992/5/17	1	6.7	3.4	5.7	W	1992/12/10	1.5	5.2	2.9	8.3	W
1992/5/22	3.5	4	3.6	8.9	SW	1992/12/11	27.5	6.2	8.8	15.3	W
1992/5/31	0.5	3.7	2	4.6	NNE	1992/12/12	8	5.2	5.5	10.7	NW
1992/6/5	12	3.4	2.2	5.1	SSW	1992/12/17	9	5	2.6	4.8	SSW
1992/6/8	6.5	5.4	3.8	6.6	SE	1992/12/18	2	4.5	7.1	11.2	W
1992/6/20	16	7.1	2.8	7	N	1992/12/19	0.5	4.4	3.8	7.3	WNW
1992/6/21	20.5	5.9	4.7	7	N	1992/12/20	9.5	4.8	2.8	4.3	SSE
1992/6/22	2.5	6.4	2.5	4.4	NNW	1992/12/21	5.5	5.7	2.5	6.7	SE
1992/6/24	16.5	6	1.5	4.1	NNE	1992/12/22	6	5.8	5.4	10.4	W
1992/6/30	22	5	2	4.2	NE	1992/12/24	4.5	5.4	8.6	13	WNW
1992/7/1	26.5	5	3.8	7.2	W	1992/12/26	0.5	4.5	4.8	7.4	WNW
1992/7/8	3	4.6	2.9	6	W	1992/12/27	6.5	5.4	2.9	6.8	WSW
1992/7/9	1	5	3.1	7.4	WSW	1992/12/29	8	6.6	3.3	7.4	NE
1992/7/12	14	4.6	1.9	4.4	NNW	1992/12/30	5	5.1	4.1	9.3	W
1992/7/14	5	4.7	2.1	4.1	NE	1993/1/2	6	4.4	3	5.7	SW
1992/7/15	7	4.7	2.8	5.2	NE	1993/1/3	9.5	4.4	4.2	10.6	W
1992/7/16	1.5	4.6	2.3	5.2	N	1993/1/4	0.5	4.6	4.7	9.8	NNW
1992/7/18	49.5	4.6	5.8	10.1	WSW	1993/1/5	0.5	6	5.7	10.1	NW
1992/7/23	1	6	3.9	7	W	1993/1/7	17.5	5	2.2	5.6	N
1992/8/9	8	5	5.4	12.4	WSW	1993/1/8	2.5	3.6	5.7	8.5	NW
1992/8/13	24	4.5	2.9	4.6	SE	1993/1/10	9.5	5.3	4	7.2	NNW
1992/8/14	1.5	4.6	2.3	5.2	NE	1993/1/13	0.5	4.7	3.1	6.9	NE
1992/8/21	3	4.7	2.4	4.5	W	1993/1/14	11	5	4.2	7.1	NNE
1992/8/26	42.5	4.6	2.1	5.9	WSW	1993/1/15	3.5	4.3	2.1	4.6	NE
1992/9/3	4.5	5.5	3.9	11.2	WSW	1993/1/16	4.5	4.2	4.9	7.2	SE
1992/9/11	0	6.5	6	8.1	NNW	1993/1/18	15	4.9	2.9	5.4	WSW
1992/9/16	0	4.5	2.2	4.6	NNE	1993/1/19	1.5	4.8	6.2	9.8	W
1992/9/20	5	5	3.9	7.6	NNW	1993/1/20	4	5.3	4.5	10.6	W
1992/9/25	6.5	4.8	5.1	11.4	WSW	1993/1/25	0.5	4.8	1.9	6.2	SE
1992/9/27	2.5	6	5.6	9.1	NW	1993/1/27	35	4.5	2.6	5.3	WSW
1992/10/4	6	4.9	3.6	8.8	N	1993/1/28	8.5	4.9	9.4	14.6	W
1992/10/6	9.5	5.9	2.4	5.4	NNE	1993/1/29	0.5	5.3	11.2	15.5	W
1992/10/9	22	5.2	3.5	7.4	WSW	1993/1/30	2.5	5.1	5.4	9.9	W
1992/10/10	16	6	4.6	9.3	W	1993/1/31	6	4.5	4.1	8.9	W
1992/10/15	7.5	4.5	1.7	4.1	N	1993/2/2		5.5			
1992/10/20	20.5	4.5	2.6	9.6	SE	1993/2/7		5.3			
1992/10/25	20	4.9	6.2	13.3	W	1993/2/9		4.8			

rainfall was dried up at *ca.*100℃ lastly on slide glass. The specimens on slide glass were examined by X-ray diffractometer. Specimens for TEM - AEM analysis was prepared by placing them on carbon coated microgrid. A JEM 200CX TEM combined with EDS detector , TN 2000 , operated at 200 kV, was used.

The electron beam was usually focussed to a diameter of *ca.* 150 - 400 nm for analysis in TEM mode. The size of the X-ray source is approximately of the order of the electron beam diameter for a thin specimen and an accelerating voltage of 200 kV. Qualitative analysis was usually carried out because qualitative AEM data combined with ED pattern was almost adequate for identification but quantitative analysis was carried out in case of necessity. It was carried out on the basis of the Cliff and Lorimer (1972) thin film tequnique using K-factors experimentally determined from synthesized glass standards.

Descriptive results

(1) Rain water

Table 1 shows pH values of rain waters collected from April 1992 to January 1993. Monthly pH value change is shown in Fig. 2.

The lowest pH was measured on rain water on June 1992. Average value is pH = 4.65. According to Reports of Research on acid rains in Niigata Prefecture (1985- 1989) (1991) averaged pH value from April 1985 to March 1989 was 4.86 .

Fig. 3 shows correlation between pH values and quantities of rain water Characteristic feature is that pH value in general, increases as rain water quantities increases but some plotted data are deviated from this general rule of straight relation. The data correspond to those still preserving low pH value of 4.5-5 even in increasing rain fall quantities. Table 2 shows dates corresponding to these data.

Fig.4 shows frequency of wind direction in the days of such type group of pH values . It is found that WSW wind direction is predominant. The polluted materials might come from western direc-

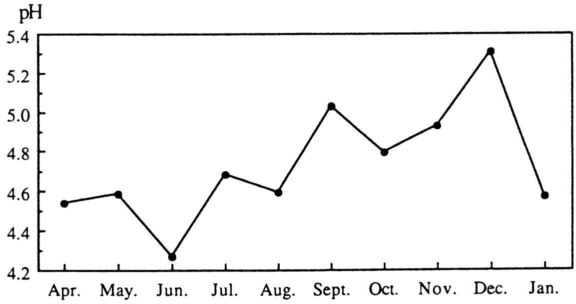


Fig.2. Monthly pH value change of rain waters (Apr. 1992 to Jan. 1993).

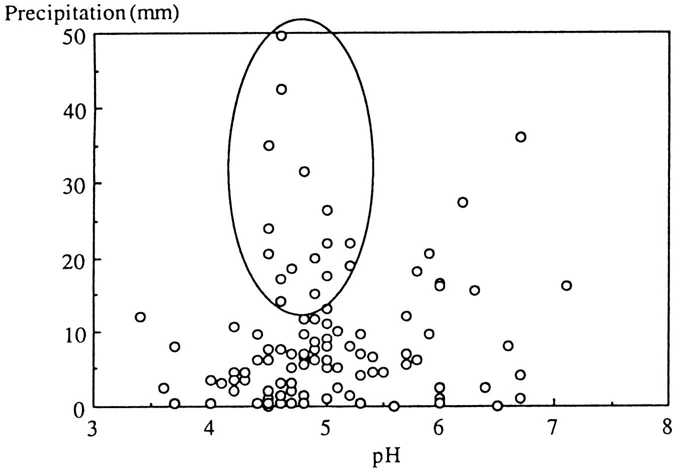


Fig. 3. Correlation between pH values and quantities of rain water. pH value in general, increases as rain water quantities increases but some plotted data which are circled are beyond this straight relation. The data correspond to those of still preserving low pH values of 4. 5-5 even in increasing precipitation.

Table 2 Dates corresponding to the circled data of Fig. 3

1992	04	19	1992	10	09
	05	14		10	20
	06	30		10	25
	07	01		10	31
	07	12		11	10
	07	18	1993	01	07
	08	13		01	18
	08	26		01	27

tion. However, no clear relation between pH values and wind strength was observed. Solution analysis was not carried out in this study because dried specimen composed of some mineral phases represents their original chemical composition if their quantities are precisely known as is suggested by Manecki *et al.* (1988), although it is best to have precise analytical results on solutions.

(2) Solid materials

X ray diffraction data

Some examples of XRD data are shown in Fig. 5. High background from 15 to 35°(2θ) suggests the presence of amorphous materials and/or organic matter. This estimation was supported by TEM observation: much amorphous materials such as carbons are found. Mineral phases confirmed are gypsum (bassanite), quartz, halite, barite, mica, amphib-

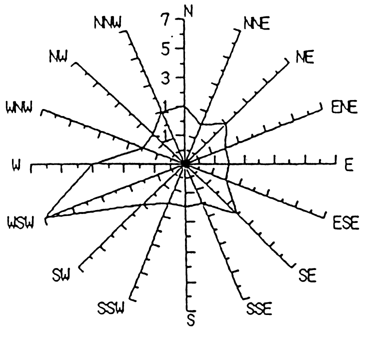


Fig.4. Frequency of wind direction in the days of low pH values even in much precipitation. It is found that WSW wind direction is predominant.

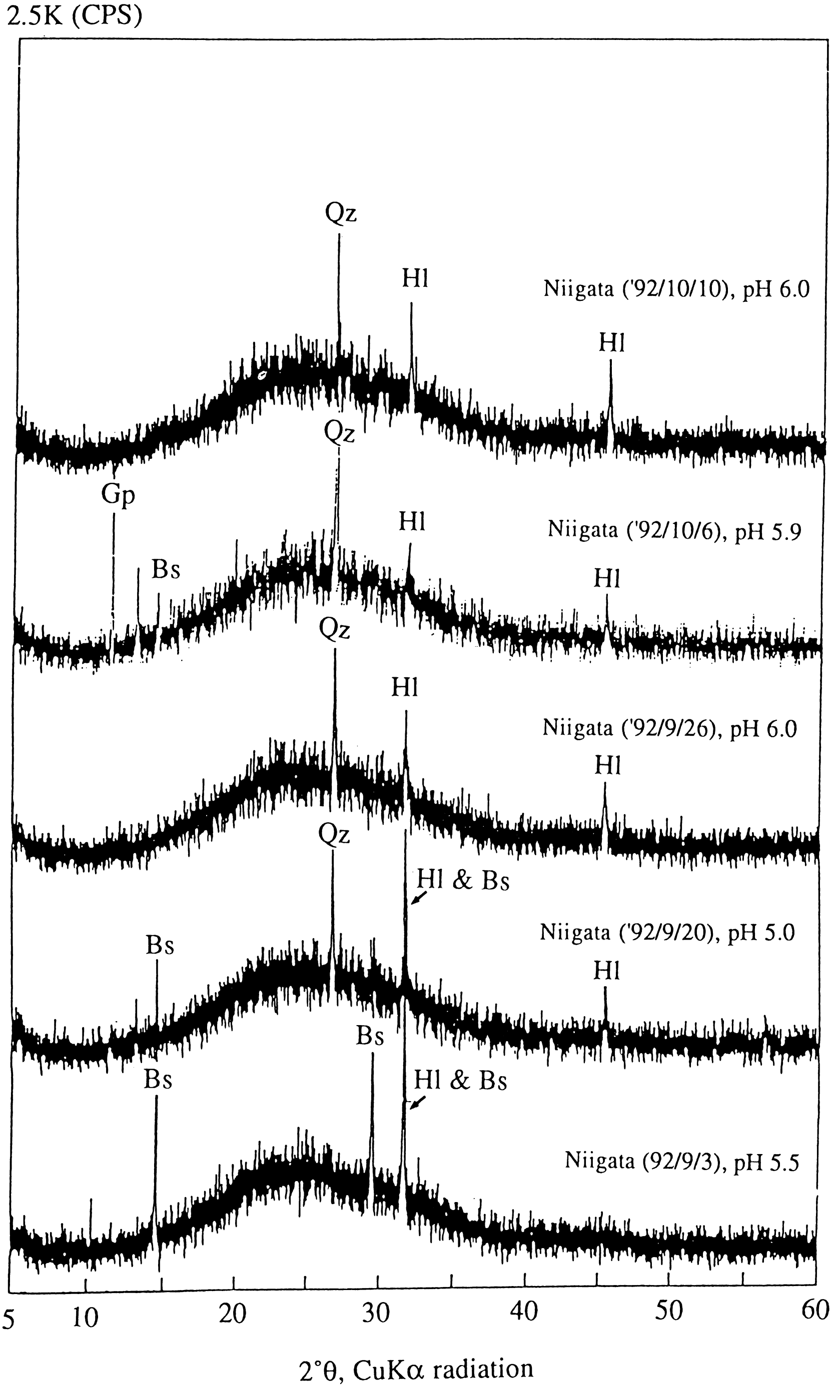


Fig.5. Some examples of XRD patterns.

Table 3 Mineral phases confirmed by X ray diffraction.
Gp: gypsum, Bs: Bassanite, Hl: Halite, Qtz: Quartz, Mica: Mica, Brt: Barite, Amph: Amphibole, Feld: Feldspar UM: Unidentified minerals

Date		Locality	pH	Gp	Bs	Hl	Qtz	Mica	Brt	Amp	Feld	UM
1992/2/20	by night	Nagaoka	3.9		*	*						*
1992/2/29	by night	Nagaoka	4.0	*	*			*				*
1992/3/5	by night	Murakami	6.7	*	*	*						
1992/3/14	by night	Nagaoka	3.7	*	*			*				
1992/3/15	by day	Nagaoka	3.4	*	*							*
1992/4/9		Niigata	3.7	*			*		*			
1992/4/19		Niigata	4.6	*	*					*		*
1992/5/9		Niigata	5.0	*	*							
1992/5/22		Niigata	4.0	*		*						
1992/6/21		Niigata	5.9	*		*	*					*
1992/6/30		Niigata	5.0	*	*	*						*
1992/7/12		Niigata	4.6			*	*	*				*
1992/7/18		Niigata	4.6		*		*					
1992/8/9		Niigata	5.0	*	*							
1992/8/13		Niigata	4.5		*		*	*				
1992/8/14		Niigata	4.6	*								
1992/8/21		Niigata	4.7	*								
1992/8/26		Niigata	4.6	*	*							
1992/9/3		Niigata	5.5		*	*						*
1992/9/20		Niigata	5.0	*	*	*	*					
1992/9/27		Niigata	6.0			*	*					
1992/10/6		Niigata	5.9	*	*	*	*					*
1992/10/10		Niigata	6.0			*	*					*
1992/10/15		Niigata	4.5	*	*		*					
1992/10/20		Niigata	4.5	*	*		*					
1992/10/25		Niigata	4.9		*	*	*				*	*
1992/10/31		Niigata	5.2	*	*	*	*					
1992/11/4		Niigata	5.1	*	*	*						
1992/11/9		Niigata	4.9	*	*	*						
1992/11/10		Niigata	4.8		*	*						
1992/11/16		Niigata	4.9	*	*	*						
1992/11/20		Niigata	5.8	*	*	*						*
1992/11/28		Niigata		*		*						

UM:Unknown Minerals

ole feldspar and so on(Table 3). Bassanite may be due to conversion from gypsum in specimen preparation procedure.

TEM observations

TEM analysis can reveal minor phases which cannot be identified by X ray analysis. Quantitative analysis may be difficult and so the identified minerals do not mean the whole picture of the specimens, but if characteristic minerals or solid particles are present and detected it may suggest specimen characteristics. Identification procedures for the observed material may be perfect if TEM image analysis, ED pattern analysis and EDS chemical analysis are combined.

However, all the solid phases are not able to be identified, and many unidentified grains are remianed.

Solid particles can be classified as follows ; natural origin and artificial, or soluble phase and insoluble phase into water.

The followings are some examples of typical inorganic minerals or materials.

Halite $NaCl$:

Distance from sea shore may be strongly related to the presence or abundance of the halite . In specimens from Nagaoka, only 1 specimens showed presence of halite. Halite is weak to electron beam radiation. Presence of halite is correlated with weak acidity or with neutral acid.

Sylvite KCl :

This mineral may also be due to sea water origin.

Carnallite $KMgCl_3 \cdot 6H_2O$:

This may also be due to sea water origin (Fig.6-a). Presence of carnallite is correlated to increasing pH values.

Sulphohalite $Na_6(SO_4)_2\,ClF$:

This hexagonal or cubic shaped grains found may also be sea water origin. The size of this mineral was about 1μm . This is weak in electron beam radiation

Kainite $KMg(SO_4)Cl \cdot 3H_2O$:

Hexagonal platy shaped kainite often have 3 - 8μm in size. They are not single crystals but have always aggregated shapes (Fig.6-b).

Thernardite Na_2SO_4 :

Parallelogram shaped grain with size of 1 to 2μm is weak in electron beam radiation. This grain is present often in low pH (~ 4.2) waters (Fig.6-c)

Aphthitalite $K_3Na(SO_4)_2$:

Aphthitalite is often hexagonal and platy and is found often in winter. Frequency of occurrence increases with decreasing pH.

Hokutolite $(Ba, Pb)SO_4$:

The size of this mineral is 0.1 - 3μm . It is often found. Various shapes are present; granular, irregular , cubic or paralleogram (Fig.6-d) .

Gypsum $CaSO_4 \cdot H_2O$:

<< Bassanite $CaSO_4 \cdot 0.5H_2$ >>

Gypsum is very commonly found and various morphological types were observed (Fig.6 - e,-f and -g).

Mullite (or Sillimanite) Al_2SiO_5 :

Mullite is very characteristic in spherical shape (Fig. 6-h and -i). Mullite is similar to sillimanite in diffraction pattern and in some cases cannot be clearly distinguished. The spherical size is 1-2μm in diameter. Not only well crystallized mullite but also intermediate type of mixture of mullite and kaolin minerals are often found. The latter type is not always distinguishable from aluminum silicate spherule.

Carbon C :

Much spherical shaped carbon grains are estimated to be present (Fig.6-j) . They are amorphous. This may be one of the causes of high background of X-ray diffraction pattern.

Graphite C :

Graphite is sometimes found in high pH water rain .

Chromium Cr :

Metal Cr is rarely found. This may be derived from plating of Cr or some unknown origin.

Stainless steel Fe - Cr(12%~) with Ni,Mo,Ti,Nb, etc :

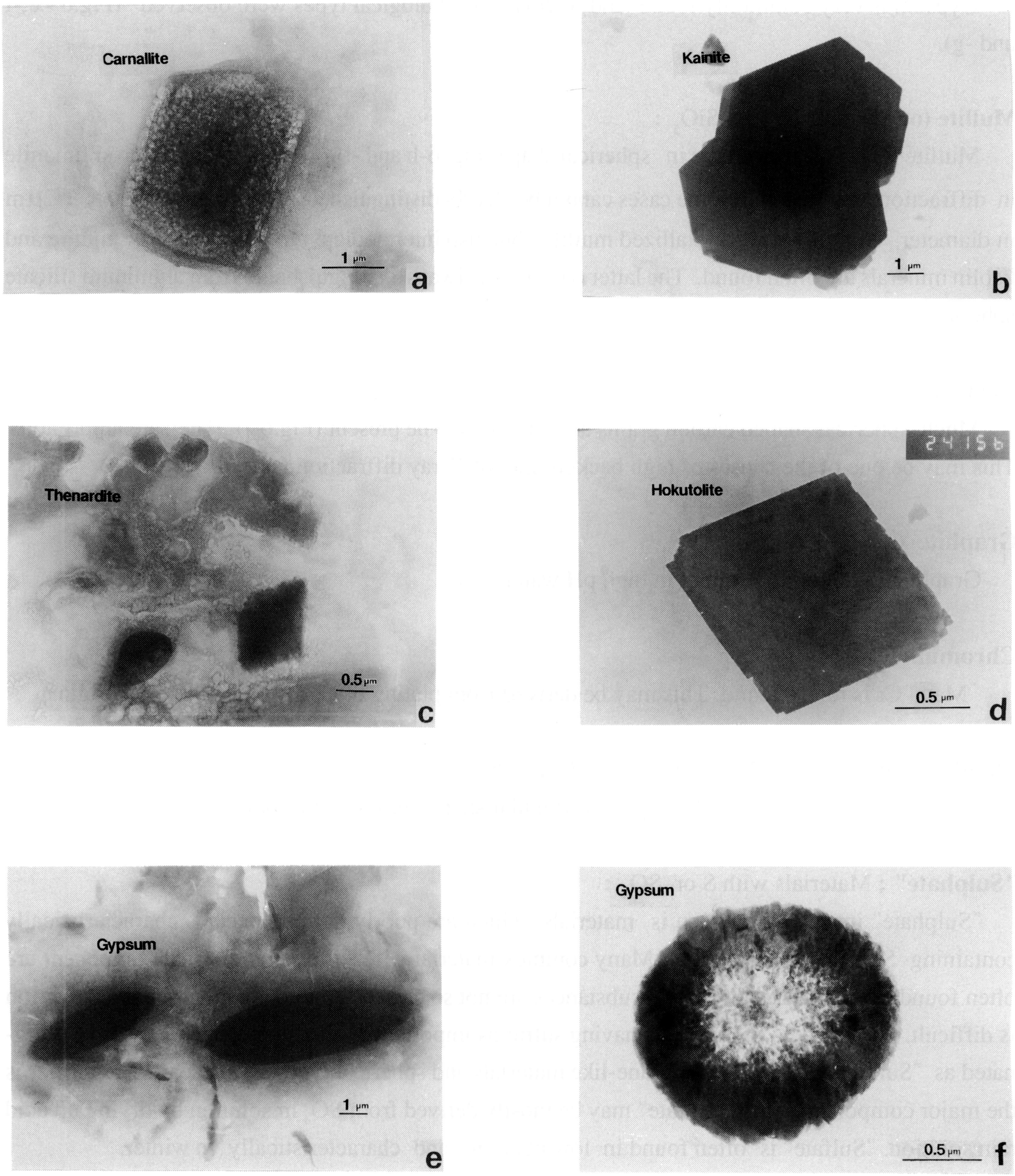
Fe-Cr type and Fe-Cr-Ni-(Mn) type of irregular shaped grains were found.

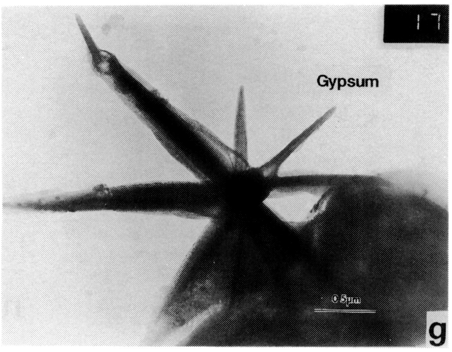
"Sulphate" ; Materials with S or SO_4 :

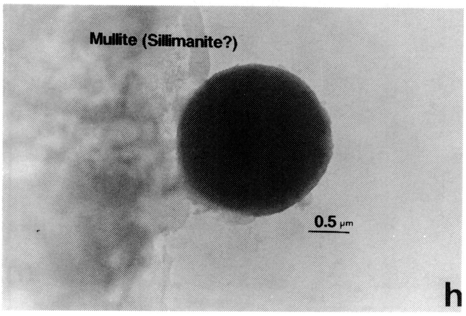
"Sulphate" in this description is materials which are poorly defined except characteristically containing S or SO_4 component. Many complex material with sulfur as importnat component are often found but the character of this substances are not so clearly defined and their characterization is difficult. So, this type of materials having sulfur as important and major component is here designated as "Sulfate". Both of membrane-like materials and spherical types are present. The former is the major component. This "Sulfate" may be mostly derived from SO_4 in solution by drying up acid rain solution. "Sulfate" is often found in low pH rains and characteristically in winter.

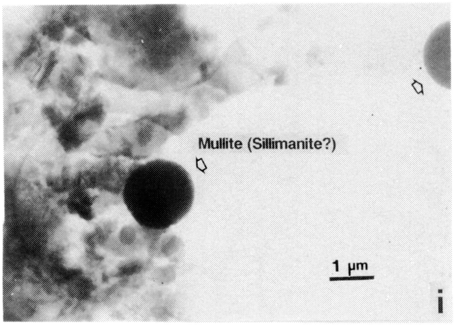
Calcite $CaCO_3$:

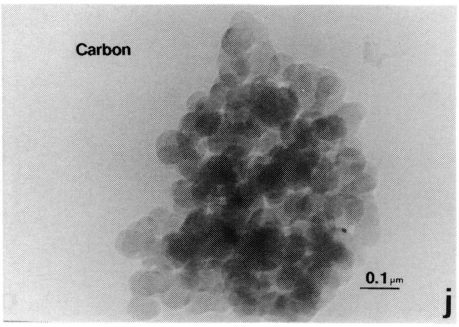
Contents of calcite increase as pH value becomes higher.

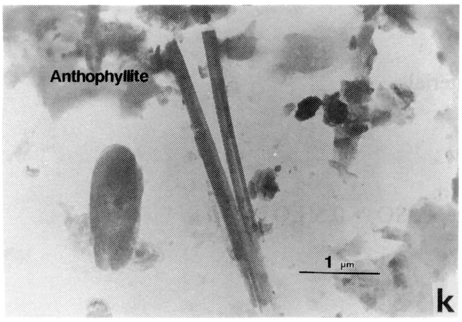

Carnallite
1 μm
a
Kainite
1 μm
b
Thenardite
0.5 μm
c
24156
Hokutolite
0.5 μm
d
Gypsum
1 μm
e
Gypsum
0.5 μm
f

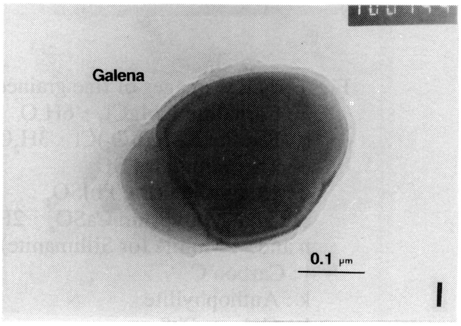

17
Gypsum
0.5µm
g


Mullite (Sillimanite?)
0.5 µm
h


Mullite (Sillimanite?)
1 µm
i


Carbon
0.1 µm
j


Anthophyllite
1 µm
k


Galena
0.1 µm
l

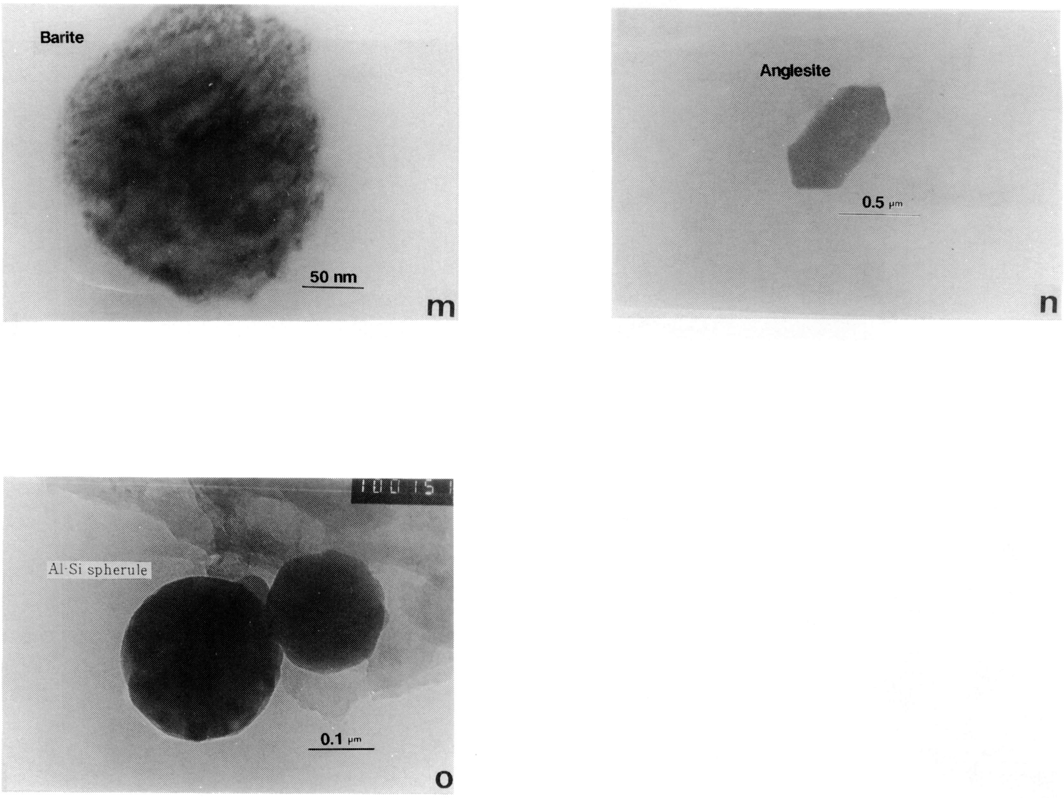


Fig. 6. TEM images of fine grained minerals or materials.
a : Carnallite $KMgCl_3 \cdot 6H_2O$
b : Kainite $KMg(SO_4)Cl \cdot 3H_2O$
c : Thernardite Na_2SO_4
d : Hokutolite $(Ba, Pb)SO_4$
e, f and g : Gypsum $CaSO_4 \cdot 2H_2O$ << Bassanite $CaSO_4 \cdot 0.5H_2O$ >>
h and i : Mullite (or Sillimanite) Al_2SiO_5
j : Carbon C
k : Anthophyllite
l : Galena PbS
m : Barite $BaSO_4$
n : Anglesite $PbSO_4$
o : Al-Si spherule

Another observed minerals and materials are as follows;

Biotite
Phlogopite
Glauconite
Chlorite
Plagioclase
K-feldspar
Hornblende
Anthophyllite (Fig.6-k)
Quartz SiO_2
Silica glass
Brookite /Rutile TiO_2
Franklinite $(Zn, Mn, Fe)(Fe, Mn)_2O_4$
Bayerite / Gibbsite $Al(OH)_3$
Galena PbS (Fig.6-l)
Carlinite

The other materials found, for examples, are barite $BaSO_4$ (Fig.6-m), Anglesite $PbSO_4$(Fig.6-n), Tridymite, dolomite $CaMg(CO_3)_2$, anatase TiO_2, teallite $PbSnS_2$ nickel Ni, cupper Cu, Zn-Al-oxide $Zn_4Al_{22}O_{37}$ and so on.

All the identified minerals or solid particles are summarized in Table 4.

Much unidentified materials were also present. For example, Al-Si spherule (Fig.6-o) is important. Its main compositions are Si and Al associated with small amount of K, Fe, Ca, Na, Mg, S, Cl, Ti, Mn. Some of this type grains show no diffraction pattern type but most of them show weak diffraction pattern of kaolinite with or without mullite diffraction. These grains may be related to mullite. Their characteristic shape of spherule suggests its artificial origin.

Discussions

Table 5 shows the classification of soluble and insoluble materials. Among soluble types, most of sulfate SO_4 ions may be due to pollution synthesis of SO (Maneckli *et al*., 1985) and presence of gypsum, thernardite and aphthitalite may largely be due to the results of neutralizing effect of acid component.

Furthermore, thernardite and aphthitalite are rarely observed but if the rain water contains these

Table 4 The identified minerals or solid particles in rain water.

	Date	'92/2/20	'92/2/29	'92/3/5	'92/3/10	'92/3/14	'92/3/15	'92/4/9	'92/5/7	'92/5/31	'92/6/20	'92/6/21	'92/6/30	'92/7/12	'92/7/23	'92/8/9	'92/8/13	'92/9/3	'92/9/20	'92/9/27	'92/10/6	'92/10/10	'92/10/20	'92/10/25	'92/10/31	'92/11/4	'92/11/9	'92/11/10	'92/11/20
	Locality	Nagaoka	Nagaoka	Murakam	Nagaoka	Nagaoka	Nagaoka	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata	Niigata
	Precipitation							8	13	0.5	16	20.5	22	14	1	8	24	4.5	5	2.5	9.5	16	20.5	20	19	10	11.5	31.5	18
Materials	Chemical Composition \ pH	3.7	4	6.7	3.9	3.4	3.4	3.7	5	3.7	7.1	5.9	5	4.6	6	5	4.5	5.5	5	6	5.9	6	4.5	4.9	5.2	5.1	4.9	4.8	5.8
Halite	NaCl	****		***				****	****	*	****	****	****		****	****	*	****	****	****	****	****	****	****	****	****		***	****
Sylvite	KCl												**																
Carnallite	KMgCl3•6H2O	***																	***	***	**	**		**		**		**	
Sulphohalite	Na6(SO4)2ClF			**																								*	**
Kainite	KMg(SO4)Cl•3H2O			**																*									
Gypsum	CaSO4•2H2O	****	***	****	****	****	****	**	****	****	***	****	****		*	****	**	****	****	****	**	**	****	***	****	****	****	**	****
(Bassanite)	2CaSO4•H2O	****	***	****		****		**	****	****	***	****	****			****	**	****	****	****	***	***	****	***	****	****	****	****	****
Thenardite	Na2SO4		*			**																							
Aphthitalite	K3Na(SO4)2		****				**			*													**						
Barite	BaSO4																				*								
Hokutolite	(Ba,Pb)SO4		**			**	**		***	**			*			**			**		**	**	****	**			****		
Anglesite	PbSO4																												
Biotite	K(Fe,Mg)3AlSi3O10(OH)2	*							*								**				*	*							
Phlogopite	KMg3Si3AlO10(OH)2														*		*												
Illite	KAl2Si3AlO10(OH)2							*			**			**			**				**	**							
Glauconite	K(Fe,Al)2(Si,Al)4O10(OH)2						*																						
Chlorite	(Mg,Fe,Al)6(SiAl)4O10(OH)8	*			**		**	**						**		**	**							**					
Plagioclase	NaAlSi3O8-CaAlSi2O8					*		*	*		*			*	*	*								**					
K-Feldspar	KAlSi3O8							*	*	*	*					*	*						**		*				
Calcite	CaCO3										*				*	*													
Dolomite	CaMg(CO3)2						*																						
Anthophyllite	(Mg,Fe)7Si8O22(OH)2	*																						*					
Actinolite	Ca2(Mg,Fe)5Si8O22(OH)2						*										*					*							
Hornblende	Ca2(Mg,Fe)3AlSi7AlO22(OH)2							*		*				**			*												
Quartz	SiO2					*		*	*	**	*			**			*				*	*	**						*
Mullite (Sillimanite?)	2Al2O3•SiO2						*																*	*					
Alminium Silicate Spherule		**			*		*		*				*	*	*								*		*				
Iron Spherule		*			*				*	*				**			*							*					*
Iron Oxide (hydroxide)					**				*	*	*	*			**					*							*		
"Sulfate"	S & Others		****	*		****	****			*						**	*						****					*	
Tridymite	SiO2																		**										
Silica glass	SiO2	*		*					*					**	*	**	*								*		*		*
TIO2 phase	TiO2	*					*	*						*	**		*		*					*	*	*			
Carlinite	Ti2S											*												*	*				
Teallite	PbSnS2											*																	
Galena	PbS	*								*								*** ,											
Graphite	C											*									*	*							*
Chromium	Cr											*				*											*		
Nickel	Ni																							*					
Copper	Cu																								*				
Franklinite	(Zn,Mn,Fe)(Fe,Mn)2O4					*			*	*					*						*	*				*	*	*	
Bayerite	Al(OH)3															*													
Zinc Alminium Oxide	Zn4Al22O37														*														
Iron Titanium Silicide	FeTiSi								*																				
Stainless Steal	Fe-Cr-Ni									*						*	*						*	*			*		
Carbon	C				**	*	**			**				****		**										*		*	

****: Major, ***: Intermediate, **: Minor, *: Trace

Table 5 Classification of the materials into soluble and insolubl phases in water.

Soluble Materials		
Natural Materials	Artifical Materials	Materials of Unknown Origin
Halite	Gypsum (Bassanite)	
Sylvite	Thenardite	
Carnallite	Aphthitalite	
Sulphohalite	Carbon	
Kainite	"Sulfate"	
	Anglesite	

Slightly Soluble Materials		
Mica & Clay Minerals	Asbestos	Barite
Feldspar	Tridymite	Hokutolite
Quartz	Chromium	Calcite
Hornblende	Nickel	Dolomite
	Copper	Silicate glass
	Franklinite	Titanium oxide
	Mulite	Teallite
	Stainless steal	Graphite
	Iron spherule	Galena
	Iron oxide (hydroxide)	
	Lanthanum oxide	
	Alminium silicate spherule	

Materials of unknown nature		
	Carlinite	
	Zinc Alminium oxide	Bayerite
	Iron Titanium Silicide	

materials its pH is very acidic. So, the presence of these two minerals may suggest 2nd stage of neutralization process rather than 1st stage of neutralization process which may correspond to formation of gypsum.

The presence of thenardite and aphthitalite may represent strong pollution.

Another artificial products are already shown in Tables 5. Figs. 7 and 8 represent correlation between the occurring mineral species , and pH values and seasonal change respectively.

It is possible to calssify these minerals based on the character of rainfall into the following three types ;

1) materials contained in strong acid rain

2) materials contained in normal (neutral) rain

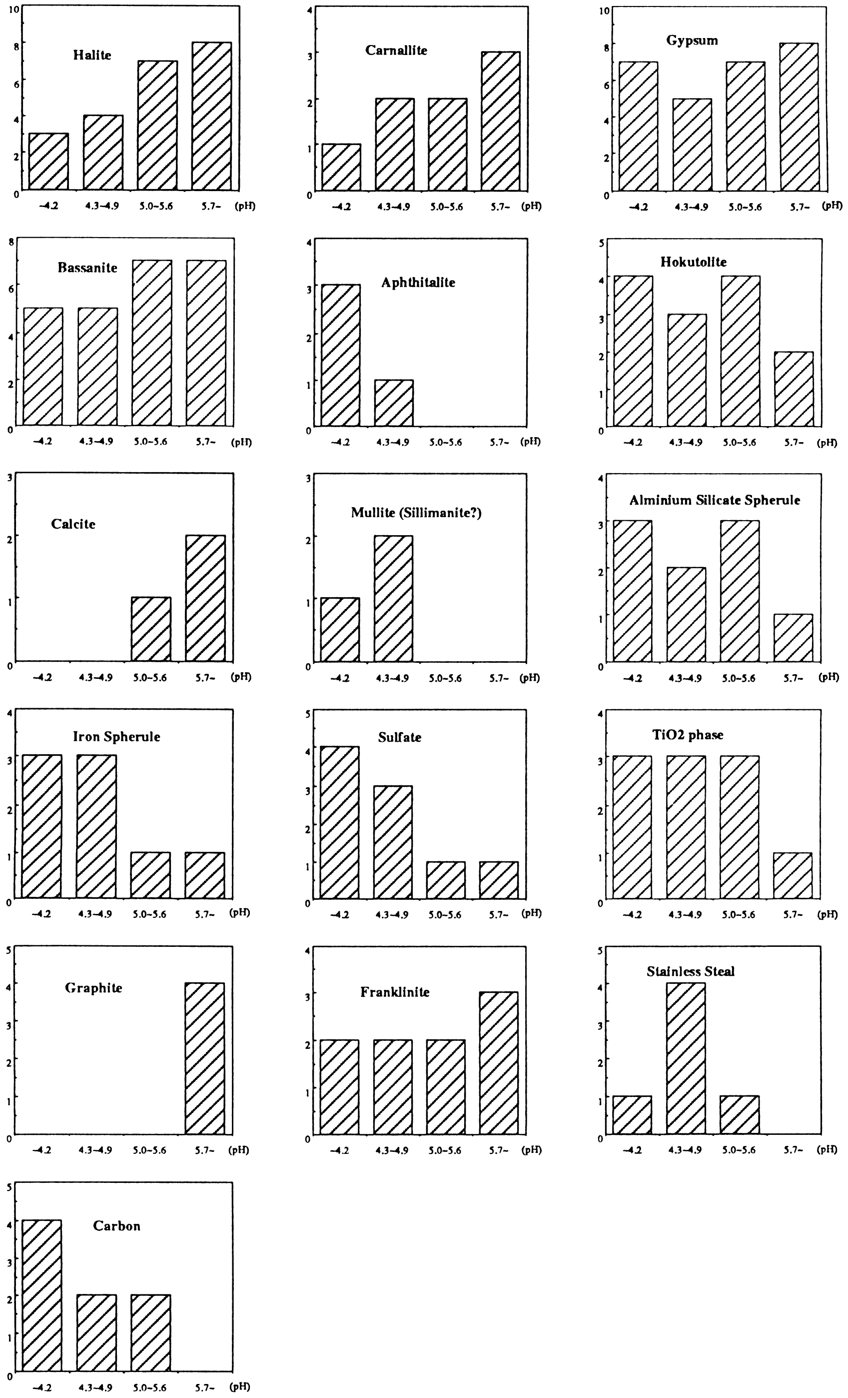


Fig.7. Correlation between mineral species and pH values.

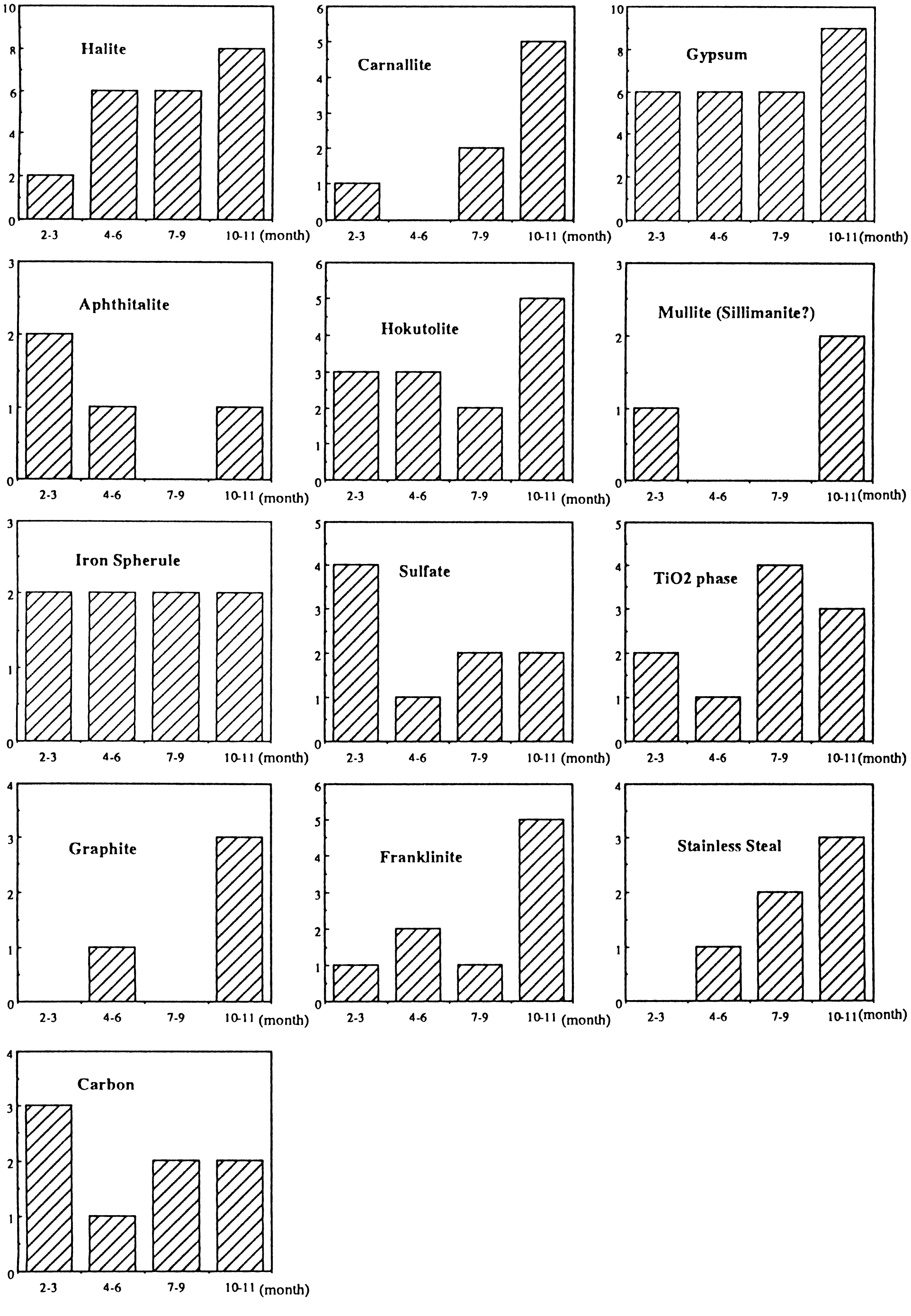


Fig. 8 . Correlation between mineral species and seasonal change

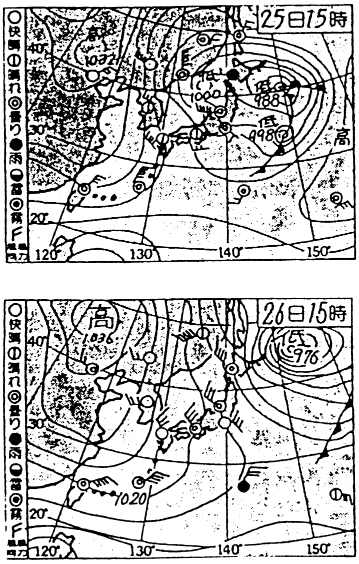


Fig.9. Weather charts of 25 and 26 October 1992 when mullite grain and related minerals were found.

3) materials being independent of acidity of rain

These types are again classified into soluble type and insoluble type.

Soluble type contains thenardite , aphthitalite , carbon and "sulphate"

"Sulphate" is much related to origin of strong acidity. So thenardite, aphthitalite and carbon are strongly correlated to coexistence of the "sulphate".

Insoluble type materials contain mullite, Al Si spherule , Iron spherule, stainless steel, galena, chlorite and hornblende. Among them, strong correlation is found in mullite and carbon. When the meteorological weather chart represents West high and East low winter type in Niigata, pH of rainfall decreases and snow shows low pH generally.

Oikawa (1992) suggests that the pollution species are due to materials from the Far East continent . If it is true, the carbon may also be due to continental origin. Mullite strongly correlates with "sulphate ". Most Al Si spherules can also be considered fundamentally the same materials as mullite. These spherules may be due to the results of burning of coal above 1000℃ (Tazaki *et al.*,1989).

There is no outstanding use of coal in Japan especially Japan Sea side and there is large qunatity of combusion in the continental region around the Japan Sea . So, these polluted materials may be transported from continent. One example of weather chart of the day when spherical mullite was confirmed in acid rain is shown in Fig. 9. This is typically winter type weather chart.

Summary

1) Large amounts of fine grained minerals or materaials were found in acid rains as in Table4 .

They contained various mineral species .

2) They were classified as artificial and natural types , and into soluble and insoluble types in water.

3) Many of them may be artificial. Examples of the most striking type are mullite and Al Si spherules. They are sherical in shape and this may be interpreted as artificial because it is formed in burning coal. Mullite and its related mineral grains are typically found when weather map is winter type . Mullite and " sulphate" may well suggest their pollution origin.

4) Some another soluble sulphates , such as thenardite and aphthitalite ,may also become indicator of strong acidity and/or polluted rain.

5) This paper may be the first report of systematic study of solid mineral and materials in acid rain water. The results of this study indicate strong possibility of suggesting origin of polluted rainwater from mineralogical view point , especially from TEM-AEM investigation method.

6) However, many problems still remain : for example, the data are not always sufficient and much larger quantities of data are necessary for detailed characteriztion. Further examinations are needed and another project of comparative study on solid materials and minerals in acid rains between western Europe and Japan is now in progress.

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Niigata : 新潟
Nagaoka : 長岡
Murakami : 村上