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Signals of pollution revealed by trace elements in recent snow from mountain glaciers at the Qinghai–Tibetan plateau

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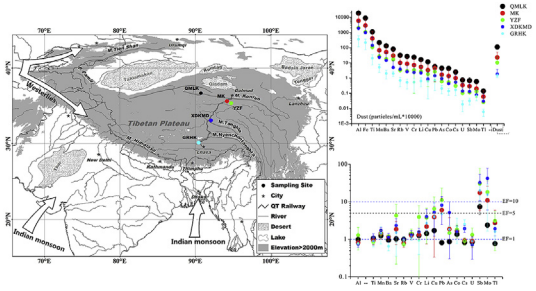
HIGHLIGHTS

- Digested concentrations of trace elements (TEs), REEs, Y and Th in snow samples from 5glaciers were mainly discussed.
- EF values were overestimated at least 4.6 times based on Ti or Al with lower mass fractions in traditional acidified samples.
- Dust were the main sources of TEs, while Pb,Cu,Sb Mo, As were occasionallycontributed from human activities.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to extract pollution signal of trace elements (TEs) in glacier snow at the Qinghai-Tibetan plateau of China by human activities, concentrations of 18 TEs (Al, Ti, Fe, Rb, Sr, Ba, V, Cr, Mn, Li, Cu, Co, Mo, Cs, Sb, Pb, Tl, and U), 14 rare earth elements (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), Y and Th in digested snow samples from five glaciers in April–May 2013 before monsoon season were measured. Results shown that higher TEs concentrations were found in glaciers at the northern plateau while lower concentrations in glaciers at the central and southern plateau. Discussion revealed that EF values calculated from elements with mass fraction <30% such as Ti and Al, etc in traditional acid leached samples, will overestimate at least 4.6 times the contribution of other sources than dust for TEs such as Sb, Sr, As, Cu and Pb etc. Analysis indicated that most TEs mainly originated from dust sources, whereas Pb, Cu, Mo and Sb showed occasionally significant contributions from polluted sources in three snow pits and the GRHK surface snow samples. The pollution probably originated from mining and smelting, road transport emissions on the plateau and some regions outside of the plateau. Dust provenance tracing results based on REEs indicated that Taklimakan Desert, Qaidam Basin, and Tibetan surface soil were the potential dust sources for the studied glaciers, while the Indian Thar Desert was an occasional dust sources for YZF,XDKMD and GRHK snow samples.

1. Introduction

Trace elements (TEs) in snow and ice in remote areas such as

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Antarctic and Arctic, especially Greenland, and Andes in South America not only preserved information about climatic changes during the last several climatic cycles (Gabrielli et al., 2005; Marteel et al., 2006) but also significant pollution of extensive mining and smelting activities linked with non-ferrous metals beginning early from 2000 to 2700 years ago (Hong et al., 1994; Krachler et al., 2009; Eichler et al., 2017). It was revealed that widespread atmospheric pollution at northern hemisphere by TEs started from industrial revolution (Candelone et al., 1995; Planchon et al., 2002), then enhanced through wide use of leaded gasoling, and decreased since late 1960s due to manners had been taken to reduce the usage of leaded gasoling (Boutron et al., 1991). At recent decades, growing interesting in TEs in snow and ice in Arctic European Alps, Soviet Union, Altai, South America glaciers further lead to many valuable findings still related with anthropogenic emission of metals from various human activities (Barbante et al., 2004; Krachler et al., 2005; Gabrieli et al., 2011; Hong et al., 2012; Eichler et al., 2012, 2014,2015). These researches give us a clue that human persistently impact global elemental metal cycles, which is also reported by Rauch1 and Pacyna (2009).

The Qinghai-Tibetan Plateau is regarded as the "Third pole" besides Antarctic and Arctic, its environment and climatic change have been drawn increasing attention due to glaciers located at the plateau are water storage for more than a billion people of south and east Asia, sending fresh melt water down the Indus, Ganges, Brahmaputra, and other river systems (Yao et al., 2012). Reliable data on TEs in snow and ice collected from several glaciers at the Qinghai–Tibetan Plateau had revealed widespread increasing of TEs resulted from pollution originated from different regions surrounding the plateau. For example, Sb and Pb etc in the Mushitag Ata ice core recorded anthropogenic pollution from central Asia since 1950s with peak in 1991 (Li et al., 2006a,b); the increasing of Bi, U, Cs, As, Mo, Sn, and Sb in Mount Everest ice cores in recent decades were due to various anthropogenic pollution responding to rapid economic growth in central Asia (Kaspari et al., 2009); long-range transported TEs from south Asia were detected in wet deposition and snow pits samples at the high altitude regions of southern plateau (Duan et al., 2009; Cong et al., 2010; Liu et al., 2011; Huang et al., 2013), as well as the findings of anthropogenic TEs in the central to northern Tibetan plateau (Dong et al., 2015; Li et al., 2011, 2012). TEs from local polluted sources were detected from snow pits samples at No.1 Glacier of Tienshan located at the north-west bonder of the plateau (Li et al., 2007). Recently, interesting findings have been observed from ice cores of Punuogangri and Guliya ice cap. One of them was that Northern Hemisphere (primarily in Western Europe) coal combustion was the likely source of Pb, Cd, Zn, and Sb during 1850–1950 period recorded from Guliya ice ice core (Sierra-Hernández et al., 2017). Another finding was that Sb, Cd, Zn and Pb reflect Central, South and East Asia metallurgies/coal-burning emissions from Punuogangri ice core (Beaudon et al., 2017).

However, most studies related with TEs in current snow as well as ice core samples at the Plateau mentioned above were based on various traditional acidification methods. Li et al. (2007) have stated these studies based on different acidification methods. Results through different acid leaching methods are unlikely to be directly comparable. Uglietti et al. (2014) found that the mass fluxes of these TEs to high altitude glaciers will be significantly underestimated even in ice core samples after acidification over one month. Our data also shown that TEs from the acid leachable fraction only accounted for about 6%–50% for Al, Ti, Rb, and V, and 60%–90% for other TEs in their full digested concentrations (Li et al., 2017). Obviously, the enrichment factor (EF) values calculated on acid leached concentrations of TEs taking Al or Ti as local soil reference will overestimate the contributions from sources other than dust, especially those from human activities.

The aim of this study was firstly to characterize the current variation of TEs, as well as their EF values based on total digested snow samples, and secondly to extract signals of anthropogenic sources of TEs in recent snow collected from five mountain glaciers on the plateau. The results of this study will provide a valuable reference for evaluating the contribution of TEs from human activities in the atmosphere at the studied glaciers in future.

2. Materials and methods

2.1. Sampling

Snow pit samples from three glaciers (MK, Meikuang glacier, YZF, Yuzhufeng glacier, and XDKMD, Xiaodongkemadi glacier), as well as surface snow samples from a further two glaciers (QMLK, Qiumianleike and GRHK, Gurenhekou) were collected between late April and late May 2013 (Fig. 1). The sampling information including sampling method, locations as well as sample numbers were shown in Li et al. (2017) and also shown in Table 1 in the supplementary material. The snow deposition time of the studied sites was within the non-monsoon season but just before the onset of Indian monsoon activities. The westerly prevailing wind was the dominant atmospheric cycling driving factor during the non-monsoon season (Fig. 1). The sites are spread across the Qinghai–Tibetan plateau from the north (QMLK, MK, and YZF), central (XDKMD, which is also located at the boundary of north and south), and to the south (GRHK).

2.2. Preparation and determination

The acid cleaning procedure, sample digestion procedures, and determination of dust content and $\delta^{18}O$, TEs, REEs, Y and Th are described in Li et al. (2017).

The measurement of TEs (Al, Ti, Fe, Rb, Sr, Ba, V, Cr, Mn, Li, Cu, Co, Mo, Cs, Sb, Pb, Tl, and U), REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu), Y, and Th was carried out using an Element 2 inductively-coupled plasma sector field mass spectrometer (ICP-SFMS; Thermo Finnigan, Bremen, Germany) at the Institute for the Dynamics of Environmental Processes, National Research Council (IDPA-CNR) Venice, Italy. Standard reference materials TMrain-95 (from National Water Research Institute, Canada, see its copy is in the Supplementary material) was used to validate the quality of the ICP-SFMS analyses. The accuracy of this determination can be found in Fig. 1 of Supplementary material. The accuracy of the digestion method for total concentrations of TEs was validated based on a soil standard reference material (SRM) GBW07423 (GSS-9, made by Institute of Geophysical and Geochemical Exploration, Langfang, China). Detailed description of the digestion method, accuracy and procedural blanks could also be found in Li et al. (2017), while treatment procedures regarding digestion not completely described in Li et al. (2017) as well as the accuracy of TEs based on six different quantities from less than 1 mg–25 mg of soil SRM were also described in Supplementary material.

3. Results and discussion

3.1. Variations of TEs and REE concentrations across the studied sites

Statistics data for TEs were shown in Table 1 while those of REEs were shown in Table 2 in Supplementary material. Obvious spatial variations of TE concentrations were observed in the snow samples of the studied sites (Fig. 2). Comparing the surface samples of QMLK and GRHK, the average TE concentrations in QMLK which located at