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 from the EPICA (European Project for Ice Coring in Antarctica) Dome C ice core have been determined using inductively coupled plasma sector field mass spectrometry (ICP-SFMS) and thermal ionization mass spectrometry (TIMS), covering the period from ~533 kyr BP to ~800 kyr BP, respectively. Our data have enabled us to extend the previous EDC records of trace elements and Pb isotopes from the Holocene back to the Marine Isotopic Stage 20.2, ~800 kyr BP. 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. 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 occurred during the interglacial periods before the MBE. Our data suggest that the main factors affecting deposition fluxes and sources of natural trace elements over Antarctica are most likely linked to a progressive coupling of the climates of Antarctica and lower latitudes over 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 that originate from various natural sources (Hong et al., 2003; Gabrielli et al., 2005a, b; Marteel et al., 2008, 2009). These changes are particularly important in understanding the future

evolution of element cycles as present-day global warming most likely affects the atmospheric circulation and the resultant elemental dispersion patterns on Earth. Despite such interest, reconstructing long-term changes in past natural biogeochemical cycles for various trace elements linked to different climatic conditions has 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.

By combining the few records of trace elements from the EPICA Dome C ice core presented previously (Gabrielli et al., 2005a; Marteel et al., 2008, 2009), we can now extend the Dome C climate-related trace element records to the full length of ~800 kyr. In addition, we now present Pb isotopic compositions as environmental indicators for identifying the sources of aerosol dust that reached 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 increases in the amplitude of glacial-interglacial cycles after the MBE and cooler interglacial cycles before the MBE (Yin and Berger, 2010). Thus, our data allows for an investigation of climate-related changes in trace element sources, transport, and deposition fluxes, under different climatic conditions 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) at Dome C (hereafter referred to as 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 ages estimated to be 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 the 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 as a whole or divided into consecutive parts, producing 42 different depth intervals. After decontamination at the KOPRI, these 42 samples were then analyzed for first measurements of Mo, Sb, and Tl, along with the 79 aliquots from the EDC ice core that were used in previous studies (Gabrielli et al., 2005a; Marteel et al., 2008, 2009).

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). Measurements of Pb isotopic compositions were then carried out using an isotope ratio thermal ionization mass spectrometer (model VG354, Fisons Instruments) at Curtin University of Technology.

Results and Discussion

Preliminary data collected from the samples include changes in concentrations of several elements (Ba, Rb, Mo, Sb, Cd, Tl, Bi) and Pb isotopic composition. It should be noted that data related to variations in Mo, Sb and Tl concentrations in deep Antarctic ice cores covering the past climatic cycles are the first ever published. For the other elements, we have combined new and existing data from EDC ice core to produce detailed records for the whole ~800 kyr period.

Our data clearly indicate that concentrations have varied significantly over 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 with the climatic conditions. Such variability has been well documented in previous studies (Gabrielli et al., 2005a, b; Marteel et al., 2008, 2009). Variations in concentrations with respect to climatic conditions occur, but they are different for each element. As illustrated in Fig. 1, Rb remains lower for warmer climatic conditions characterized by δD values that are less negative. Conversely, higher concentrations of Rb are observed during colder climate periods when δD values are more negative. Rb is an element derived primarily from the continental crust, and previous study has observed similar relationships for crustal trace elements (Marteel et al., 2009). This may be attributed to a strengthening of South America dust sources, in combination with a lengthening of the lifetime of atmospheric dust particles as they are transported from lower latitudes to East Antarctic Plateau. This prolonged lifetime is proposed to be a result of 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 more negative, the increase in this pattern is less pronounced in comparison to that of
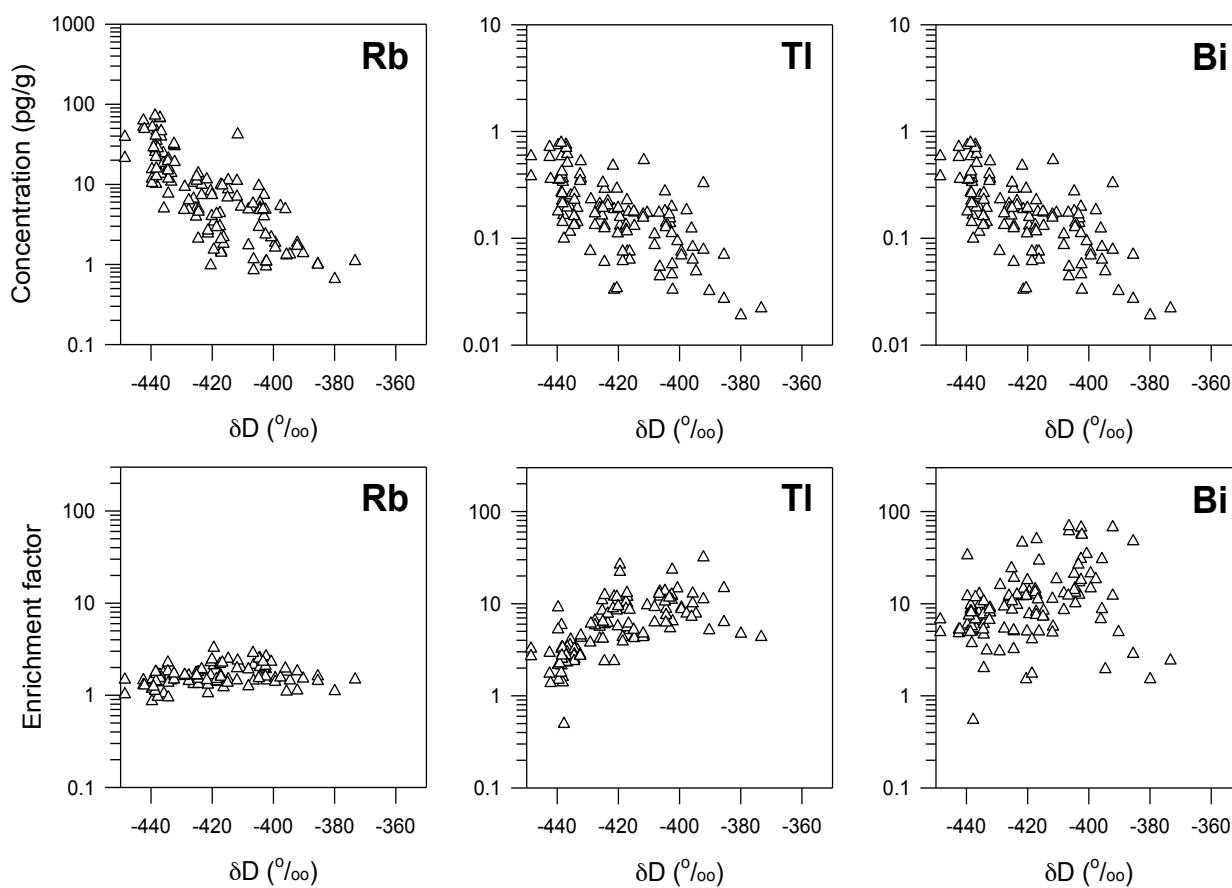
Fig. 1. Changes in concentrations and EF values of Rb, Tl and Bi as a function of δD values over the past 800 kyr. A logarithmic scale is used for both concentrations and crustal enrichment factors.

Rb. This may be due to differences in the primary factors (such as the sources and pathways) that control 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, we calculate the crustal enrichment factors (EF) for each element. The EF value 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, This was expected, as Rb originates mainly from the continental crust. In comparison, EF values for Tl and Bi show systematic increases toward those much larger than unity during the warmer periods and approach to unity during the coldest climatic periods. This indicates that contributions from crustal dust were very important during the coldest periods, while contributions from volcanoes seem to become more significant during the warmer periods (Marteel et al., 2008). Interestingly, EFs for Tl and Bi appear to be slightly more elevated when δD values are between about −390‰ and −410‰ (Fig. 1). In these cases, we posit that different atmospheric circulations prevailed during these intermediate climatic periods, probably due to a slightly northward migration of the Antarctic Polar Front, which may have pushed more meridional transport of volcanogenic Tl and Bi from lower latitudes toward Antarctica.

Finally, in Fig. 2, we present the preliminary [206]Pb/[207]Pb profile as a function of δD values. Our data correspond to the time period between ~533 kyr BP and ~800 kyr BP, while data from Vallelonga et al. cover the past 220 kyr. The [206]Pb/[207]Pb ratios before and after the MBE tend to be within a relatively similar range. A few data points before the MBE show less radiogenic values. This 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), who pointed out that Australian dust is not a major component of Antarctic

dust, whatever the period.

Conclusion

In extending the previous EDC records of various trace elements to the full length of ~800 kyr, this study has allowed us to discuss changes in past natural biogeochemical cycles for these elements linked to different climatic conditions. Both detailed records of trace elements as well as records of Pb isotopes suggest that changing atmospheric circulation patterns over Antarctica in conjunction with a progressive coupling of the climates of Antarctica and lower latitudes have governed the deposition fluxes and sources of trace elements during the past 800 kyr.
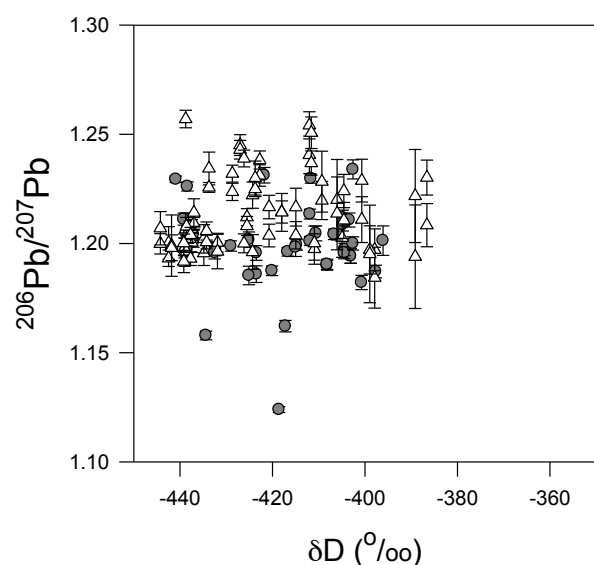
Fig. 2. Changes in ^{206}Pb/^{207}Pb ratios as a function of δD values. Open triangles show the data from Vallelonga et al. (2010) and grey circles from this work.

Acknowledgements

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