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REAL SCALE EXPERIMENT OF SULFUR DIOXIDE DISSOLUTION INTO CLOUD DROPLETS GENERATED IN ARTIFICIAL CLOUD EXPERIMENTAL SYSTEM(ACE)

Sadamu Yamagata [1]
Satoru Baba [1]
Naoto Murao [1]
Sachio Ohta [1]
Tsutomu Fukuyama [2]
Masahiro Utiyama [2]
Tadasi Yamada [3]
Yasushi Fujiyoshi [4]
Toshio Harimaya [5]
Masaaki Inage [6]

Abstract

The processes of sulfur dioxide dissolution into cloud droplets and its successive oxidation to sulfate were studied in an artificial cloud experimental system(ACE) in a vertical shaft of a mine. Sulfur compounds in droplets, aerosols and gas were collected by serial samplers at several heights. The concentrations of sulfur compounds at each height indicate that the released sulfur dioxide at the bottom of the shaft was absorbed by cloud droplets but the oxidation rate of sulfite to sulfate was slow which may be due to the absence of light and oxidants in the shaft.

KEYWORDS: *shaft, cloud, sulfur dioxide, oxidation, soil particle*

1. Introduction

The chemical species relating to the quality of rain are mainly sulfur dioxide and nitrogen oxide. These chemical substances are released into the atmosphere by human activities such as power stations with coal or oil, automobiles, smelters and so on, then oxidized to sulfuric acid and nitric acid which deposit on the surface. Therefore acid rain, one of the most serious

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[1] D.Eng., Research Assistant, Dept. of Environments and Resources, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan
[2] D.Sci., Section Chief, National Institute for Environmental Studies, Tsukuba, Ibaraki 305-0053, Japan
[3] D.Eng., Professor, Dept. of Civil Eng., Chuo University, Kasuga Bunkyo-ku, Tokyo 112-8551, Japan
[4] D.Sci., Professor, Institute of Low Temperature Sciences, Hokkaido University, Sapporo 060-0819, Japan
[5] D.Sci., Professor, of Graduate school of Science Hokkaido University, Sapporo 060-0810, Japan
[6] Mitsui Construction Co. Nakase Mihama-ku, Chiba 261-0023,Japan

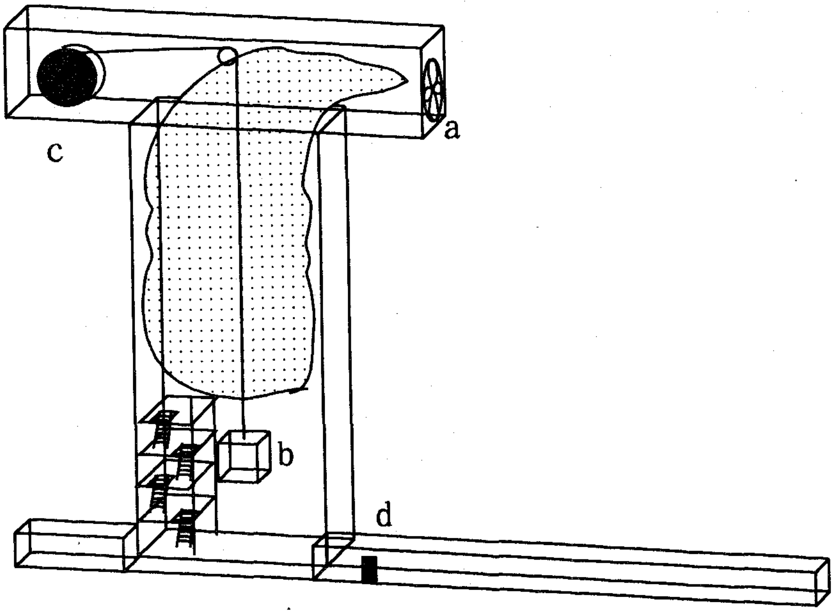

Figure 1. Scheme of the ACE(Artificial Cloud Experimental System) in Kamaishi Mining Co. Electric fan(a); Sampling cage(b); Cage wire winder(c); sulfur dioxide gas cylinder(d). The wall of the shaft is naked rock and gets wet from the bottom to the top by high relative humidity

global environmental problem, should be regarded as the reflection to rains of the acidification of the atmosphere. It means that we must study how the atmosphere is acidified; the total amount of acidifying substances, the process and its speed of chemical transformation and removal from the atmosphere. The first point can be estimated in each country and the second point is being studied by many researchers through field observations (Hegg and Hobbs, 1982; Liu, *et al.*, 1993; Collett, *et al.*, 1994; Snider and Vali, 1994; Laj, *et al.*, 1997) and laboratory experiments as reviewed(Hoffman and Jacob, 1984; Martin, 1984;Schwartz, 1984;Seinfeld, 1986; Hidy, 1990). The studies about chemical processes in laboratories so far are mainly those in bulk phase; those in small droplets like cloud droplets(Hansen, *et al.*, 1991; Steele, *et al.*, 1981) and rain drops are not studied so much because of difficulties in keeping them in the air for enough time. We succeeded to produce a constant cloud in Artificial Cloud Experimental System(ACE), vertical shaft of a mine with high-powered electric motor fan and studied the dissolution of sulfur dioxide gas into cloud droplets and its oxidation there. Several chemical species other than sulfur were also measured.

2. Experimental

2.1 Facilities

For a cloud experiment we used Nippou-central shaft(Kamaishi Mining Co.) which locates Kamigou-machi Tohno-city Iwate Pref., Japan. The scheme of the ACE is shown in Fig.1.

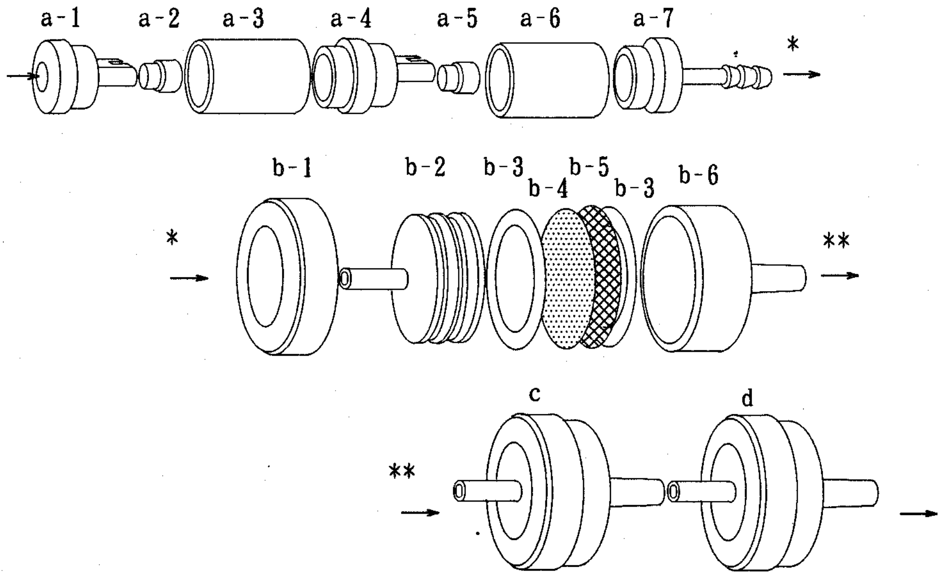

Figure 2. The components of samplers for cloud droplets, aerosol particles and sulfur dioxide gas. a-1:one 9.6mm jet for the separation of particles lager than 10μm; a-2: first impaction stage; a-3: upper holder; a-4: five 2mm jets for the separation of particles lager than 2μm; a-5: second impaction stage; a-6: middle holder; a-7: bottom holder. b-1: holder(top) ; b-2: gas inlet; b-3: silicone packing; b-4: teflon filter; b-5: filter supporting net; b-6: holder(bottom). c,d: sulfur dioxide filter holder.

The electric fan at the top of the shaft(680m a.s.l.) evacuates the air from the bottom(250m a.s.l.). The shaft has $5.5m \times 2.8m$ section; one third is ladder space with which we can access any level; the central one third of the shaft is kept for an up-and-down cage loaded with various observational instruments, the last one third is free space through which the air flows up without any interference. The experiments were carried out five times on 4,5,6 September, 1996.

2.2 Sulfur dioxide Gas Release at the Bottom

In some runs sulfur dioxide gas was released at the bottom from the cylinder towards upwind direction then diffused by a small electric fan to mix sulfur dioxide gas with the air. Its concentration was monitored by sulfur dioxide meter and about 50ppbv during the gas release.

2.3 Sampling and Analysis of Sulfur Species

The sampler for sulfur species in cloud droplets, aerosols and gas shown in Fig.2 consists of serially combined an impactor, an aerosol filter and two gas filters.

The impactor is designed to trap cloud droplets lager than 10μm in diameter(at the first stage (a-2) in the figure) and those between 10μm and 2μm in diameter(at the second stage(a-5)), respectively under volumetric flow rate of 15[L/min]. When the liquid water contents of clouds are 0.01[g/m^3], which correspond to a sparse fog, this impactor in two hours collects enough amount of water(18mg) for weighing with an electric balance. The following aerosol filter(b-4) collects particles smaller than 2μm and the paper filter impregnated with sodium carbonate is used for sulfur dioxide gas collection. From the amount of trapped sulfur dioxide in each gas filter collection efficiency was calculated. This sampler connected in series has an advantage that one sulfur species analyzed only once which is not so easy with samplers collecting droplets, aerosols and gas separately. It is, however, inevitable that large particles other than droplets are also collected at the impactor which may result in an overestimate of chemical species in cloud droplets. The amount of soil particles, one of the main components in aerosol in the shaft, may suffer large influence by the sampling with this sampler because the diameters of soil particles in the shaft sometimes exceed 2μm. On the other hand soluble sulfur may not influenced so much because such a large soluble sulfur should act as a cloud nuclei and exists in a cloud droplet. The impacting part of each stage are paper pad impregnated with formaldehyde to prevent the oxidation of sulfite to sulfate which enable us to analyze the oxidation state of sulfur in cloud droplets. By this method we can estimate the oxidation process of sulfite to sulfate in cloud droplets. The sampling were performed alternatively; one is automatic sampling using a cage and the other is fixed-point sampling on landings of ladder at several levels. While the former has an advantage that we can collect samples at any level, it is impossible to sample air at several levels exactly the same time because only one cage can be used during one run. It is also difficult to synchronize the transportation schedule of cage with the time table of automatic sampler which results in a deterioration of the height resolution of data. The latter sampling on the landings is desirable for chemical analysis because we can sample air at the same time for long enough time for chemical analyses and at fixed heights. The problem is its danger and annoyance to go up and down ladders to exchange filters. The analyses of sulfur species were all performed with ion chromatography(DIONEX DX500). Before the analysis impactor pads and aerosol filters were extracted with ion exchanged water under ultrasonication while gas filters were extracted with hydrogen peroxide solution to oxidize dissolved sulfur dioxide to sulfate for the analysis.

2.4 Metal Elements in Cloud Droplet and Aerosols

The extracts of the paper pads in the impactors and Teflon filters were also analyzed its metal components by ion chromatography and ICP-MS(Hewlett Packard HP4500). Furthermore aerosols on Teflon filters were decomposed with the mixture of nitric acid and hydrofluoric acid then diluted with ion exchanged water for ICP-MS analysis of non soluble metals.

2.5 Ozone, Ammonia and Hydrogen Peroxide at the Bottom

Ozone concentration was monitored by automatic ozone monitor(Dylec 1006-AHJ); its concentration was constantly less than 1ppb. Ammonia was sampled by paper filters impregnated with hydrochloric acid then analyzed by ion chromatography. Hydrogen peroxide in gas phase at the bottom was sampled by bubbling air into ion exchanged water then reacted with reagent(parahydroxy-phenylaceticacid). The intensity of the fluorescence of the product was measured by a handy fluorescence meter(Turner Designs 10AU-005) at the bottom of the shaft. Though this sampling methods suffers artifacts by ozone in gas phase, the ozone concentration was low enough to neglect this interference.

2.6 Diameter of Cloud Droplets

Cloud droplets were sampled by impaction on a transparent plastic sheet coated with waterblue, a water-soluble blue dye. The sheet was fixed on a slide glass by sticking tape and preserved in a case until sampling. For cloud droplets sampling the slide glass was moved quickly to impact cloud droplets on the sheet. The trace of the droplets were observed with an optical microscope and measured its diameter one by one.

3. Results and Discussion

Table 1 shows the experimental parameter of all 5 runs; the temperature was between 12.1 and 15.2 degree Celsius at the bottom and 9.7 and 12.0 at the top, relative humidity were more than 95% at the bottom, atmospheric pressure were 980hPa and 940hPa at the bottom and top, respectively. The height of cloud bottom which was recognized with eye were about 280m a.s.l. These conditions were almost same as the ones performed in April and Octorber 1995(Yamada, 1996).

Table 1. The conditions of experiments for each run

No.	Date	Time(LST)	Temperature (℃)		Wind Speed(m/s)*		SO_2	Sampling
		start - stop	bottom	top	Sensor1	2		
#1	4 Sep	11:16-12:55	12.3-14.0	9.7-12.0	0.1-0.3	-**	Release	Cage
#2	4 Sep	14:28-17:40	12.9-13.4$^{\$}$	11.0-11.5	0.2	0.5-0.6	Release	Cage
#3	5 Sep	11:34-13:04	13.4-15.2	10.9-13.3	-	-	Not	Landing
#4	5 Sep	14:17-17:11	13.5-14.2$^{\$}$	10.8-11.5	-	-	Release	Landing
#5	6 Sep	10:37-14:11	12.1-12.7	10.9-12.0	0.2-0.3	0.6-0.9	Not	Landing

*: Wind speed sensors(Shibaura Denshi, PA1000) 1 and 2 were mounted on the same cage but at different position. The difference between them can be understood as the nonuniformity of the wind speed in the cross section.

**: "-" indicates no data.

$: data at 350m a.s.l.(Run #2) and at 480m a.s.l.(Run #5)

3.1 Sulfur Species in the Shaft

The molar concentration of total sulfur species in droplets, aerosols and gas at each level were shown in Fig.3(left half). Runs #1 and #2 were samples obtained with the cage and the others were ones at the fixed level.

The sampling heights of #1 and #2 must be noted because they are different from other runs. Although the samplings in #1 and #2 at each level contained small amounts of air during transportation, no correction was carried out. According to the sampling methodology sulfur species in this study are categorized in following 4 ones; sulfite in cloud droplets resulted from the dissolution of sulfur dioxide gas, sulfate in cloud droplets which may be from sulfate aerosols and/or the oxidation of sulfite, sulfates in aerosols, and sulfur dioxide gas. Sulfite and sulfate in cloud droplets are further classified into two, respectively by the diameter of the droplets which include them. In all experiments sulfur mainly exist as sulfur dioxide in the gas phase and its concentrations were highest at the bottom and decreased as the altitude. Although there were no entrance of air other than the bottom, the total sulfur concentration were not kept constant, which may be illustrated by the deposition of sulfur dioxide gas onto the wet wall of the shaft.

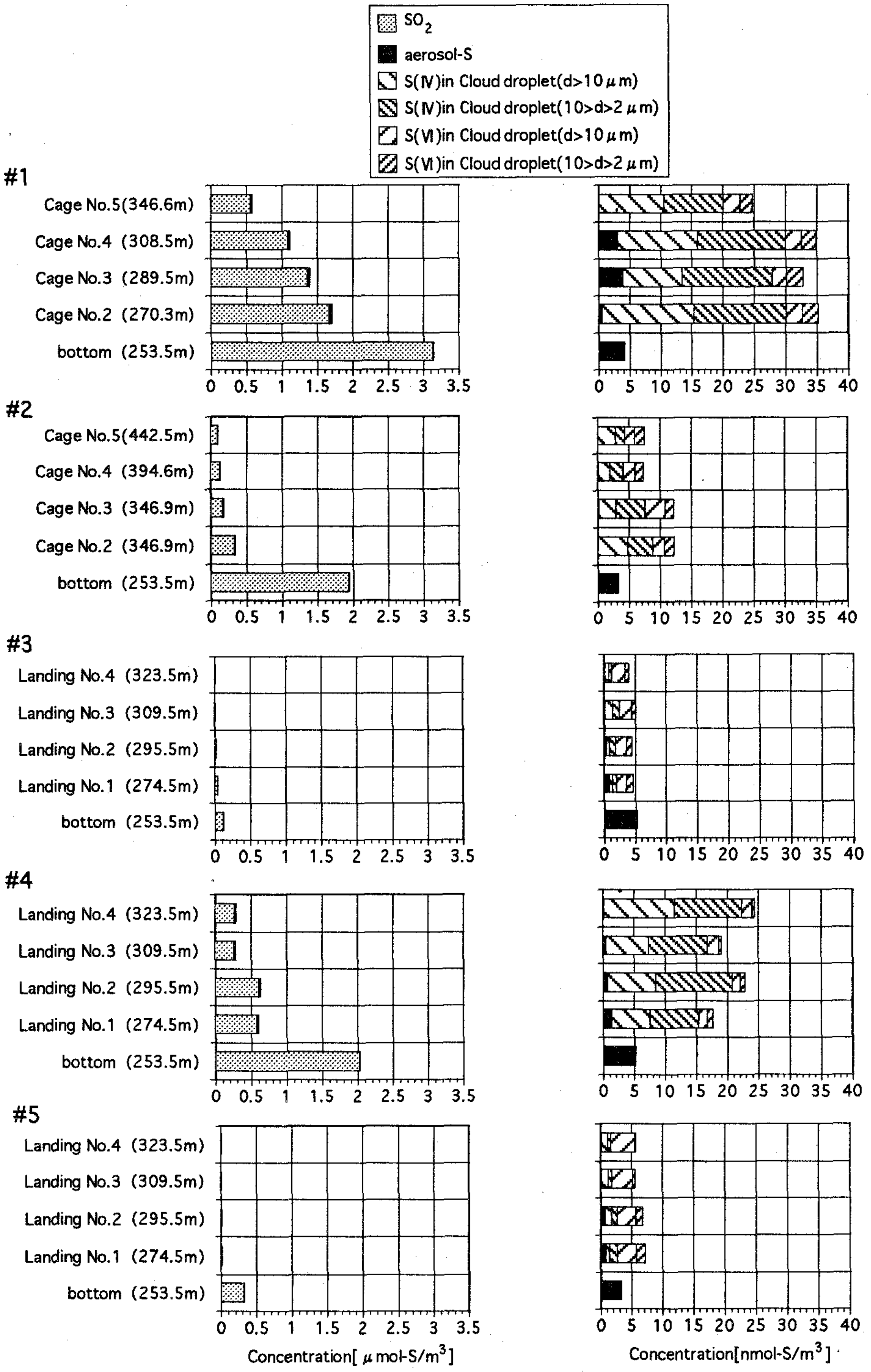

Figure 3. The concentrations of sulfur species(left half) and those without sulfur dioxide gas(right half). The unit of X axis in left and right is different. The sampling altitudes in #1 and #2 are different from others because of the cage sampling.

The right half of Fig.3 shows the concentration of sulfur species except sulfur dioxide gas. As is expected sulfite concentration increased at the height around the cloud base. The concentration of sulfite in the cloud droplets, however, increased even at the height lower than cloud base. This indicates that even under cloud base aerosols already got wet, swelled and accompanied with sulfur dioxide(analyzed as sulfite) to be collected by the impactor as "cloud droplets".

The concentration of sulfite in cloud droplets must be noted; it is kept constant almost all height which means that dissolution of sulfur dioxide finished at the beginning of cloud formation and the little oxidation of sulfite to sulfate proceeded in the droplets. If the rate of oxidation is fast, the concentration of sulfate in the droplets increased as the droplets went up and the total concentration of sulfur in droplets increased because enough amount of sulfur dioxide were still in gas phase. Although during no sulfur dioxide gas release(#3 and #5) the concentration of total sulfur is much lower than those of during the gas release, the concentration of sulfur dioxide is relatively high part of which may be residue of released sulfur dioxide gas during before runs.

We will use the data in #4 which were the only samples during sulfur dioxide release and collected at fixed levels which has enough time for chemical analysis. From the amount of liquid water contents(24[mg/m^3air]) the concentration of sulfite in the cloud droplets were calculated. At the Point #2(295.5m a.s.l.) the concentration of sulfur dioxide was 600[nmol-S/m^3air], the concentration of sulfite was 20[nmol-S/m^3air] which is almost equilibrated with the sulfur dioxide in the gas phase under pH range between 6 and 7. Although the precise value of pH was not measured, the pH values were measured for cloud water collected separately by a fog water collector. We should use pH values of the cloud water only for references because they were sampled at higher levels than this study during no sulfur dioxide release. The pH values dispersed from 6.5 to 7.2 which must be by some degree higher than the pH values of cloud waters in this study.

Although the concentration of hydrogen peroxide were 0.27ppb(run #1 and #2) and 0.42ppb(#3 and #4), the amount were one order lower than sulfur dioxide even no gas release at the bottom. In the atmosphere other oxidation reagents such as OH radical are commonly known. Many oxidation reagents are produced by the photo dissociation of ozone, whose concentration in this study should be lower than the atmosphere due to low ozone concentration.

There have been several experiments in laboratories and measurements in fields which demonstrate sulfite oxidation to sulfate in clouds. Hansen, *et al.*(1991) performed laboratory experiments with a concurrent-flow atmospheric pressure cloud chamber and found very fast sulfite oxidation. Their experimental conditions are different from ours in some aspects; the concentrations of sulfur dioxide is about ten times higher, the cloud is formed not by adiabatic expansion but mixing, the cloud nuclei were NaCl and soot particles, experiments were performed under room light, and so on. On the other hand Steele, *et al.*(1981) constructed a large(6.6m^3) expansion type cloud chamber and carried out investigations of chemical interactions between sulfur dioxide and cloud droplets. Their experimental conditions are rather similar to our experiments in this study; the cloud is generated by adiabatic expansion, experiments were performed under dark condition. The concentration of sulfur dioxide, however, is almost same as ones by Hansen et al. and about one order higher than ours. In this study we did not observe the clear evidence for the sulfite oxidation to sulfate even in the run #4 of which sampling was performed under sulfur dioxide release and at the fixed levels for c.a.3hrs enough for chemical analysis. Although the main reason why in our system sulfite oxidation proceed little is not clear, slow oxidation rate of sulfite in our system implies large advantage to investigate the chemical reactions in clouds. This is because it is much easier to add various kinds of oxidation reagents such as ozone, hydrogen peroxides than to eliminate specific oxidation reagents from the system. Another advantage of this system is that no light in the system which is an original energy of the chemical reactions in the atmosphere.

Field measurements intended to clarify the role of cloud in oxidizing sulfur dioxide to sulfate were also carried out by several researchers. Hegg and Hobbs(1982) presented sulfate production in wave clouds with analyses of 28 cases and derived an empirical rate equations for sulfate production in those clouds. Chandler, *et al.*(1988) measured the concentrations of hydrogen peroxide in the liquid phase and sulfur dioxide in the gas phase in cloud at the same time and found the anti-correlation between them. Levin, *et al.*(1990) measured the sulfate content in individual aerosol, haze, and cloud droplets to conclude the importance of sulfate particles in pH control. As is supposed with all field measurements , it is almost impossible to repeat one measurements with the same conditions including the concentrations of trace components in the atmosphere. Furthermore it is also necessary to obtain meteorological parameters which may be used to reproduce the atmospheric structure by numerical calculations afterward. It should become a big project with a number of researchers, one of such example is a sub-project of EUROTRAC, Ground based Cloud Experiment(GCE). In GCE Laj, *et al.*(1997) reported the increase of the sulfate concentration down-wind of the cloud and illustrated some events by in-cloud sulfate formation and others by the entrainments of sulfate aerosols. Even in these dense measurements, it is inevitable to exclude the artefact by an entrainment of new air into the cloud. One of the advantage of ACE is that we can control the entrainment; there are several horizontal openings to ACE which are closed during experiments. We may be able to introduce air from this openings and realize controlled entrainments. Another advantage is that we can generate gases and aerosols at the bottom one of which is sulfur dioxide gas in this study. Our ACE takes significant role which will bridge the distance between laboratory experiments and field measurements.

3.2 Chemical Species Other than Sulfur

The concentrations of other chemical species in cloud droplets and aerosol in run #4 were tabulated in Table 2 and 3, respectively.

Table 2. The concentration of chemical species in cloud droplets in #4

Site	Altitude	Droplet Size	Concentrations[ng/m^3]							
			Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	Al	Cu	Fe	Mn
No.1	274.5m a.s.l.	d>10um	-*	-	23	24	-	1.9	-	1.4
		10um>d>2um	120	540	23	22	-	4.3	-	3.1
No.2	295.5m a.s.l.	d>10um	73	280	11	16	-	0.42	-	0.48
		10um>d>2um	-	-	-	14	-	2.8	22	4.1
No.3	309.5m a.s.l.	d>10um	-	-	14	16	-	2.8	-	2.4
		10um>d>2um	-	-	12	16	-	2.0	15	3.7
No.4	323.5m a.s.l.	d>10um	88	350	15	16	-	1.0	-	1.5
		10um>d>2um	120	400	14	14	2.1	2.6	-	3.1

*: "-" indicates "under the detection limits".

Table 3. The concentration of chemical species in aerosol in #4

Site	Altitude	Concentrations[ng/m^3]							
		SO_4^{2-}	NH_4^+	K^+	Mg^{2+}	Al	Cu	Fe	Mn
bottom	250.0m a.s.l.	500	-*	-	-	-(-)**	20(32)	37(1700)	18(140)
No.1	274.5m a.s.l.	100	420	360	40	-(-)	10(16)	20(1500)	15(140)
No.2	295.5m a.s.l.	60	-	-	-	-(2.1)	22(27)	-(2500)	4.6(160)
No.3	309.5m a.s.l.	50	-	-	38	-(-)	40(40)	14(1900)	8.6(110)
No.4	323.5m a.s.l.	-	220	-	-	-(-)	6.4(14)	-(1100)	4.1(80)

***: "-" indicates "under the detection limits".**
****:concentrations of water soluble components out of parentheses and total concentrations in parentheses.**

There are several data which are under detection limits because the sampling and the analysis strategies were tuned for the analyses of sulfur species including its oxidation state in cloud droplets. Among such data the concentration of Mn presented in Fig.4 were rather clear although the concentration of the nonsoluble component in cloud droplets were not obtained by the high background of the paper pads used for sampling.

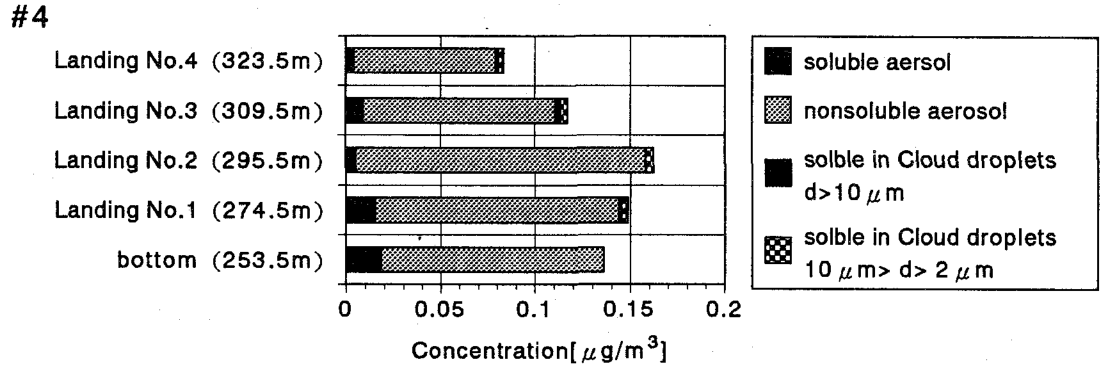

Figure 4. The profile of Mn concentration in ACE.

At all height the main components of Mn existed as nonsoluble aerosols. The total amount of Mn decreased above the cloud base which may be illustrated by the involvement into the cloud droplets which was not detected by the analysis. This result must be noted because the involvement of soil particles into cloud droplets has significance from the two standpoints; one is the chemical reactions caused by involved soil particles such as photocatalysis (Yamagata, *et al.*, 1994) and the other is dissolution of mineral components from the soil particles which may be an origin of nutrient for biological ecosystem such as open ocean where mineral components are in short(Zhuang, *et al.*, 1992). Another supports for the involvements of soil particle into cloud droplets were obtained by the microscopic image shown in Fig.5

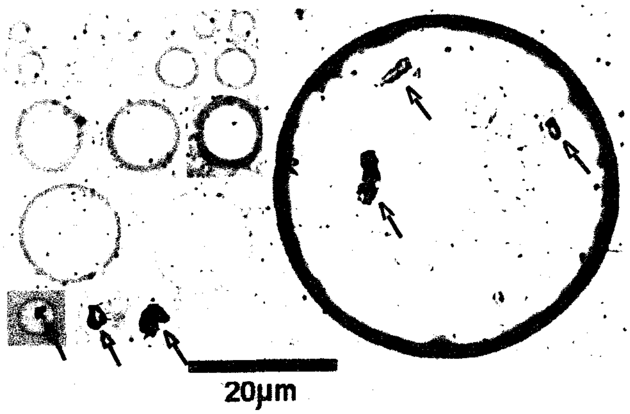

Figure 5. The traces of cloud droplets impacted on waterblue film. The dark shadows indicatede by arrows are shown in some traces.

The waterblue film method used for cloud droplets collection were succeeded only at the height 321.5m a.s.l. From the images of traces the diameter of cloud droplets were calculated, which showed that it ranged from several μm to 20μm. In some trace of droplets dark shadows were observed which can be regarded as the soil particles in cloud droplets although impaction of soil particles after the cloud droplets impaction is not ruled out. Further studies about the distribution of soil particles must be continued.

4. Conclusion

Sulfur dioxide dissolution into the cloud droplets and its successive oxidation were studied in Artificial Cloud Experimental System(ACE) in a shaft. The dissolution process is almost finished at the base of cloud where the sulfite in cloud droplets and sulfur in gas phase is nearly in equilibrium. The oxidation process from sulfite to sulfate was not observed even in the best experimental condition which indicated the low oxidants in ACE which is its advantage to study chemical reaction in droplets. The concentration of Mn and microscopic images of the traces of the droplets suggested soil particles are involved in cloud droplets which attracts scientific interests from the atmospheric chemistry and the material circulation including ecological system in the ocean.

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