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Methanesulfonic Acid and Major Ions in the Ice Core from Site-J, Greenland

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Abstract

The emission rate of dimethyl sulfide from the oceans corresponds to 38 % of the total biological emission of sulfur. Dimethyl sulfide is transformed in the atmosphere into H_2SO_4 and methanesulfonic acid (MSA) by photo-oxidation. In the remote marine atmosphere, methanesulfonic acid is well correlated with nssSO_4^{2-}, and can be used as a tracer for biogenic SO_4^{2-} in remote areas such as the Arctic. We have determined electrical conductivity, pH and concentrations of major soluble species (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) and MSA of sixty-eight ice core samples from Site-J, South Greenland.

1. Introduction

Man-made emissions of sulfur (104×10^{12} gS/year) are estimated to be over two-thirds of total natural emissions (Cullis and Hirschler, 1980). Man's contribution is increasing at the rate of 2.2 %/year. Global emissions of atmospheric sulfur from volcanoes and sea-spray are 5×10^{12} gS/year and 44×10^{12} gS/year, respectively (Cullis and Hirschler, 1980). Andreae and Raemdonck (1983) have estimated the emission rate of biogenic sulfur. The total biological emission of sulfur is estimated to be 103×10^{12} gS/year.

Dimethyl sulfide (CH_3SCH_3, DMS) produced by marine phytoplankton is considered to be the major source of organic sulfur to the marine atmosphere. The biogenic DMS emission from the oceans is estimated to be 39×10^{12} gS/year (Andreae and Raemdonck, 1983). The emission rate of DMS from the oceans is 38 % of the total biological emission of sulfur.

DMS is transformed in the atmosphere into H_2SO_4 and methanesulfonic acid (CH_3SO_3H, MSA) by photo-oxidation (Hatakeyama et al., 1985). The production rate of MSA from DMS depends upon air temperature. Significant seasonal trends in aerosol MSA are observed, with higher MSA occurring during warm months (Saltzman et al., 1986). In the remote marine atmosphere MSA is well correlated with nssSO_4^{2-} (Ayers et al., 1986 ; Saltzman et al., 1986), and can be used as a tracer for biogenic SO_4^{2-} in remote areas such as the Arctic (Li and Winchester, 1989).

Deep ice cores contain detailed records of paleoclimatic atmospheric environments. The distributions of chemical constituents along ice cores provide information on past conditions of aerosols and precipitation. In this study, we present profiles of Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-} and MSA along the 205.9 m ice core from Site-J (South Greenland, 66°51.9'N, 46°15.9'W, 2030 m elevation).

2. Methods

Ice core drilling was carried out at Site-J from May to June 1989 (Watanabe and Fujii, 1990). Ice core samples were collected between 2.5 m and 205.9 m depth at approximately 10 cm intervals.

Electrical conductivity and pH of liquid samples were measured in-situ. Sixty-eight core samples were selected for this study. For each individual sample (50

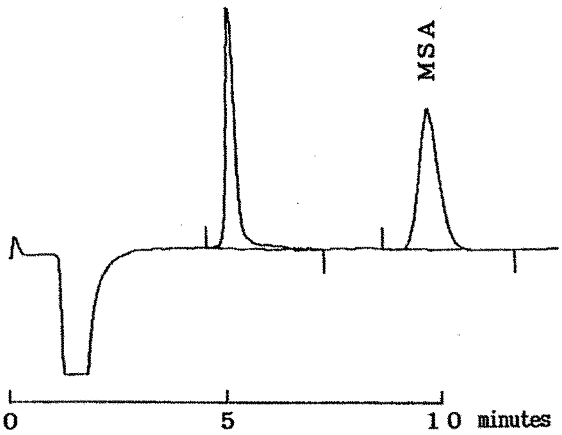

Fig. 1. Ion chromatographic analyses of MSA.

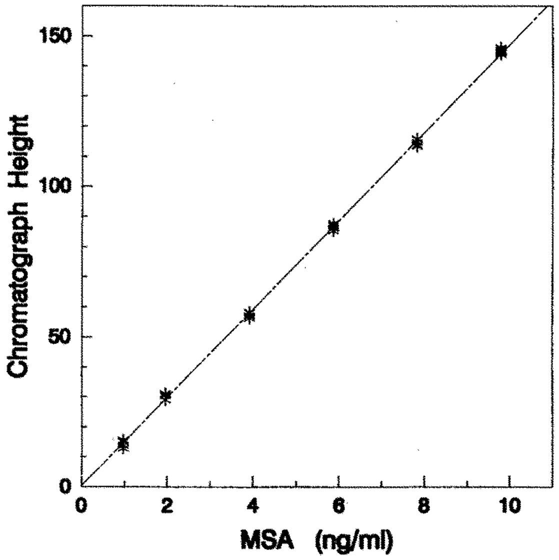

Fig. 2. Calibration curve for MSA.

ml), we have determined the concentrations of major soluble species (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) and MSA.

All ions were determined by ion chromatography (Dionex−2020i/SP). Melt water samples were concentrated 100 times by using a Dionex-TAC-1 column for anions and MSA. MSA was measured by using Dionex-AG4A, AS4A columns, 0.3 mM $NaHCO_3$ eluent, Dionex AMMS-I suppressor and 0.025N H_2SO_4 regenerant. Anions were measured by the same columns, suppressor and regenerant of MSA with the exception of 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ eluent. Samples were concentrated 100 times by using a Dionex-TCC-1 column for cations, and cations were measured by using Dionex-Fast Cation I, Fast Cation II columns, 12 mM HCl/0.18 mM DAP eluent, Dionex CMMS-II suppressor and 50 mM $Ba(OH)_2$ regenerant.

With these analytical conditions, good separation in the MSA chromatogram was achieved (Fig. 1). A calibration curve for MSA was prepared as concentration versus peak height (Fig. 2). No detectable MSA was found in blank water.

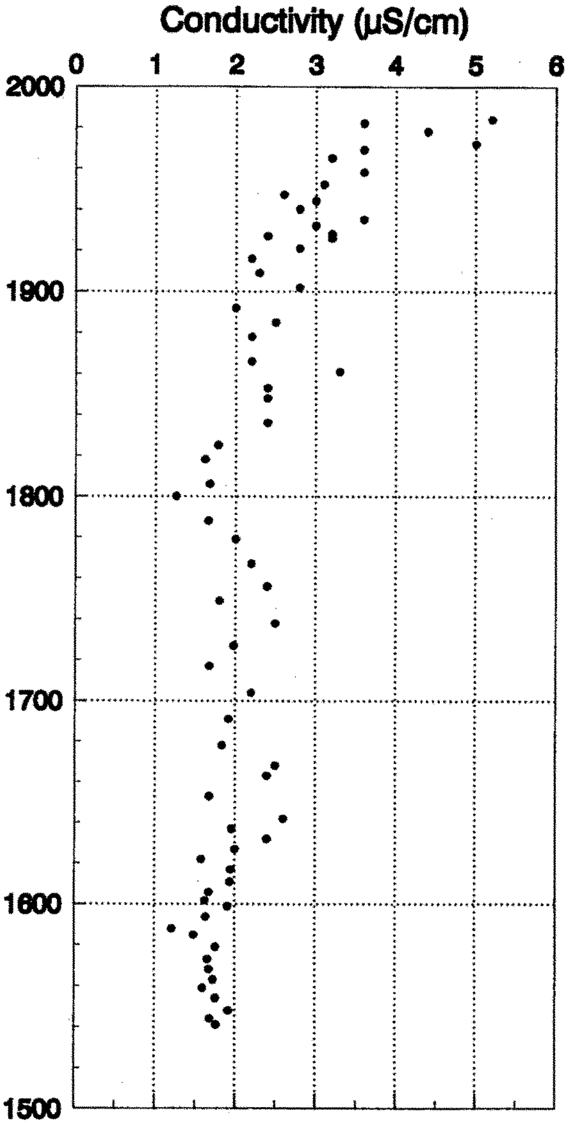

Fig. 3. Profile of conductivity of core samples.

3. Preliminary results

3.1. Conductivity and pH

The profiles of electrical conductivity and pH are shown in Figs. 3 and 4. The ice core is dated with the accumulation rate of water equivalent (Shoji *et al.*, 1991).

Conductivity and pH exhibit very weak variation before A.D. 1900. On the other hand, conductivity increases from 2 to 5μS/cm at 25 ℃ after A.D. 1900, and pH decreases to about 5.1. Correlation matrices of the measured components are given in Table 1. Conductivity is well correlated with pH (r=0.828), NO_3^- (r=0.818) and SO_4^{2-} (r=0.654) after A.D. 1900. Recent changes of conductivity and pH have been caused by anthropogenic emissions of acidic materials.

3.2. Anions

The profiles of NO_3^- and SO_4^{2-} concentration are shown in Figs. 5 and 6. The NO_3^- profile presents large variations, and NO_3^- concentration has increased in this century. SO_4^{2-} concentration exhibits very weak variation before A.D. 1900, and has increased radically

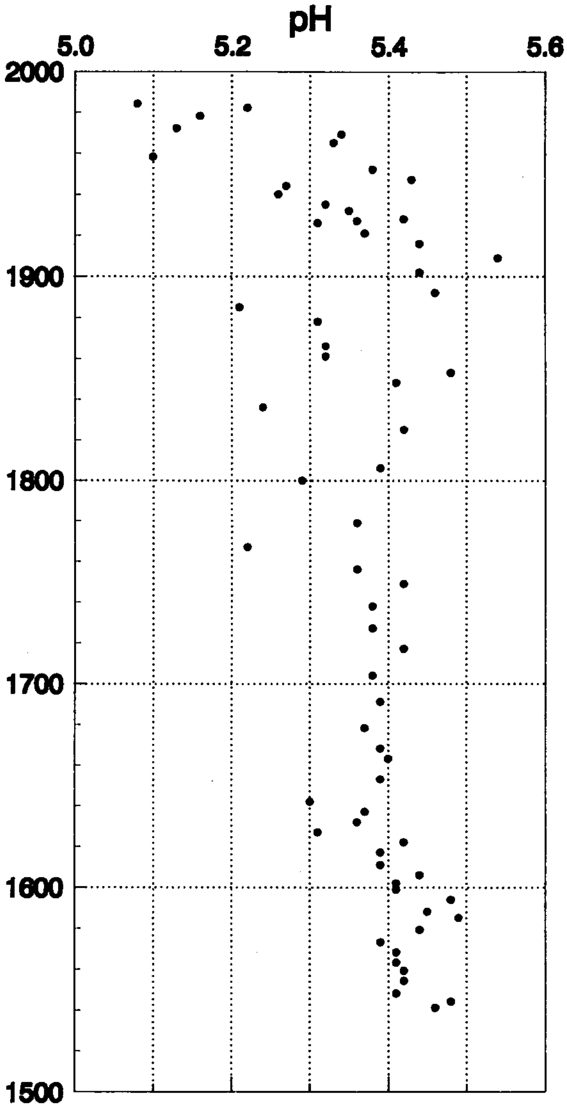

Fig. 4. Profile of pH of core samples.

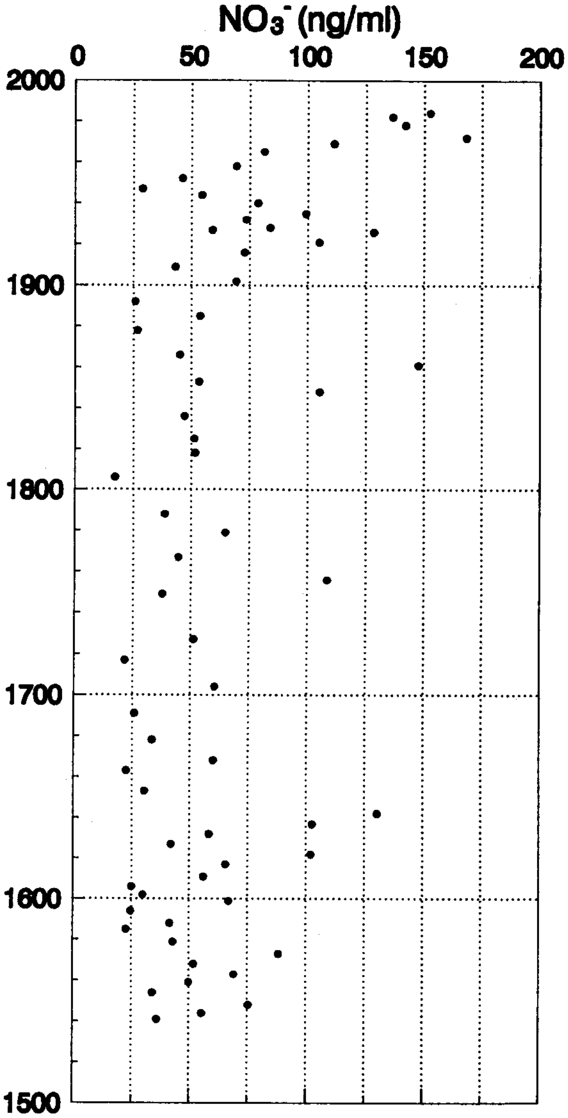

Fig. 5. Profile of NO_3^- concentration of core samples.

in this century. The man-made emissions of sulfur and nitrate are well recognized to be increasing in this century.

The profiles of anion concentration and anion components are shown in Fig. 7. Cl^- is the most abundant anion before A.D. 1900 ; SO_4^{2-} has increased to the comparable level to that of Cl^- in this century.

3.3. MSA

The MSA concentration profile is shown in Fig. 8. A clear fluctuation pattern in the MSA profile is not found. MSA, which is considered to be from marine biogenic production, has not shown a clear secular trend since A.D. 1540. Saltzman et al. (1986) report significant seasonal trends in marine atmosphere MSA concentration. Higher concentrations are observed during warmer months. The amplitude of these variation is a function of latitude, with the greatest seasonal changes occurring at higher latitudes (Saltzman et al., 1986). Short term variations of MSA concentration shown in Fig. 8 are considered to represent seasonal variability.

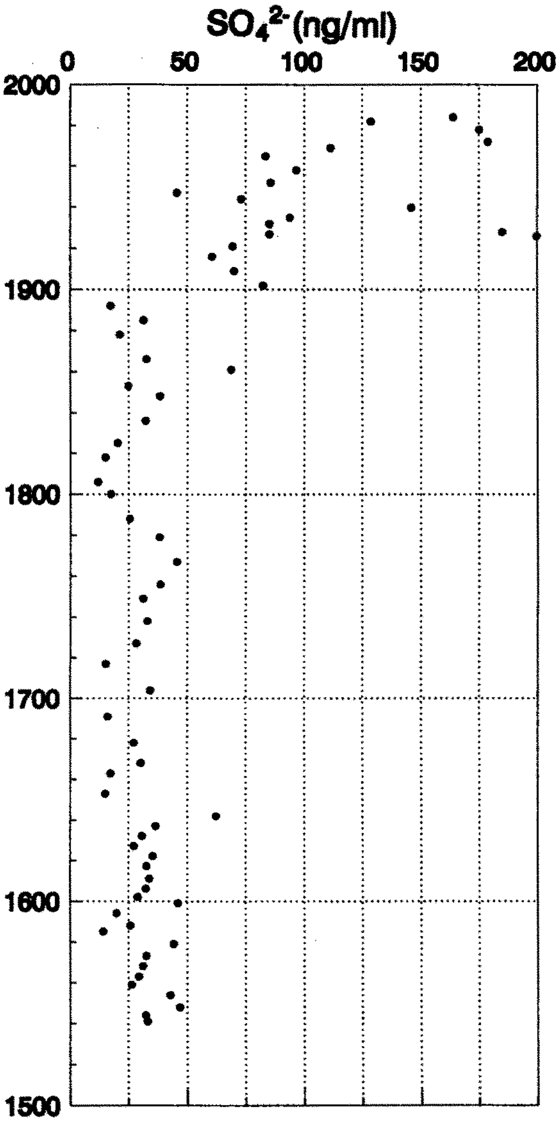

Fig. 6. Profile of SO_4^{2-} concentration of core samples.

Good correlations between MSA concentration and $nssSO_4^{2-}$ concentration in the marine atmosphere are reported by Ayers et al. (1986) and Saltzman et al. (1986). Fig. 9 shows the relationship between MSA concentration and $nssSO_4^{2-}$ concentration of the core samples. MSA concentrations are slightly correlated with $nssSO_4^{2-}$ concentration before A.D. 1900 (r=0.354).

4. Concluding remarks

We have determined electrical conductivity, pH and concentrations of major soluble species (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}) and MSA of sixty-eight ice core samples from Site-J, South Greenland. The preliminary results of this study are summarized as follows :

1. Conductivity has increased from 2 to 5μS/cm at 25°C in this century, and pH has decreased to about 5.1. Conductivity is well correlated with pH (r=0.828), NO_3^- (r=0.818) and SO_4^{2-} (r=0.654) in this century. Recent changes of conductivity and pH are caused by anthropogenic emissions of acidic materials.
2. SO_4^{2-} concentration exhibits very weak variation before A.D. 1900, and has increased radically in this century. Man-made emissions of sulfur and nitrate are well recognized to be increasing in this century.
3. Cl^- is the most abundant anion before A.D. 1900 ; SO_4^{2-} has increased to the comparable level to that of Cl^- in this century.
4. A clear fluctuation pattern is not found in the MSA profile. Short term variations of MSA concentration are considered to represent seasonal variability. MSA concentrations are slightly correlated with $nssSO_4^{2-}$ concentration before A.D. 1900 (r=0.354).

Table 1. Correlation matrices of the measured components.

	pH	MSA	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	SO_4^{2-}	$nssSO_4^{2-}$
E.C.	0.677 0.828 0.406	0.064 0.125 0.059	0.705 0.255 0.375	0.642 0.112 0.522	0.466 0.071 0.294	0.480 0.136 0.545	0.696 0.498 0.262	0.721 0.818 0.478	0.838 0.654 0.529	0.832 0.666 0.449
pH		0.043 0.065 0.022	0.464 0.252 0.420	0.313 0.059 0.391	0.309 0.135 0.205	0.289 0.095 0.432	0.397 0.366 0.051	0.493 0.672 0.149	0.524 0.537 0.220	0.517 0.543 0.134
MSA			0.026 0.144 0.081	0.029 0.065 0.000	0.021 0.005 0.052	0.030 0.097 0.042	0.029 0.017 0.111	0.222 0.208 0.294	0.077 0.058 0.374	0.086 0.074 0.354
Na^+				0.802 0.476 0.749	0.557 0.306 0.334	0.598 0.264 0.410	0.768 0.533 0.542	0.463 0.395 0.003	0.789 0.615 0.058	0.746 0.558 0.143
K^+					0.566 0.299 0.463	0.635 0.382 0.496	0.775 0.688 0.394	0.491 0.343 0.180	0.681 0.301 0.136	0.651 0.274 0.015
Mg^{2+}						0.659 0.888 0.185	0.619 0.520 0.388	0.266 0.141 0.018	0.552 0.502 0.022	0.537 0.501 0.089
Ca^{2+}							0.620 0.411 0.408	0.401 0.057 0.335	0.592 0.358 0.205	0.577 0.353 0.121
Cl^-								0.488 0.578 0.013	0.755 0.636 0.195	0.734 0.621 0.085
NO_3^-									0.712 0.750 0.724	0.721 0.754 0.719
SO_4^{2-}										0.998 0.997 0.980

all after 1900
before 1900

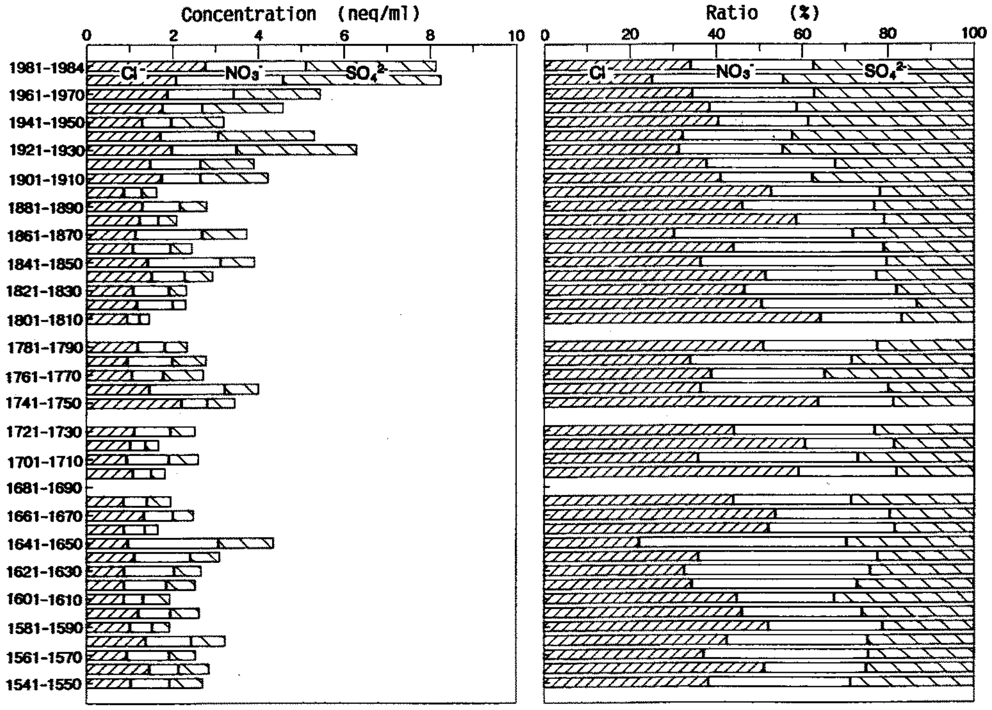

Fig. 7. Profiles of anion concentrations and anion components.

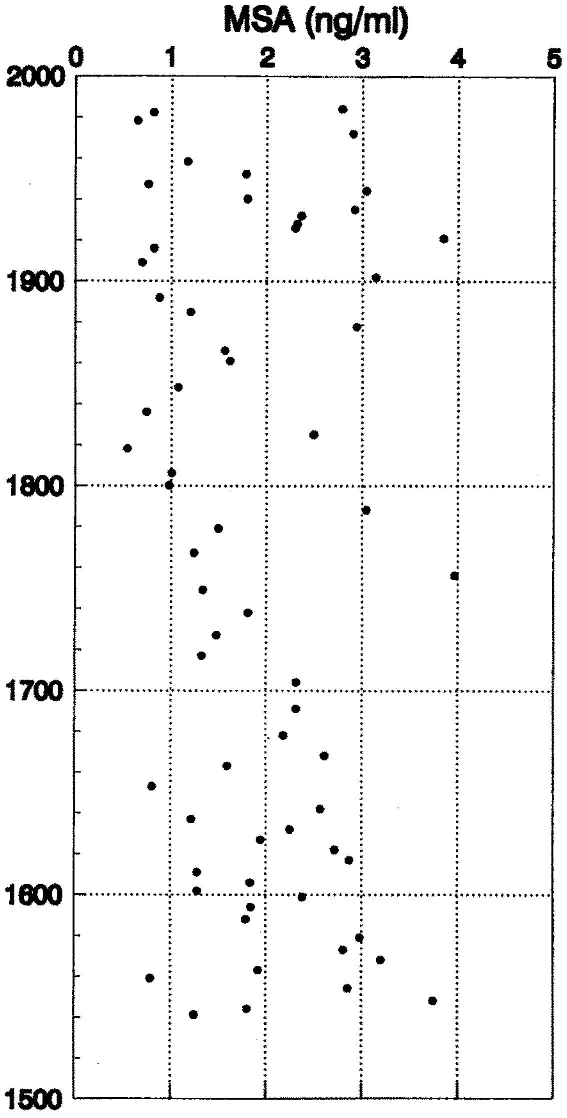

Fig. 8. Profile of MSA concentration of core samples.

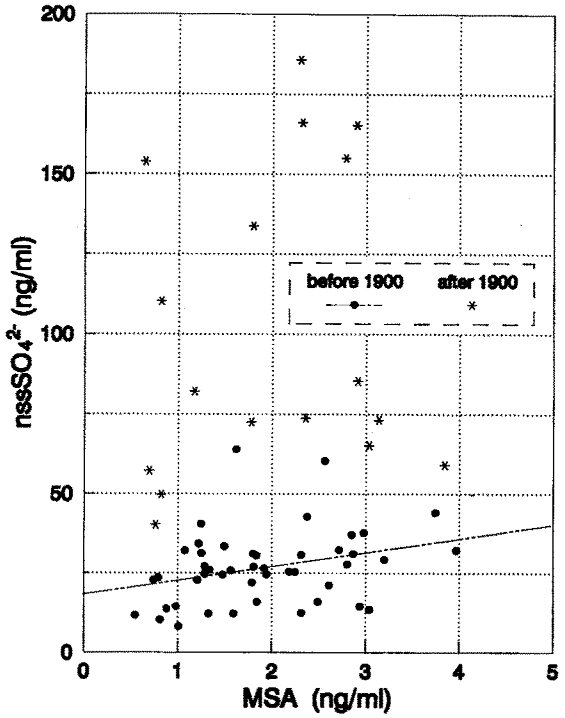

Fig. 9. Relationship between MSA concentration and nssSO$_4^{2-}$ concentration of core samples.

Acknowledgments

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