Recent 180 Year Oxalate (C2O42-) Records Recovered from the Mount Everest Ice Core: Some Environmental Implications

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Recent 180 year oxalate (C₂O₄²⁻) records recovered from the Mount Everest ice core: some environmental implications

Carboxylic acids (e.g. formate, acetate, glycolate and oxalate) are common constituents of global precipitation (Galloway and others, 1982) and are major contributors to the acidity of precipitation in the remote atmosphere at low and mid-latitudes (Kene and Galloway, 1986). Since their potentially important roles in tropospheric chemistry, few investigations of snow carboxylic acids have been conducted in remote areas, particularly in Asia. There is only one report of organic acids in snow from the Guliya ice cap in the northwestern Qinghai–Tibetan Plateau, which covers the period 1977–91 (Sun and others, 1998), and a few from polar regions (Legrand and others, 1992; Legrand and Angélis, 1995). To get a first understanding of atmospheric organic-acids variations and their environmental significance, we present the ice-core record of oxalate (C₂O₄²⁻) from Far East Rongbuk (FER) Glacier, Mount Everest.

During the Sino-U.S. Cooperative Glaciological Expedition to Mount Everest in May 1997, a 41 m core, covering the period AD 1814–1997, was collected from a site at 6500 m a.s.l. on FER Glacier on the northern slope of Mount Everest. Detailed methods of ice-core sampling and chemical analysis are described by Kang and others (2000) and Qin and others (2000). The ice core was dated by Qin and others (2000), and ice-core sampling was similar to the method of Legrand and De Angelis (1995), in order to reduce contamination for trace carboxylic acid determination.

Variations of the 10 year mean of C₂O₄²⁻, Ca²⁺ and NH₄⁺ concentrations and δ¹⁸O values during the past 180 years from the FER ice core are shown in Figure 1. The mean C₂O₄²⁻ concentration is 137 ng g⁻¹ for the last 180 years (Table 1). During the 19th century, C₂O₄²⁻ concentrations were 0.0–45.5 ng g⁻¹ with a mean value of 7.9 ng g⁻¹. In the 20th century, C₂O₄²⁻ concentrations were 0.0–3225 ng g⁻¹ with a mean value of 186 ng g⁻¹, and the highest values occurred during the 1960s. Considering 10 year averages, C₂O₄²⁻ concentrations were lowest from the 1840s to the 1870s and have increased since the beginning of the 20th century, reaching their highest values in the 1960s. The highest C₂O₄²⁻ mean concentration, which occurred from the 1950s to the 1980s with a mean value of 24.8 ng g⁻¹, is three times higher than that of the 19th century. From error bars (±1 std dev) (Fig. 1) and standard deviations (Table 1), the fluctuations of C₂O₄²⁻ are small in the 19th century, suggesting that the variations of C₂O₄²⁻ may be seasonal fluctuations around the background level. During the 20th century, however, especially during the 1950s–80s, many peaks of C₂O₄²⁻ concentration occur and the fluctuations are dramatic, indicating that short episodes with high C₂O₄²⁻ concentrations account for elevated mean values in the 20th century.

In order to investigate the environmental implications of C₂O₄²⁻ variations, the sources of C₂O₄²⁻ should be considered. Carboxylic acids come from vegetation emissions and biomass burning (Andreae and others, 1988; Talbot and others, 1988; Legrand and others, 1992), the oxidation of various alkenes (Jacob, 1986) and anthropogenic emissions (Talbot and others, 1988; Legrand and others, 1995).

The apparently increasing tendency of C₂O₄²⁻ concentrations during the 20th century is not consistent with that of Ca²⁺, which is representative of atmospheric dust (Kang and others, 2000) in the Himalaya (Fig. 1), suggesting that the source of C₂O₄²⁻ has very little relation to atmospheric dust. NH₄⁺ comes mainly from biogenic sources in the Himalaya (Mayewski and others, 1983; Davidson and others, 1986), and the general trend of variations is not obvious (Fig. 1), suggesting that the distinct increase of C₂O₄²⁻ concentrations is not mainly related to biogenic sources and hence may be caused by other sources. Ice core δ¹⁸O (as a temperature proxy) has increased since the beginning of the 20th century, and the general tendency broadly follows that for the C₂O₄²⁻ variations (Fig. 1). However, the increase of C₂O₄²⁻ in the 20th century is more dramatic than that of δ¹⁸O. The temperature increase may influence the C₂O₄²⁻ concentration (e.g. the strength of the emissions by vegetation or the oxidation of various alkenes) but is not the dominant factor for higher C₂O₄²⁻ concentrations in the 20th century, particularly during the 1950s–80s.

Oxalate has been mass-produced by industry since the 1940s (e.g. in Germany) (Hong, 1997). Thus we assumed that C₂O₄²⁻ concentrations in the 19th century are not influenced by industrial emissions and may represent the background values, while higher C₂O₄²⁻ concentrations, especially those peaks due to short episodes during the 1950s–80s, may be caused by industrial emissions. As industrial chemicals, oxalate and its derivatives are used
extensively in the chemical industry (e.g. the medical, textile and metallurgical sectors) [Hong, 1997]. Though the transportation and deposition for these industrial C$_2$O$_4$$_2^-$ pollutants from source regions to mountain glaciers are not well known, the ice-core C$_2$O$_4$$_2^-$ records from Mount Everest provide a unique opportunity to assess the contribution of anthropogenic emissions to the background C$_2$O$_4$$_2^-$ concentration.

In the mid-20th century, industrial pollution by oxalate was very serious, and was less effectively controlled than today. More recently, strict controls have been imposed on industrial pollution, and many oxalate-producing factories have been closed around the world (Hong, 1997). This may be the reason for the lower C$_2$O$_4$$_2^-$ concentrations in the 1990s. On the other hand, the C$_2$O$_4$$_2^-$ concentrations start to increase around 1900, possibly related to the temperature increase (Fig. 1). In summary, the C$_2$O$_4$$_2^-$ concentration during the 1950s–80s, which may mainly reflect anthropogenic emissions, is about three times higher than the background value in the 19th century.

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