Ice core dust particulate by XPS-SEM/EDAX

-Impact of dust particulate on SO₄²⁻ record in ice cores

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Abstract The ice core dust particulate sampled from Mt. Xixabangma has been analyzed by means of X-ray photoelectron spectrometer (XPS) and scanning electron microscope with energy dispersion X-ray analysis (SEM/EDAX). The results show that the contents of SO_4^2 and SO_3^2 in the surface layer of the dust are significantly higher than those in the subsurface layer (with the exception of organic sulfide). This difference indicates that the surface SO_x has been captured and then chemically converted by the atmospheric dust particulate before its deposition with snow, which is obviously different from those inner layer sulfates and sulfites contained by dust itself. In addition, it has been determined by SEM/EDAX that the dust contains relatively high concentrations of transition metal elements such as Fe and Ti oxides which could function as photocatalysts to the conversion of SO_x adhered on the surface of the dust, and consequently accelerate the deposition of SO_x to snow. Our research also demonstrates that the adsorptive carrying and the catalytic performance of the dust to the atmospheric SO_x are most important causes of the positive correlation between SO₄²⁻ and dust concentration records in ice cores.

Keywords: ice core records, dust particulate, sulfate ions.

AMONG the ice core records, both SO_4^2 and dust (microparticle) records have their own certain indicative significance on environment respectively. In polar and most mid- to low-latitude glaciers, for instance, SO₄²⁻ record represents the information of anthropogenic pollution, oceanic biological activity, volcanic eruption, etc. In central Asia including northwestern China, where the seasonal dust storms are mainly created and driven by the cold front weather system, dust record can represent not only atmospheric dust burden but also air temperature. In despite of the difference of the environmental indications between SO_4^2 and dust records in ice cores, the positive correlation of the two ice core records has been widely found^[1, 2]. It can be inferred that one of the most important reasons for it is that dust particulate could capture SO, in the atmosphere, which makes SO, deposit together with dust and subsequently builds up a correlation in glaciers. The "capture effect" of dust may influence and possibly change the distribution, the transportation way and the deposition process of element S in the atmosphere, which result in the SO_4^2 record hardly to indicate its environmental significance directly, thus it adds more difficulties to the reconstruction of the environmental history from the SO_4^{2-} ice core record. In this research the XPS and SEM/EDAX technique were used to obtain surface information of ice core dust and its main composition. The objective of it is, from a microcosmic angle, to explore and evaluate the impact of atmospheric dust on the formation of SO_4^{2-} ice core record, to reveal the relationship between the two ice core records and eventually to improve our precision in the interpretation of SO_4^{2-} and dust records in ice cores.

1 Preparation and analysis of samples

The ice core with a total length of 13 m was extracted from the top of Kangwure glacier $(28^{\circ}28'32'' \text{ N}; 85^{\circ}49'09''\text{E}, 6\ 140 \text{ m a.s.l.})$ in the Mt. Xixabangma area in September 1991. After being transported back to LIGG, the ice core was continuously well preserved in a frozen state in the low-temperature laboratory of LIGG (below -15° C). For the sample preparation, 2-m-long segment was intercepted from

Chinese Science Bulletin Vol.44 No.15 August 1999

the upper part of the core (no cranny and in good shape) and 1.5-cm-thick surface ice was eliminated. The inner core was then divided evenly into two segments as samples 1 and 2 respectively from the top down. When the two samples dissolved into liquid naturally, the solutions were filtered with ashless filter papers, then dried in the nature condition. Each of the two samples weighed about 0.2g. Samples 1 and 2 correspond to the period from the early 1990s to the middle 1980s and the period from the middle 1980s to the early 1980s, respectively. Due to the chemical constituents in an ice core from dry and wet deposition of atmospheric aerosol, the two samples represent an average chemical composition of atmospheric insoluble particles of mid-to-upper-troposphere over the Mt. Xixabangma area at the corresponding period of time. Analyses of the samples were conducted in the OSSO. Elemental compositions of samples 1 and 2 were measured by SEM/EDAX (SEM-1200/EDAX-9100). XPS (VG-ESCLAB210) was used to determine the properties of certain chemical elements of the particle sample made by mixing of samples 1 and 2. Under the condition of the particles being sputtered by different intensity Ar⁺ beam, the properties of S species in different dust layers (generally from the surface down to tens angstroms) were obtained through high-resolution S_{2p} spectrum measurements. The high-resolution Fe_{2p} spectra in different layers of the sample were also measured for parallel analysis.

2 Results and discussions

(i) Experimental results. Figure 1 is the S_{2p} spectrum of the dust sample without being sputtered by Ar⁺ beam, showing chemical states of S species on the surface of dust. Three strong peaks appear, corresponding to binding energy values of 166.6, 168.5, and 162.4 eV, demonstrating the existence of Na₂SO₃, FeSO₄ and organic sulfides, respectively. The strongest peak of 162.4 eV indicates that there is relatively high concentration of organic sulfide on the surface of the ice core dust. Moreover, the amount of sulfates seems higher than that of sulfites.



Fig. 1. $$S_{2p}$$ spectrum of the ice core dust not sputtered by Ar^{\star} beam.

Figure 2 is the S_{2p} spectrum of the dust sample after being sputtered by 4 kV Ar⁺ beam for 15 min, revealing the chemical states of S in the subsurface layer of the dust. In fig. 2 there is no apparent change of 162.4 eV peak, but the 168.5 and 166.6 eV peaks are weakened significantly. The change in the two figures verifies that most of sulfates and sulfites in the ice core dust are adhered to the surface of the ice core dust, which are not a $_{730}$ part of dust itself.

In the parallel analysis of Fe element, the dust sample was sputtered twice by 4kV Ar⁺ to explore ¹ the chemical states of Fe in different layers of the ¹



Fig. 2. S_{2p} spectrum of the ice core dust sputtered for 15 min by 4 kV Ar⁺ beam.



Fig. 3. Fe_{2p} spectra of the ice core dust experienced different periods' sputtering.

dust. The Fe2n spectra of dust experienced without being sputtered and being sputtered for 5 and 10 min

Chinese Science Bulletin Vol.44 No.15 August 1999

1425

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are given in fig. 3-1, -2 and -3 respectively, which reveal the chemical states of Fe from the surface down to different inner layers of the ice core dust. It can be seen from the figure that the appearances of three spectra of Fe_{2p} are nearly the same. 710.7 eV is the typical binding energy of Fe^{3+} in Fe_2O_3 . Fig. 3 indicates that the chemical states of Fe are very constant in different layers of the ice core dust and apparently are different from S element. It is obvious that Fe and its compounds such as Fe_2O_3 are the original constituents of the ice core dust.

The main elemental composition of the dust sample is given in table 1, which was measured through the SEM/EDAX technique. Although there are differences in quantity of some elements between the two samples, both of them show Fe and Ti in a relatively high concentration. Fe and Ti oxides such as Fe_2O_3 and TiO_2 are known photocatalysts, which can form the hole-electron redox pair under the illumination of sunlight. The hole-electron redox pair is highly active in redox reaction^[3].

Element -	Average concentration (%)		Flement	Average concentration (%)	
	sample 1	sample 2	Element .	sample 1	sample 2
Al	1.7	15.73	Cl	0.23	nd
Si	11.17	43.87	S	7.38	1.52
Ca	6.88	1.06	Ti	5.38	1.52
Mg	11.42	2.11	Cr	4.26	nd
K	4.08	10.33	Zn	nd	0.14
Fe	12.70	22.25	Pb	10.12	nd

Table 1 Elemental composition of the ice core dust by means of SEM/EDAX

nd, not detected.

(\parallel) Analysis and discussion. The existence of sulfates and sulfites in the form of adhering to the surface of the ice core dust confirms that the dust does have the capability to capture SO_x in the atmosphere. On the other hand, it indicates that the dust and some S species in ice cores can be derived from different sources. On the basis of the above study, it can be concluded that the positive correlation between SO₄²⁻ and dust records appearing in ice cores can result from the capture of dust to SO_x in the atmosphere to a large extent, and derivation from the same source is not a single cause for the correlation. As a matter of fact, most dust particulate in Kangwure ice core evidently originated from the influx of "Asian dust" during the high dust season of the Tibetan Plateau. The SO₄²⁻ in the ice core, which is the final deposition production of atmospheric SO_x, has experienced a series of physical and chemical processes under the effect of atmospheric dust. The SO_x in the atmosphere can be derived from both natural emission and anthropogenic pollution. Although the atmospheric dust over many areas on the Tibetan Plateau contains sulfates derived from salt lake stratum of northern Tibet Plateau, which surely relates to the concentration of dust, they are not the only source of SO₄²⁻ in the ice core, besides, they can be easily identified from their distinct form in ice cores.

We believe that the way of dust particulate capturing SO_x depends upon its property in the atmosphere. Generally, the dust has two different forms in the air. One is that the dust is surrounded by a thin layer of water under the condition of high humidity. The SO_2 dissolved in the water can be oxidized into $SO_4^{2^-}$ directly or by the effect of photocatalysis^[4, 5]. The other case is that there is no water layer surrounding the dust under the condition of low humidity. The SO_x absorbed on the surface of the dust can be oxidized into $SO_4^{2^-}$ under the photocatalysis of transition metal oxides. The feasibility of this process has been approved by several researches^[6-8]. In this case, the transition metal oxides in dust (such as Fe₂O₃ and TiO₂) play a crucial role.

In addition, adhering to the surface of the dust in a physical or chemical way, the sulfur oxides and their ultimate products $(SO_4^{2^-})$ sink into snow through dry or wet deposition. After having experienced a series of subsequent change processes such as evaporation, washing out by melting water, densification, etc. in snow, they transform into the ice core records ultimately. A portion of $SO_4^{2^-}$ and $SO_3^{2^-}$ on the sur-

Chinese Science Bulletin Vol. 44 No. 15 August 1999

face of the dust must be avulsed away during these processes, even though it apparently does not wipe out the correlation between the dust and SO_4^2 records in ice cores. We extrapolate that the capacity of dust carrying SO_x mainly depends on the adsorbing intensity of dust to SO_x in the atmosphere. The pertinent research is under way.

The formation, transportation and deposition of atmospheric dust follow its own rule. However, because of its capability of adsorbing, carrying and catalyzing the atmospheric sulfuric oxides, it may exert a significant impact on the transportation, distribution and deposition of SO_x , and eventually change the natural circulation of S. Since the SO_4^{2-} in ice cores is the final deposition production of SO_x under the influence of atmospheric dust, the proper interpretation of the record extremely depends upon the intensive researches of every process relative to the formation of the record.

Acknowledgement This work was supported by the National Natural Science Foundation of China (Grant No. 49501004), a special funding for crysphere research from the CAS, the National Climbing Project (Grant No. 95-Yu-40) and Key Project of the CAS (Grant No. KZ951-Al-402).

References

- 1 Li Zhongqin, Yao Tandong, Xie Zichu et al., Modern atmospheric environmental records in Guliya Ice Cap of Qinghai-Xizang Plateau, Chinese Sciences Bulletin, 1995, 40: 874.
- 2 Prospero, J. M., Savoie, D. L., Effect of continental sources on nitrate concentrations over the Pacific Ocean, Nature, 1989, 339(6227): 687.
- 3 Michael, R. H., Scot, T. M., Wonyong Choi et al., Environmental application of semiconductor photocatalysis, Chem. Rev., 1995, 95(1): 69.
- 4 Martin, L. R., Good, T. W., Catalysed oxidation of sulfur dioxide in solution: the iron-manganese synergism, Atmos. Environ., 1991, 25A: 2395.
- 5 Grigic, I., Hudnik, V., Bizjak, M. et al., Aqueous S (N) oxidation I. Catalytic effect of some metal ions, Atmos. Environ., 1991, 25A: 1591.
- 6 Faust, B. C., Hoffmann, M. R., Bahnemann, D. W., Photocatalytic oxidation of sulfur dioxide in aqueous suspensions of α-Fe₂O₃, J. Phys. Chem., 1989, 93: 6371.
- 7 Yasumichi Matsumoto, Hideakl Nagal, Ei-ichi Sato, Photocatalytic oxidation of sulfur on titanium dioxide, J. Phys. Chem., 1982, 86: 4664.
- 8 Christian, B., Rudi van Eidik, Transition metal-catalysed oxidation of sulfur (IV) oxides: Atmospheric-relevant processes and mechanisms, Chem. Rev., 1995; 119.

(Received December 4, 1998)

The Nd-Sr isotope study of Mesozoic granitoids in Jiangxi Province

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Abstract Nd-Sr isotopic compositions of 12 Mesozoic granitoids from Jiangxi Province have been reported. They show low- $\epsilon_{Nd}(-13.8--8.3)$, high- $I_{Sr}(0.71069-0.73981)$ and old t_{DM} (2087-1635 Ma). Comparison between the Sm-Nd isotopic compositions of the granitoids and those of the basement metamorphic rocks suggests that these granitoids were mainly derived from the metasedimentary rocks. There is an east-west trend Mesozoic granitoid zone with low- t_{DM} from S. Jiangxi to S. Fujian. The origin of these granites was preliminarily discussed.

Keywords: Nd-Sr isotopic compositions, material source, low-t_{DM} zone, Mesozoic granitoids, Jiangxi Province.

1 Geological setting

There are many granitoids with various ages in Jiangxi Province. Jinning granitoids are located over the north of the Zhejiang-Jiangxi Railway where is part of the Yangtze Block. Caledonian granitoids are

Chinese Science Bulletin Vol.44 No.15 August 1999

1427