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SHORT CONTRIBUTIONS

Variation of Mg, S, K and Ca contents in individual sea-salt particles

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ABSTRACT

Elemental composition of individual sea-salt particles collected over the Pacific Ocean was examined by an electron microscope equipped with an energy-dispersive X-ray analyzer. We found a significant variation of Mg, S, K and Ca contents. Moreover, the weight ratio of S/Na was well correlated with those of Mg/Na, K/Na and Ca/Na. This property can be explained by the fractionary recrystallization within evaporating drops followed by shattering.

1. Introduction

Sea salt is the principal component of marine aerosols of $\geqslant 1$ μm radius (Mészáros and Vissy, 1974; Gras and Ayers, 1983). For decades, much research has been devoted to the chemistry of sea-salt particles, as reviewed by Podzimek (1980). Since, however, these studies are mainly based on bulk chemical analyses, our knowledge is far from complete.

We report here the results of X-ray spectrometry of 200 individual sea-salt particles. The sampling was carried out over the equatorial Pacific Ocean onboard the research vessel *Natsushima* during the cruise of JAPACS 91 (Japan Pacific Climate Studies: 28 December 1990–13 March 1991). The particles were collected on a carbon-coated nitrocellulose (collodion) film by using an impactor of 1-mm diameter jet at the deck 5 m above the sea level. The flow rate of air was ~ 1 l min^{-1}. In this condition, the collection efficiency is evaluated to be 50 % at 0.5 μm radius and 100 % at > 0.7 μm for particles of 2 g cm^{-3} density. The location, time and weather conditions are listed in Table 1.

For elemental composition analysis, every 50 sea-salt particles collected at 4 sites were examined with an electron microscope (Hitachi, H-600) equipped with an energy-dispersive X-ray analyzer (EDX) (Kevex, Delta 5). The sample particles were selected with a criterion that they are larger than 1 μm in diameter and are *not* surrounded by numerous smaller particles; this appearance may suggest the fractionary recrystallization (explained later) on the collecting surface. The electron beam was irradiated at the center of a particle. X-ray spectra were obtained at an accelerating voltage of 50 kV and a counting time of 50 s. The abundance of Na, Mg, S, Cl, K and Ca in individual particles was then calculated by means of a thin-film method. These elements were detected at 2σ significance level in 196 of the 200 particles.

2. Results and discussion

Fig. 1 shows an electron micrograph of sea-salt particles in the sample II. The X-ray spectra of particles A and B are also indicated. As shown in Fig. 1, particle A is composed predominantly of Na and Cl. On the other hand, particle B contains higher fractions of Mg, S, K and Ca. The scatter of the amounts of Mg, S, K and Ca in individual sea-salt particles will be examined below.

In Fig. 2, the weight ratios of Mg/Na, Cl/Na, K/Na and Ca/Na are plotted as a function of S/Na

Table 1. *Location, period and weather conditions of aerosol sampling; mean weight ratios of Mg/Na, S/Na, Cl/Na, K/Na, and Ca/Na are also listed; the number of particles analyzed is indicated in parenthesis*

Sample		I	II	III	IV
location		03°S, 178°W	10°S, 175°W	00°S, 180°E	04°N, 160°E
day (GMT)		25 Jan. 1991	4 Feb. 1991	7 Feb. 1991	18 Feb. 1991
time (GMT)		20:30–21:30	23:40–24:50	20:50–21:50	03:00–04:00
weather		Fine	Fine	Rainy	Cloudy
wind speed (m/s)		6.1	6.7	13.3	8.3
humidity (%)		71	75	86	74
Mg/Na*	($r \geq 1$ μm)	$0.08 \pm 0.04^{\#}$ (20)	$0.06 \pm 0.08^{\#}$ (25)	$0.05 \pm 0.03^{\#}$ (15)	$0.02 \pm 0.02^{\#}$ (3)
	($r < 1$ μm)	0.13 ± 0.09 (30)	0.13 ± 0.17 (25)	0.09 ± 0.06 (35)	0.06 ± 0.07 (47)
S/Na*	($r \geq 1$ μm)	0.12 ± 0.05 (20)	0.09 ± 0.07 (25)	0.09 ± 0.03 (15)	0.04 ± 0.01 (3)
	($r < 1$ μm)	0.18 ± 0.15 (30)	0.19 ± 0.25 (25)	0.12 ± 0.06 (35)	0.06 ± 0.04 (47)
Cl/Na*	($r \geq 1$ μm)	1.9 ± 0.1 (20)	1.8 ± 0.1 (25)	1.9 ± 0.1 (15)	1.9 ± 0.1 (3)
	($r < 1$ μm)	1.8 ± 0.1 (30)	1.6 ± 0.2 (25)	1.9 ± 0.2 (35)	1.9 ± 0.1 (47)
K/Na*	($r \geq 1$ μm)	0.03 ± 0.01 (20)	0.01 ± 0.01 (25)	0.02 ± 0.01 (15)	0.01 ± 0.00 (3)
	($r < 1$ μm)	0.04 ± 0.02 (30)	0.02 ± 0.02 (24)	0.03 ± 0.01 (35)	0.02 ± 0.01 (47)
Ca/Na*	($r \geq 1$ μm)	0.04 ± 0.03 (20)	0.03 ± 0.03 (25)	0.03 ± 0.02 (14)	0.01 ± 0.00 (3)
	($r < 1$ μm)	0.07 ± 0.08 (30)	0.08 ± 0.15 (25)	0.04 ± 0.03 (35)	0.02 ± 0.02 (45)

* The weight ratios of Mg/Na, S/Na, Cl/Na, K/Na, and Ca/Na are 0.12, 0.084, 1.80, 0.037, and 0.038 for seawater, respectively (Berg and Winchester, 1978).

$^{\#}$ A standard deviation.

for all the samples. For reference, the concerned ratios of seawater are indicated by arrows. As shown in Fig. 2, the sea-salt particles exhibit considerable diversity in their values of Mg/Na, K/Na, Ca/Na and S/Na, while Cl/Na values are nearly constant at the seawater value. Further, the ratios of Mg/Na, K/Na and Ca/Na are well correlated with that of S/Na. It should be noted that this finding would be masked in bulk chemical analyses, since the mean values of Mg/Na, K/Na, Ca/Na and S/Na for the sample are close to those of seawater (Table 1). Therefore, the analysis of *individual* particles is essential to obtaining the results shown in Fig. 2.

Fig. 3 shows the dependence of S/Na ratio on particle radius. The radius used here is an apparent one on the collecting surface. The S/Na ratio shown in Fig. 3 appears to approach that for seawater at large particle sizes (say, ≥ 1 μm in radius), although there are only a few data points for particles larger than 1.5 μm.

To understand the correlation between S/Na and Mg/Na, K/Na and Ca/Na, we examine the several mechanisms which can change the elemental composition of sea-salt particles from that of seawater. They are (1) fractionation, i.e., change in the composition during the production of particles; (2) modification, i.e., chemical reactions with acidic material; (3) cycling of aerosol particles through clouds; and (4) fractionary recrystallization within evaporating drops followed by shattering.

First, we examine the fractionation. The surface of seawater, where sea-salt particles are generated, has a chemical composition which is different from that of deeper water. In fact, from bulk chemical analyses, some researchers reported a possible enrichment of Mg, K and Ca (relative to Na) in sea salt (e.g., MacIntyre, 1974; Liss, 1975; Duce and Hoffman, 1976). These elements are argued to be associated with organic materials that have affinity for an air/water interface. However, on the other hand, no/little enrichment of S has been reported (see above references). Thus the fractionation cannot explain the correlation observed in this study.

Next, we examine the modification. The enrichment of S in sea salt has been frequently observed,

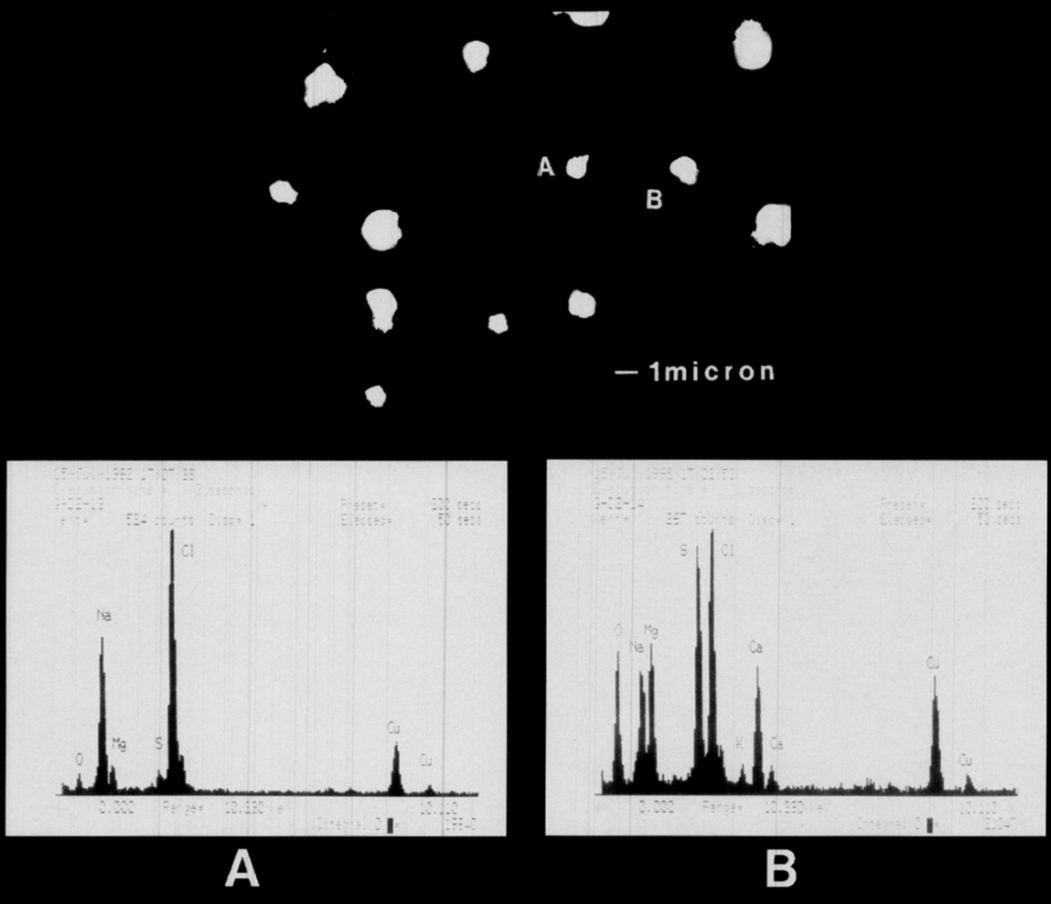

Fig. 1. Electron micrograph of sea-salt particles in the sample II. The X-ray spectra of particles A and B are also indicated. The Cu peaks in the spectrum originate from the copper grid used in the examination.

especially in the coastal atmosphere. This excess is attributed to chemical reactions with H_2SO_4 and/or SO_2 (Okada et al., 1978; Hitchcock et al., 1980; Miura et al., 1991). In the reaction, Cl^- is replaced by SO_4^{2-}. Thus the weight ratios of Cl/Na in modified sea-salt particles are smaller than that of seawater. However, in our sample, the Cl/Na ratios are consistent with the seawater value (Fig. 2). Hence our sample appears not to have been modified.

Next, we examine the cloud process. In the marine atmosphere, ammonium sulfate particles dominate the number of cloud condensation nuclei (e.g., Gras and Ayers, 1983). When a cloud forms, both the sea salt and the ammonium sulfate will be scavenged. It is likely that a fraction of sulfate-containing droplets coagulates with sea-salt-containing droplets. As a result, after the cloud evaporates, the sea-salt particles left behind tend to have excess sulfur (Andreae et al., 1986). However, this process alone cannot explain the presence of sea-salt particles whose S/Na ratios are lower than that for seawater (Fig. 2).

Finally, we examine the fractionary recrystallization followed by shattering. When drops evaporate, different compounds recrystallize separately according to each solubility product. For example, in the numerical calculation of Eugster et al. (1980), the evaporation of seawater produces many alkali sulfates (e.g., $CaSO_4 \cdot 2H_2O$,

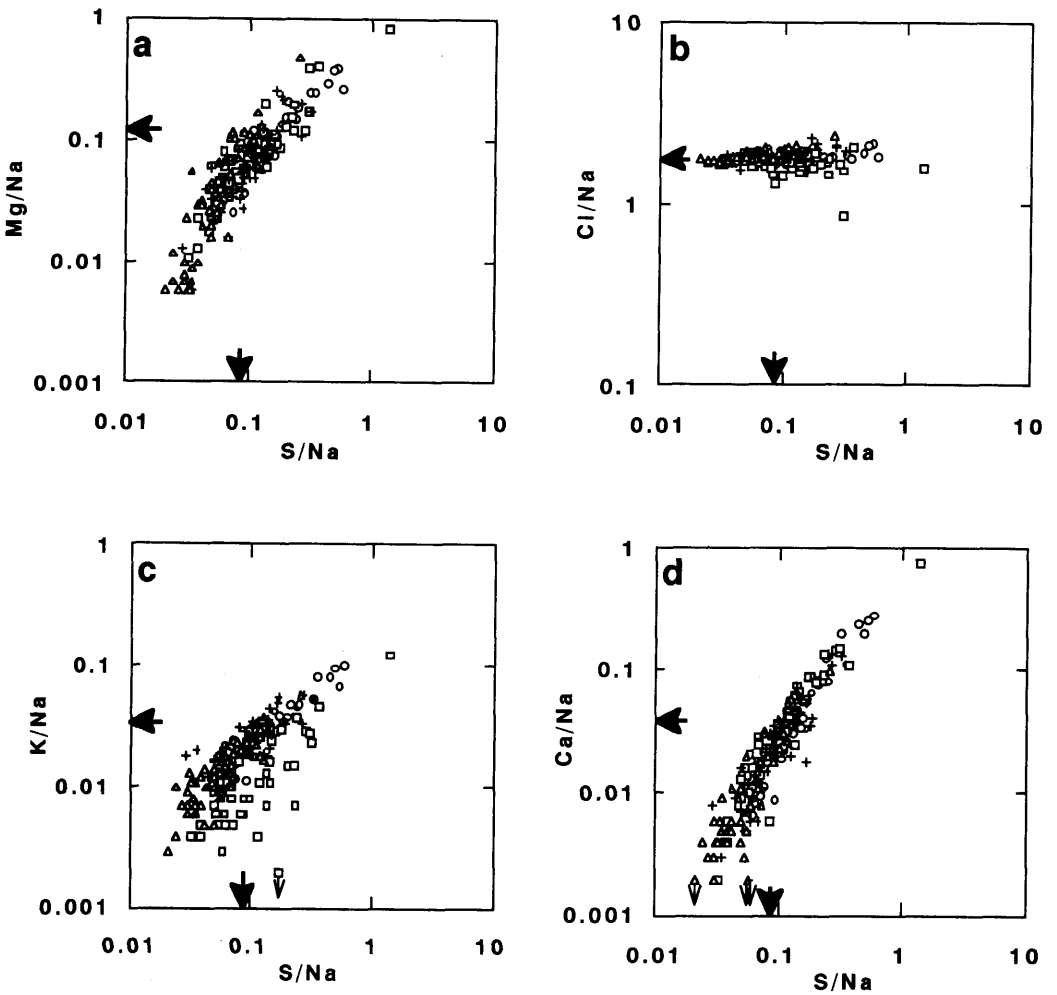

Fig. 2. Weight ratios of S/Na versus those of Mg/Na (a), S/Na (b), Cl/Na (c) and Ca/Na (d) for individual sea-salt particles. Circles, squares, crosses and triangles stand for particles in the samples of I, II, III and IV, respectively. Arrows indicate the weight ratios for seawater taken from Berg and Winchester (1978).

$CaSO_4$, $Na_2Ca(SO_4)_2$, $K_2MgCa_2(SO_4)\cdot 2H_2O$, and $MgSO_4\cdot H_2O$), as well as NaCl. After drops evaporate, the particles form aggregates of loosely attached crystals. The aggregates will easily shatter to produce pure crystals and their mixtures (Parungo et al., 1986).

In this way, the fractionary recrystallization can explain the variation for Mg/Na, S/Na, K/Na and Ca/Na. If this is the case, one can expect good correlations between S/Na and Mg/Na, K/Na and Ca/Na, since alkali ions are easily combined to SO_4^{2-}. Moreover, this scenario is consistent with the possible large diversity in S/Na for small particles (Fig. 3), since the variation in chemical composition is predicted to be large in small particles. It should be noted that the fractionary recrystallization does *not* change the bulk chemistry of sea salt, contrasting to the cases of fractionation, modification, and cloud process. This property can explain the fact that the averaged chemical composition of sea-salt particles is roughly close to that of seawater (Table 1).

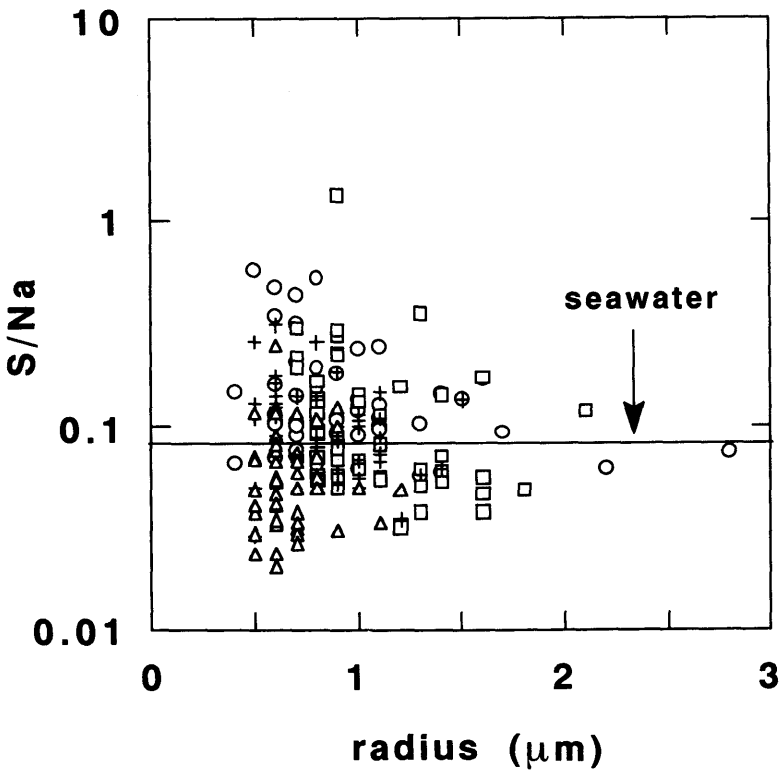

Fig. 3. Weight ratio of S/Na versus particle radius. Symbols are the same as in Fig. 2.

3. Summary

The weight ratio of S/Na was found to be correlated with those of Mg/Na, K/Na and Ca/Na in sea-salt particles collected over the Pacific Ocean. These correlations are consistent with the fractionary recrystallization within evaporating drops followed by shattering. This scenario was first proposed by Sugawara et al. (1949) to explain the atmospheric distribution of elements of sea-salt origin, while has not been confirmed observationally. Our results suggest that this process may be at work in the maritime atmosphere.

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