Trace elements and Pb isotope records in Dome C (East Antarctica) ice over the past 800,000 years

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Abstract
Trace elements (V, Cr, Mn, Fe, Co, Cu, Zn, As, Rb, Sr, Mo, Cd, Sb, Ba, Tl, Pb, Bi, Th and U) and Pb isotopic compositions have been determined in various sections from the EPICA (European Project for Ice Coring in Antarctica) Dome C ice core, covering the period from ~533 kyr BP to ~800 kyr BP, by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) and thermal ionization mass spectrometry (TIMS), respectively. Our data enable us to extend the previous EDC records of trace elements and Pb isotopes to the full record of ~800 kyr from the Holocene back to Marine Isotopic Stage. We here discuss the EDC records of Ba, Rb, Mo, Sb, Cd, Tl, Bi and Pb isotopes. Crustal elements such as Ba and Rb show well defined variations in concentrations in relation to climatic conditions with lower values during the interglacial periods and much higher values during the coldest periods of the last eight climatic cycles, while volcanogenic Cd, Tl and Bi show a less pronounced relationship between concentrations and climatic conditions. The isotopic signatures of Pb suggest that changes in the provenance of dust reaching the East Antarctic Plateau from Potential Source Areas have occurred during the interglacial periods before the MBE. Our data suggest that the main factors affecting the deposition fluxes and sources of natural trace elements over Antarctica are most likely linked with a progressive coupling of the climate of Antarctica and lower latitudes during the past 800 kyr.

Key words**:** Trace elements, Pb isotopes, Antarctic ice, Climate change, Mid-Brunhes Event

Introduction

Deep Antarctic ice cores allow us to reconstruct climate-related changes in the biogeochemical cycles of atmospheric trace elements originating from various natural sources (Hong et al., 2003; Gabrielli et al., 2005a, b; Marteel et al., 2008, 2009). These changes are particularly important to understand the future evolution of their cycles due to present-day global warming probably affecting the atmospheric circulation and the resultant dispersion patterns of trace elements on Earth. Despite such interest, however, the reconstruction of long-term changes in past natural biogeochemical cycles of various trace elements linked to different climatic conditions has been proved to be extremely difficult, because the purity of Antarctic snow and ice is extremely high and drilling operations do heavily contaminate the outside of deep ice cores.

Combining a few available records of trace elements previously presented from the EPICA Dome C ice core (Gabrielli et al., 2005a; Marteel et al., 2008, 2009), we here extend the Dome C climate-related records of various trace elements of interest to its full length of ~800 kyr. In addition, Pb isotopic compositions are also presented as environmental indicator for identifying the sources of aerosol dust reaching the East Antarctic Plateau during different climatic stages. The climate of the EPICA ice core is characterized by the difference in amplitude of climatic cycles and climate conditions before and after the Mid-Brunhes Event (MBE, ~430 kyr BP) with significant increase in amplitude of glacial-interglacial cycles after the MBE and cooler interglacials before the MBE than after the MBE (Yin and Berger, 2010). Therefore, our data would enable the investigation of the progressive changes in deposition fluxes, transport and sources of trace elements in conjunction with the difference in climate variability before and after the MBE.

Materials and Methods

A total of 23 core sections were selected from the 3,259.7 m ice core drilled by the European Project for Ice Coring in Antarctica (EPICA) drilled at Dome C (hereafter EDC) in East Antarctica (75°06′S, 123°21′E, altitude 3233 m above sea level). The depth of the 23 sections ranged from 2973.85 m to 3190 m, which correspond to an estimated age between about 572 kyr BP and 800 kyr BP, covering the MIS 15.1 to MIS 20.2.

Each core section was mechanically decontaminated using ultra-clean procedures at Korea Polar Research Institute (KOPRI) (Hong et al., 2003), which has proved to be the most effective method for obtaining the clean inner core after removing the outside contamination of the core originated mainly from drilling operations. The inner core so obtained was then either collected whole or divided into consecutive parts, giving the 42 depth intervals. Together with the 42 samples obtained after decontamination at KOPRI, the 79 aliquots from the EDC ice core, which were used for previous studies (Gabrielli et al., 2005a; Marteel et al., 2008, 2009), were additionally analyzed for the first measurement of Mo, Sb and Tl.

All sample handling and analytical operations were carried out under a Class 10 laminar airflow bench or booth in clean laboratories (Class 1000) located at KOPRI. Concentrations of various trace elements (V, Cr, Mn, Fe, Co, Cu, Zn, As, Rb, Sr, Mo, Cd, Sb, Ba, Tl, Pb, Bi, Th and U) were determined using Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS) (Element2, Thermo Fisher Scientific, Bremen, Germany) equipped with an Apex high-sensitivity inlet system (Apex IR, Elemental Scientific Incorporated, Omaha, Nebraska, United States). The measurements of Pb isotopic compositions were carried out using a VG354 magnetic sector field, multi-collector Thermal Ionization Mass Spectrometer at Curtin University of Technology (Triton, Thermo Finnigan).

Results and Discussion

The preliminary data on changes in concentrations of several elements (Ba, Rb, Mo, Sb, Cd, Tl, Bi) and Pb isotopic composition measured in the samples are here presented. It should be noted that concentrations of Mo, Sb and Tl are the first data ever published on past variations of these elements in deep Antarctic ice cores covering the past climatic cycles. For the other elements, new data are combined with those previously obtained from EDC ice core to produce detailed records for a ~800 kyr period.

Our data clearly show that concentrations have strongly varied during the past ~800 kyr. Mean concentrations range from 0.09 pg/g for Bi to 60 pg/g for Ba. The maximum/minimum concentration ratios are observed to be between 51 for Tl and 526 for Bi. A pronounced variability in concentrations is closely linked to the climatic conditions. Such variability has been well documented in previous studies (Gabrielli et al., 2005a, b; Marteel et al., 2008, 2009). The feature of variations in concentrations with respect to climatic conditions appears however to be different for each element. As illustrated in Fig. 1, Rb remains lower values for warmer climatic condition characterized by less negative δD values. Conversely, higher concentrations of Rb are observed during colder climate periods with more negative δD values. Rb is an element mainly derived from the continental crust and such relationship for crustal trace elements such as Rb has been well observed in previous study (Marteel et al., 2009), which may be attributed to a strengthening of South America dust sources, together with a prolonged lifetime of atmospheric dust particles whey they are transported from lower latitudes to East Antarctic Plateau due to a reduced hydrological cycle during colder periods (Lambert et al., 2008).

The situation appears to be different for Tl and Bi. Although concentrations of these two elements generally increase when δD values are

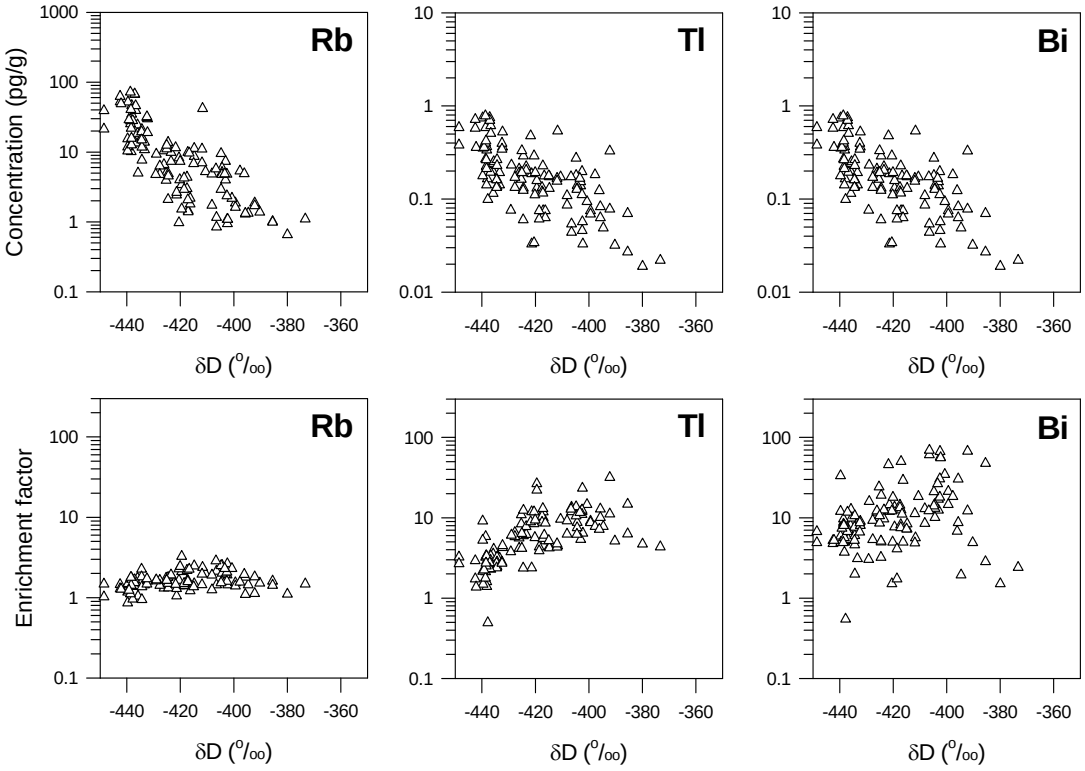

Fig. 1. Changes in concentrations and EF values of Rb, Tl and Bi as a function of δD values over the past 800 kyr. A logarithmic scale is used for both concentrations and crustal enrichment factors.

more negative, however, an increase pattern is less pronounced in comparison to that for Rb. This may be due to the difference in the main factors such as the sources and pathways controlling the input of Tl and Bi into the Antarctic atmosphere. Indeed, crustal dust is not a dominant source for these two elements.

In order to evaluate the relative magnitude of rock and soil dust contribution, the crustal enrichment factors (EF) were calculated for each element. The EF is defined as the concentration ratio of a given element to that of a conservative crustal element, normalized to the same concentrations ratiod characteristic of the upper continental curst (Wedepohl, 1995). Using Ba, as a crustal reference element, for example, the calculation of EF for Rb is as follows:

$$EF(Rb) = (Rb/Ba)_{ice}/(Rb/Ba)_{crust}$$

In Fig. 1, EF values for Rb appear to be close to unity with more or less constant values whatever the period, as expected by the fact that Rb originated mainly from the continental crust. In comparison, EFs values for Tl and Bi show systematic increase toward those much larger than unity during warmer periods and approach to unity during the coldest climatic periods. This indicates that contribution from crustal dust were very important during the coldest period, while contribution from volcanoes seems to become significant during warmer periods (Marteel et al., 2008). Interestingly, EFs for Tl and Bi appear to be slightly more elevated for δD values between about –390‰ and –410‰ (Fig. 1). For this aspect, we suppose that different atmospheric circulations prevailed during such intermediate climatic periods, probably due to slightly northward migration of the Antarctic Polar Front, may have governed more meridional transport of volcanogenic Tl and Bi from lower latitudes toward Antarctica.

Finally, the preliminary $^{206}Pb/^{207}Pb$ profile is shown as a function of δD values in Fig. 2. Our data correspond to the time period between ~533 kyr BP and ~800 kyr BP, while data from Vallelonga et al. cover past 220 kyr. The $^{206}Pb/^{207}Pb$ ratios after and before the MBE tend to be within a relatively similar range. A few data points before the MBE show less radiogenic values. Such less radiogenic signature is representative of dust aerosols generated in southeastern Australia (Deckker et al., 2010). Our Pb isotopic signature for the pre-MBE indicates that dust transported to Antarctica could be sourced from Australia, which is inconsistent with

the findings of Vallelonga et al. (2010), which pointed out that Australian dust is not a major component of Antarctic dust whatever the period.

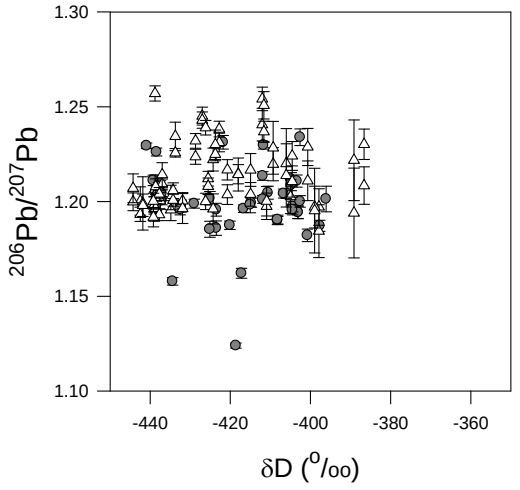

Fig. 2. Changes in $^{206}Pb/^{207}Pb$ ratios as a function of δD values. Open triangles show the data from Vallelonga et al. (2010) and grey circles from this work.

Conclusion

Our study has extended the previous EDC records of various trace elements to its full length of ~800 kyr, which enable us to discuss changes in past natural biogeochemical cycles of these elements linked to different climatic conditions. The detailed records of trace elements as well as Pb isotopes suggest that changing atmospheric circulations in conjunction with a progressive coupling of the climate of Antarctica and lower latitudes governed the deposition fluxes and sources of trace elements over Antarctica during the past 800 kyr.

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References

Deckker PD, Norman M, Goodwin ID, Wain A, Gingele F. Lead isotopic evidence for an Australian source of aeolian dust to Antarctica at times over the last 170,000 years. Palaeogeogr Palaeoclimatol Palaeoecol 2010; 285:205-223.

Hong S, Kim Y, Boutron CF, Ferrari CP, Petit JP, Barbante C, et al. Climate-related variations in lead concentrations and sources in Vostok Antarctic ice from 65,000 to 240,000 years BP. Geophys Res Lett 2003; 30: doi:10.1029/2003GL018411.

Gabrielli P, Barbante C, Boutron CF, Cozzi G, Gaspari V, Planchon F, et al. Variations in atmospheric trace elements in Dome C (East Antarctica) ice over the last two climatic cycles. Atmos Environ 2005a; 39: 6420-6429.

Gabrielli P, Planchon FAM, Hong S, Lee KH, Hur SD, Barbante C, et al. Trace elements in Vostok Antarctic ice during the last four climatic cycles. Earth Planet Sci Lett 2005b; 234: 249-259.

Lambert F, Delmonte B, Petit JR, Bigler M, Kaufmann PR, Hutterli MA, et al. Dust-climate couplings over the past 800,000 years from the EPICA Dome C ice core. Nature 2008; 452:616-619.

Marteel A, Boutron CF, Barbante C, Gabrielli P, Cozzi G, Gaspari V, et al. Changes in atmospheric heavy metals and metalloids in Dome C (East Antarctica) ice back to 672.0 kyr BP (Marine Isotopic Stages 16.2). Earth Planet Sci Lett 2008; 272: 579-590.

Marteel A, Gaspari V, Boutron CF, Barbante C, Gabrielli P, Cescon P, et al. Climate-related variations in crustal trace elements in Dome C (East Antarctica) ice during the past 672 kyr. Clim Change 2009; 92:191-211.

Jouzel J, Masson-Delmotte V, Cattani O, Dreyfus G, Falourd S, Hoffmann G, et al. Orbital and millennial Antarctic climate variability over the past 800,000 years. Science 2007; 317:793-796.

Vallelonga P, Gabrielli P, Balliana E, Wegner A, Delmonte B, Turetta C, et al. Lead isotopic compositions in the EPICA Dome C ice core and Southern Hemisphere Potential Source Areas. Quat Sci Rev 2010; 29:247-255.

Wedepohl KH. The composition of the continental crust. Geochim Cosmochim Acta 1995; 59:1217-1232.

Yin QZ, Berger A. Insolation and CO_2 contribution to the interglacial climate before and after the Mid-Brunhes Event. Nature Geosci 2010;3:243-246.