



## Lead isotopic compositions in the EPICA Dome C ice core and Southern Hemisphere Potential Source Areas<sup>☆</sup>

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### ABSTRACT

A record of Pb isotopic compositions and Pb and Ba concentrations are presented for the EPICA Dome C ice core covering the past 220 ky, indicating the characteristics of dust and volcanic Pb deposition in central East Antarctica. Lead isotopic compositions are also reported in a suite of soil and loess samples from the Southern Hemisphere (Australia, Southern Africa, Southern South America, New Zealand, Antarctica) in order to evaluate the provenance of dust present in Antarctic ice. Lead isotopic compositions in Dome C ice support the contention that Southern South America was an important source of dust in Antarctica during the last two glacial maxima, and furthermore suggest occasional dust contributions from local Antarctic sources. The isotopic signature of Pb in Antarctic ice is altered by the presence of volcanic Pb, inhibiting the evaluation of glacial–interglacial changes in dust sources and the evaluation of Australia as a source of dust to Antarctica. Consequently, an accurate evaluation of the predominant source(s) of Antarctic dust can only be obtained from glacial maxima, when dust–Pb concentrations were greatest. These data confirm that volcanic Pb is present throughout Antarctica and is emitted in a physical phase that is free from Ba, while dust Pb is transported within a matrix containing Ba and other crustal elements.

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<sup>☆</sup> This paper is dedicated to the memory of our friend and colleague Professor Kevin J.R. Rosman who, among other achievements, pioneered the accurate determination of lead isotopic compositions in polar snow and ice.

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### 1. Introduction

Dust is an active component of the Earth's climate system, both contributing to and responding to changes in radiative forcing and ocean biogeochemistry (Mahowald et al., 2005). The polar ice sheets are an ideal archive for monitoring variations in dust fluxes and other climate parameters, and have been crucial to understanding the role of dust in climate variability (Fischer et al., 2007). It has recently been suggested that variations in Antarctic dust fluxes are primarily driven by strengthened Aeolian deflation in source regions and weakening of the hydrological cycle rather than variations in atmospheric transport parameters or moderations in meridional transport (Lambert et al., 2008).

Grousset and co-workers have demonstrated the utility and selectivity of Sr and Nd isotopic systems for investigation of dust provenance in ice cores (Grousset and Biscaye, 2005). Initial studies required kg-size samples, limiting analytical resolution and sample availability to a few glacial samples, but ongoing development of the analytical technique has seen improvements in sample resolution and recently low-concentration interglacial samples have been analysed (Delmonte et al., 2007).

In parallel, the isotopic signature of dust from Potential Source Areas (PSAs) has been documented. The recent work of Gaiero (2007) reported Sr and Nd isotopic composition for PSA in Southern South America (SSA) indicating the importance of considering high-latitude areas such as Patagonia as well as low-latitude sources located at high altitude such as the Puna-Altiplano plateau in the Andean Cordillera. Revel-Rolland et al. (2006) reported an extensive data set of Sr and Nd isotopic signatures in East Australian PSA samples, suggesting the presence of a non-trivial Australian dust contribution to Antarctica during interglacial climate phases. They suggested a 10–20% Australian dust contribution during glacial phases and up to 50% during interglacial phases. The changing proportions of dust sources was attributed to changes in primary production of dust in SSA during glacial climate phases resulting from glacial and periglacial processes related to the growth and recession cycles of the Patagonian ice cap.

The use of Pb isotopes for dust provenance has been limited on account of the extreme contamination controls required to accurately determine Pb isotopic ratios in pg-level quantities, as well as a dearth of Pb isotope data for PSAs. Initial studies of Pb isotopes in Antarctic ice (Rosman et al., 1994) and seawater (Flegal et al., 1993) reported the extent and origins of industrial pollution in the Antarctic environment. Vallelonga et al. (2002a,b) demonstrated that industrial Pb emissions were efficiently transported to Antarctica from Australia from 1880 AD on, with the influence of leaded gasoline emissions from South America evident since the 1960s. This work demonstrated the efficacy of fine particle transport mechanisms from Australia to coastal Antarctica, and established the extremely low concentrations of Pb present in Antarctic ice during the Holocene of  $\sim 0.3$  pg/g ( $0.3 \times 10^{-12}$  g/g).

Determination of the provenance of Antarctic dust using Pb isotopes has been hampered by the presence of volcanic Pb in Antarctica, which has a different isotopic composition to that of dust Pb. Matsumoto and Hinkley (2001) demonstrated the overwhelming presence of highly radiogenic volcanic Pb in the Taylor Dome ice core, located west of the Transantarctic mountains, with volcanic sources accounting for  $\sim 60\%$  of total Pb in Taylor Dome ice during the glacial phases and  $\sim 95\%$  during the Holocene. Determinations of volcanic Pb inputs are usually based on Pb/Ba or Pb/Al ratios measured in ice samples, with Ba or Al used as a continental dust proxy, and the dust-Pb contribution calculated using an estimate of the ratios of the elements in the upper continental crust (e.g. Wedepohl, 1995). Data from other locations in Antarctica indicate comparable or lower volcanic Pb contributions during the Holocene: 80–90% volcanic Pb contributions to Law Dome (Vallelonga et al., 2002a,b) and Victoria Land (Van de Velde et al., 2005), 30–80% volcanic Pb contributions to Coats Land (Planchon et al., 2003),  $\sim 20\%$  volcanic Pb contributions to Vostok (Hong et al., 2003) and  $\sim 15\%$  volcanic Pb contributions to Dome C (Vallelonga et al., 2005). Hinkley (2007) demonstrated that these volcanic Pb contributions converge on a radiogenic Pb isotopic composition of  $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.26$ , which corresponds to the Pb isotopic signatures of ocean island volcanoes as well as Antarctic volcanic provinces, including Mount Erebus.

The availability of data for PSAs has been another limitation to dust provenance studies using Pb isotopes. Lead isotopic compositions have been reported for South Atlantic and South Pacific

Ocean pelagic sediments (Chow and Patterson, 1962) but no land-based loess or soil data were available before this study. Geochronological studies of volcanic provinces of Antarctica [Erebus: Sun and Hanson (1975), Sims et al. (2008); Marie Byrd Land: Hart et al. (1997); Antarctic Peninsula: Hole et al. (1993)] and the South Sandwich Islands (Barreiro, 1983) ensure that the volcanic Pb component is already well defined. These studies support the radiogenic signature of Antarctic volcanic emissions indicated by Vallelonga et al. (2002a,b) and Hinkley (2007). Rosman et al. (1998) also identified rocks from a Th-rich province in Enderby Land with matching Pb isotopic compositions in Law Dome ice.

Recent analysis of Sr and Nd isotopic compositions in targeted locations of Southern South America and Australia have greatly stimulated the interpretation of Antarctic ice core data. This work seeks to provide a similar stimulus for the analysis of Antarctic Pb isotope compositions, by presenting Pb isotopic compositions in a set of targeted Australian soil and loess samples in arid locations of identified dust production and prolonged aridity during the Quaternary. Furthermore, Pb isotopes are reported for selected samples previously analysed for Sr and Nd by Delmonte et al. (2004) for comparison with existing proxies of PSAs, such as pelagic sediments and volcanic lavas. New data from the EPICA Dome C ice core are also presented, to improve the statistical reliability of dust provenance evaluations. This work contributes to evaluations of the provenance of Antarctic aerosol, distinguishing between dust and volcanic contributions, and provides an important data set for interpretation of Pb isotopes in Antarctic ice and snow in future studies.

## 2. Regional setting

### 2.1. Ice core samples

All ice core samples presented here are from the EPICA Dome C (hereafter EDC) core drilled between 1996 and 2005. The location and site characteristics of EDC have already been extensively described (EPICA community members, 2004). Sample dating was assigned using the EDC3 chronology of Parrenin et al. (2007) with paleo-temperature information provided by the high-resolution record of deuterium/hydrogen ratios (represented here as  $\delta\text{D}$ ) reported by Jouzel et al. (2007). A preliminary data set of 30 EDC samples (Vallelonga et al., 2005) has here been extended to 74 samples covering the period 2–217 kyr BP (86.6–2193.4 m depth). Some of the EDC samples previously reported have also been remeasured to improve the precision of the Pb isotopic compositions (sample depths: 229.1 m, 432.6 m, 489.0 m, 598.1 m, 709.0 m, 1093.1 m, 1643.1 m, 2094.4 m).

### 2.2. Australian PSA samples

PSA samples from Australia were collected in July 2007 from various loess and soil deposits for which chronologies and geomorphological descriptions have already been reported. The sites sampled include Lake Mungo dunefield (Kershaw and Nanson, 1993), Brachina Gorge (Glasby et al., 2007), Lake Eyre (Magee et al., 2004), Strzelecki desert (Fitzsimmons et al., 2007) and Innamincka/Tilcha Waterhole (Nanson et al., 2008). These sites represent locations of present dust production or loess deposits, which can be considered isotopically representative of dust produced in previous glacial periods.

### 2.3. Other PSA samples

Lead isotopic compositions were determined in a selection of soil and loess samples previously reported by Delmonte et al. (2004). These samples derive from locations within SSA (in particular from

the Pampas region and Patagonia), Southern Africa (Namibia), New Zealand (Southland, Otago) and Coastal East Antarctica (Dry Valleys and Northern Victoria Land).

### 3. Materials and methods

#### 3.1. Ice core samples

The methods of preparation and analysis of the ice core samples have been previously described (Vallelonga et al., 2002a,b; Gabrielli et al., 2004). To summarize, the decontaminations were carried out in France, within a bench supplied with HEPA-filtered air maintained at  $-20^{\circ}\text{C}$  and using acid cleaned polyethylene tools and stainless steel chisels. The samples were decontaminated manually using a chiseling procedure in which the pristine inner core samples were mechanically separated from the outer contaminated layers of each ice core section. Each inner core section was usually broken into two pieces, each approximately 20 cm long. The decontaminated samples were bottled and sent to Australia for Pb isotopes analysis by Thermal Ionization Mass Spectrometry (TIMS) using a Fisons Instruments VG-354. Approximately 10 mL of each inner core sample was evaporated, after the addition of a  $\text{HNO}_3/\text{HF}/\text{H}_3\text{PO}_4$  acid mixture and a  $^{137}\text{Ba}/^{205}\text{Pb}$  isotopic tracer solution. Twelve samples were analysed at a time, with blanks and a NIST 981 SRM added to each sample batch for quality control and monitoring of instrumental mass fractionation. The instrumental mass fractionation of  $0.24 \pm 0.06\%$  per mass unit was applied to the measured isotopic ratios. Reported uncertainties on Pb isotopic compositions in EDC ice are 95% confidence intervals which represent the combination of uncertainties associated with the sample measurement, the isotopic composition of the Pb blank and the instrumental mass fractionation correction. The total analytical blank was usually 0.4 pg Pb and 2.5 pg Ba. The accuracy of the Pb and Ba concentrations is estimated to be  $\pm 10\%$  (95% confidence interval), attributed mainly to the accuracy of dispensing the spike into the sample.

#### 3.2. Australian PSA samples

Australian PSA samples were initially prepared at University Ca' Foscari of Venice, Italy, then sent to Ghent University, Belgium for Pb isolation and measurement. The bulk samples were initially dried at  $50^{\circ}\text{C}$  for 12 h, then two 0.3 g aliquots were taken of each sample for treatment by two different methods: extraction and digestion. Each extraction involved adding 8 mL of 65%  $\text{HNO}_3$  and 2 mL of 30%  $\text{H}_2\text{O}_2$  to 0.3 g of sample while each digestion involved adding 6 mL of 65%  $\text{HNO}_3$ , 3 mL of 50% HF and 2 mL of 30%  $\text{H}_2\text{O}_2$  to 0.3 g of sample. Each extraction and digestion mixture was then microwaved for 2 h. The mixtures were then evaporated and redissolved in 2 mL of dilute HBr before being passed through an AG1-X8 anion exchange column. The Pb was eluted in concentrated HCl, evaporated and then redissolved in 1%  $\text{HNO}_3$  solution with 20 ng of NIST 997 SRM ( $^{205}\text{Tl}/^{203}\text{Tl} = 2.38714$ ) added. The samples were then analysed using a ThermoScientific Neptune MC-ICP-MS located at Ghent University. The NIST 997 SRM added to each sample allowed the real-time monitoring of plasma variations and correction of instrumental mass discrimination. Mass discrimination was corrected using the Russell law (White et al., 2000), with total analytical blanks consistently lower than 1% of the signal intensity of the samples.

#### 3.3. Other PSA samples

PSA samples described by Delmonte et al. (2004) were analysed in Australia using TIMS. All fine-particulate samples (total dust

mass  $< 5\ \mu\text{m}$  diameter) were isolated by humid sedimentation and checked by coulter counter analysis prior to chemical processing. Three bulk (coarse-grained) samples were also chemically processed. Aliquots of these samples were then evaporated and redissolved in dilute HBr prior to Pb isolation by anion exchange chemistry (Dowex AG1-X8, 100–200 mesh). The column was flushed with 0.5 M HBr with the Pb then eluted in MQ water.  $\text{H}_3\text{PO}_4$  was added to the sample prior to evaporation, with the evaporated sample then loaded onto a Rhenium filament using silica gel. The samples were then analysed using the aforementioned Fisons Instruments VG-354 TIMS. Total analytical blanks were consistently less than 400 pg Pb, corresponding to less than 0.5% of the sample size analysed. Coarse-grained PSA samples (SA1, SA3, A7) have not been used to evaluate Antarctic dust provenance because they cannot be considered representative of the  $< 5\ \mu\text{m}$  diameter dust particulates found in Dome C ice.

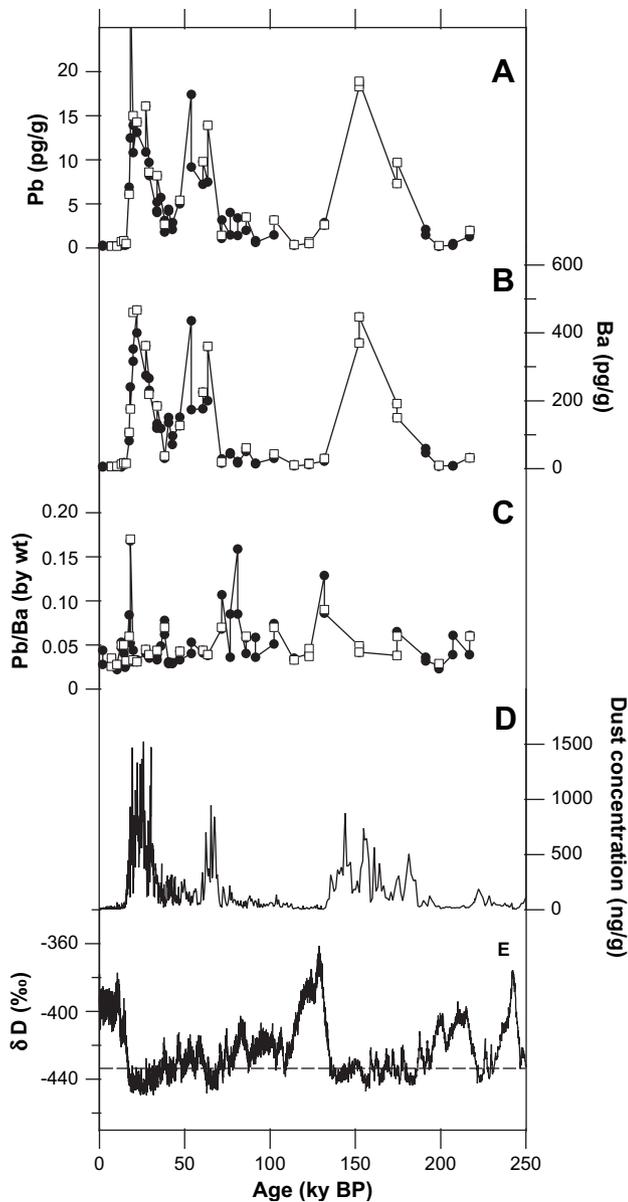
### 4. Results

#### 4.1. EDC ice samples

The preliminary data set of Pb isotopic compositions reported in 30 samples from EDC has here been extended to 74 samples covering the period 2–217 kyr BP (Table S1, supplemental data). The Pb and Ba concentrations (Fig. 1a,b) follow well-defined glacial–interglacial variations, with the lowest concentrations during the Holocene MIS 1 (14 samples, average 0.36 pg Pb/g, 10.2 pg Ba/g) and Eemian MIS 5.5 (4 samples, average 0.41 pg Pb/g, 11.2 pg Ba/g) and the highest concentrations during the Last Glacial Maximum (LGM) MIS 2 (10 samples, average 13.4 pg Pb/g, 278 pg Ba/g). The data are in good agreement with LGM/Holocene REE concentrations ratios found in the EDC ice core (Gabrielli et al., 2010). A comparison of Pb and Ba concentrations to  $\delta\text{D}$  demonstrates the well-reported non-linear sensitivity of dust fallout to climate (Gabrielli et al., 2005), in which low Pb and Ba concentrations are observed at warmer temperatures ( $\delta\text{D} > -435\text{‰}$ ) while Pb and Ba concentrations increase steeply at colder temperatures ( $\delta\text{D} < -435\text{‰}$ ). This is in good agreement with the  $\delta\text{D}$  value of  $-425\text{‰}$  at which Lambert et al. (2008) observed a correlation between dust flux and temperature. Only two samples dated to 53.8 ky BP do not follow this trend by displaying high Pb and Ba concentrations at a  $\delta\text{D}$  value of  $-429\text{‰}$  – these samples correspond to the cool climate phase between glacial Antarctic warm events A3 and A4, during which dust fluxes approached LGM levels.

In contrast to the well-defined variations of Pb and Ba concentrations, a high level of variability is observed in the  $^{206}\text{Pb}/^{207}\text{Pb}$  profile (Fig. 2). The overall trend matches that previously reported, with low  $^{206}\text{Pb}/^{207}\text{Pb}$  values during the coldest climate phases followed by higher  $^{206}\text{Pb}/^{207}\text{Pb}$  during the transitions to warmer climate phases. The level of variability in the data suggests that, for Dome C ice records, changes in Pb isotopic compositions need to be evaluated with respect to changes in dust concentration as well as changes in temperature.

Lead isotopic compositions in the EDC samples are also consistent with the preliminary data set reported by Vallelonga et al. (2005), being distributed along a mixing line between two end-members. Fig. 3 shows that this mixing line is common to all pre-industrial Antarctic ice and snow samples reported, with a radiogenic end-member of  $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.27$  and  $^{208}\text{Pb}/^{207}\text{Pb} \sim 2.52$  (the most radiogenic Taylor Dome sample) and a relatively unradiogenic end-member of  $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.17$  and  $^{208}\text{Pb}/^{207}\text{Pb} \sim 2.44$  (the least radiogenic Coats Land samples). Lead isotopic compositions in Antarctic ice and snow samples are distributed according to location, with Pb from Taylor Dome (Matsumoto and Hinkley, 2001) and Law Dome (Vallelonga et al., 2002a,b) generally being more radiogenic



**Fig. 1.** Variations in concentrations of Pb (A) and Ba (B), Pb/Ba ratios (C), dust concentrations (D) and  $\delta D$  (E) in EPICA Dome C ice core. Filled circles indicate new data (this work) and hollow squares indicate previously reported data (Vallelonga et al., 2005). The horizontal dashed line indicates a  $\delta D$  value of  $-435\text{‰}$ ; below this temperature Pb and Ba concentrations increase rapidly. The  $\delta D$  data are from Jouzel et al. (2007). Dust concentrations were determined by Coulter counter as reported by Lambert et al. (2008). The accuracies of the Pb and Ba concentrations are described in the main text.

than that from EDC or Coats Land (Planchon et al., 2003). Considering the distribution of Pb isotopic compositions in Antarctic ice samples, two Coats Land samples appear to be anomalously unradiogenic, but these two samples (dated to 1846 AD and 1851 AD) feature very low Pb concentrations and consequently large uncertainties were reported for their Pb isotopic compositions.

The overall trend of the data is consistent with that reported previously, with more-radiogenic Pb signatures during warmer climatic periods and less-radiogenic values during colder climate periods, but there appears to be a substantial level of variability. This is most clearly demonstrated by comparing  $\delta D$ , a paleo-temperature proxy, with  $^{206}\text{Pb}/^{207}\text{Pb}$  isotope ratio (Fig. 4). It is clear that for most climate temperature conditions,  $^{206}\text{Pb}/^{207}\text{Pb}$  values

vary between  $\sim 1.19$  and  $\sim 1.24$ . It is only for  $\delta D$  values below  $-432\text{‰}$  that the distribution of  $^{206}\text{Pb}/^{207}\text{Pb}$  values narrows, decreasing consistently within the smaller range of values between 1.19 and 1.21. These paleotemperatures correspond to the coldest climatic conditions, when dust fluxes are at their maximum.

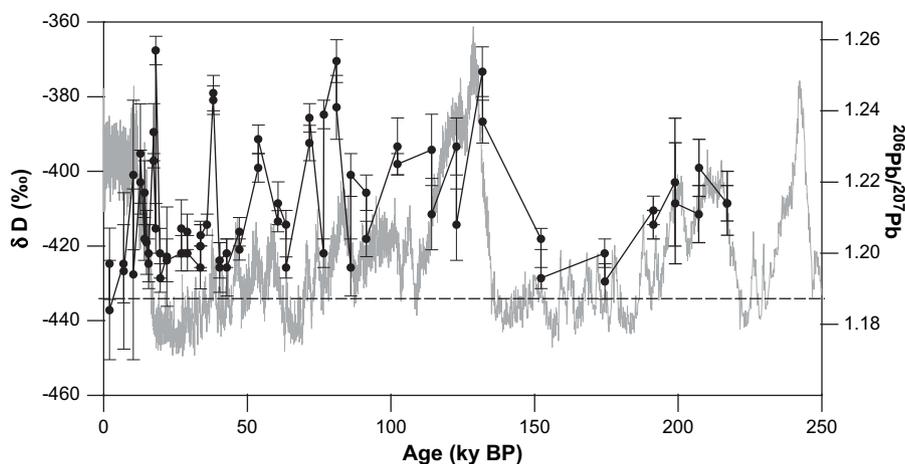
#### 4.2. Australian PSA samples

Lead isotopic compositions in PSA samples from Australia display intermediate values, not dissimilar to Southern South American PSAs but less-radiogenic than the Antarctic McMurdo-Erebus volcanic province. Australian PSA data are reported in Table S2 (supplemental data). As shown in Fig. 5a, the HF-digested samples ( $^{206}\text{Pb}/^{207}\text{Pb}$ : 1.175–1.195,  $^{208}\text{Pb}/^{207}\text{Pb}$ : 2.49–2.53), representing the large-grained silicate fraction, can be distinguished from the extracted fine-fraction of these samples ( $^{206}\text{Pb}/^{207}\text{Pb}$ : 1.19–1.24,  $^{208}\text{Pb}/^{207}\text{Pb}$ : 2.47–2.55) which are more radiogenic, exhibiting greater  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$  values. This is most extreme in the case of the two samples from Brachina Gorge ( $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.24$ ,  $^{208}\text{Pb}/^{207}\text{Pb} \sim 2.55$ ), which have quite radiogenic values. This Th-rich signature is compatible with Pb isotopic compositions reported for source rocks in Northern Australia (Bollhöfer et al., 2006). Of the Australian PSA samples only the extracted fine-fraction data have been used to evaluate Antarctic dust provenance.

#### 4.3. Other PSA samples

With the exception of Antarctic PSA samples, Pb isotopic compositions of the PSA regions are well constrained and show only minor variations (Table S3, supplemental data). Southern African samples display relatively unradiogenic values ( $^{206}\text{Pb}/^{207}\text{Pb}$ : 1.194–1.200,  $^{208}\text{Pb}/^{207}\text{Pb}$ : 2.452–2.463) while Southern South American samples ( $^{206}\text{Pb}/^{207}\text{Pb}$ : 1.193–1.199,  $^{208}\text{Pb}/^{207}\text{Pb}$ : 2.460–2.477) overlap with those of New Zealand which have more-radiogenic values ( $^{206}\text{Pb}/^{207}\text{Pb}$ : 1.197–1.208,  $^{208}\text{Pb}/^{207}\text{Pb}$ : 2.470–2.484). These samples are generally similar in  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio to those from Australia, but with lower  $^{208}\text{Pb}/^{207}\text{Pb}$  values, indicating more Th in Australian source rocks. The Antarctic samples display quite large variations in Pb isotopic composition even though they were sampled within a relatively small area between Ross Island, the adjacent Dry Valleys and Northern Victoria Land (NVL). Dividing the samples according to their East–West locations, the three Pb isotopic signatures observed are: 1) a pure volcanic signature ( $^{206}\text{Pb}/^{207}\text{Pb}$ : 1.251–1.262,  $^{208}\text{Pb}/^{207}\text{Pb}$ : 2.488–2.518) corresponding to the McMurdo-Erebus volcanic field [Corroborated with Sr and Nd isotopic data (Sims et al., 2008)]; 2) a less-radiogenic signature from Northern Victoria Land ( $^{206}\text{Pb}/^{207}\text{Pb}$ : 1.174–1.189,  $^{208}\text{Pb}/^{207}\text{Pb}$ : 2.467–2.475) similar to those of Southern South America and Australia which has not been previously identified, and 3) a Th-rich signature ( $^{206}\text{Pb}/^{207}\text{Pb}$ : 1.197–1.199,  $^{208}\text{Pb}/^{207}\text{Pb}$ : 2.523–2.606) from Pearse Valley, similar to that reported by De Paolo et al. (1982) for rocks from Enderby Land in East Antarctica.

Lead isotopes in fine-grained and coarse-grained PSA samples do indicate some minor variation in isotopic composition, which may be attributable the specific characteristics of the sampling locations. Only two Southern South American and one Antarctic sample are available for comparison, with divergent trends: the two Southern South American fine-grained samples have less-radiogenic signatures compared to the bulk samples, while for Antarctica the fine-grained PSA sample has a more-radiogenic signature compared to the bulk sample. These different trends can be explained by considering the different conditions in which these samples were collected. In Southern South America, the fine-grained fraction would be more susceptible to anthropogenic Pb



**Fig. 2.** Variations in  $^{206}\text{Pb}/^{207}\text{Pb}$  isotope ratios and  $\delta\text{D}$  in EPICA Dome C ice core. The horizontal dashed line indicates a  $\delta\text{D}$  value of  $-435\text{‰}$ ; below this temperature Pb and Ba concentrations increase rapidly. The  $\delta\text{D}$  data are from Jouzel et al. (2007). All uncertainties are 95% confidence intervals.

from leaded petrol and industrial emissions, which is reasonably unradiogenic (Bollhöfer and Rosman, 2000). In the Victoria Land region of Antarctica, the fine-grained fraction would be more susceptible to influence from local, highly radiogenic, Pb sources such as Mount Erebus. Coarse-grained PSA samples (SA1, SA3, A7) have not been used to evaluate Antarctic dust provenance because they cannot be considered representative of the  $<5\ \mu\text{m}$  diameter dust particulates found in Dome C ice.

## 5. Discussion

### 5.1. Sources of Pb in pre-industrial Antarctic ice

Hinkley (2007) recently reviewed the sources of natural Pb in Antarctica based on Pb isotopic compositions reported in Taylor Dome, EDC, Law Dome, Victoria Land and Coats Land. It was reported that in most of these locations, dust inputs (usually based on Ba concentrations) could only account for a minor proportion of total Pb in the ice, and that the remainder of the Pb originates from a radiogenic source compatible with the isotopic signatures of worldwide ocean volcanoes and some Antarctic volcanoes. Of the samples used to formulate this argument, the EDC samples show the greatest proportion of Pb from dust. This argument is supported further by the Pb isotopic compositions observed in Antarctic ice from all locations studied – Pb signatures do not vary from a broad mixing line between PSA signatures of mineral dust and McMurdo-province volcanic signatures (Fig. 5b). Rosman et al. (1998) reported the only pre-industrial Antarctic ice sample for which an extreme deviation from this trend was observed: ice from Law Dome with a markedly high  $^{208}\text{Pb}/^{207}\text{Pb}$  ratio of 2.784 indicative of a Th-rich source such as those identified in Antarctica [Pearce Valley (this work); Enderby Land (De Paolo et al., 1982)] or Australia (Bollhöfer et al., 2006).

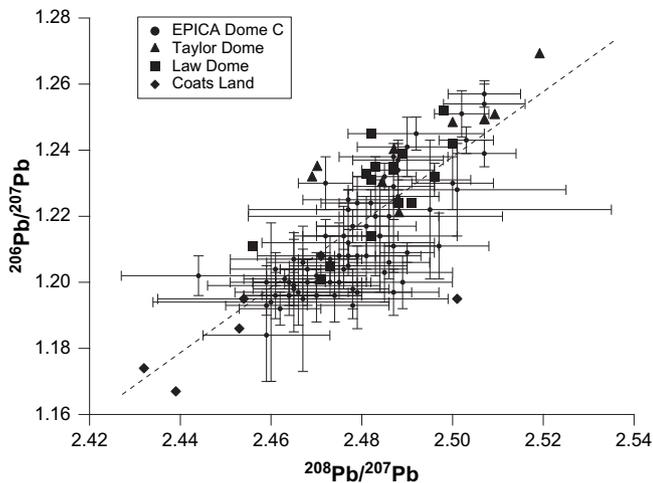
As with Sr and Nd, variations in Pb isotopic compositions of different geographical regions of dust production potentially allow the application of this element for dust provenance studies. Hinkley (2007) identified a potential limitation of the Pb isotopic system for dust provenance, in that the Pb found in Antarctic ice does not originate solely from dust but also from quiescent volcanism. This is evident in the distribution of Pb isotopes in Antarctic ice in Fig. 3, along a mixing line with a radiogenic volcanic Pb end-member and a less-radiogenic dust-Pb end-member. Considering that different locations in Antarctica display different proportions of volcanic Pb and dust Pb, those locations which display the greatest proportion

of dust Pb are likely to offer the best opportunity for dust provenance using Pb isotopes. When volcanic Pb is present in Antarctic ice, the Pb isotopic composition determined reflects a mixture of the dominant source (or mixture of sources) of dust and the characteristic radiogenic signature of volcanic Pb. While this does not inhibit the evaluation of the Pb isotopic signature of the predominant Antarctic dust source in EDC samples, it does limit the potential for identifying minor dust sources, particularly during interglacial climate phases when dust-Pb concentrations are low. Minor dust sources can only be identified as a deviation from the predominant mixture of volcanic and dust-Pb sources, requiring that the isotopic signature of the minor dust source is distinct from that of the predominant dust source and/or that the analytical precision is sufficient to resolve variations in Pb isotopic composition from one ice sample to the next. Currently, the required analytical precision cannot be achieved for the low Pb concentrations found in Antarctic ice, but new analytical techniques such as multiple ion collectors may lead to advancements in this field (Wieser and Schwieters, 2005). In Sections 5.4 and 5.5, the distinctiveness of the Australian and Antarctic PSA signatures are considered in terms of identifying minor dust contributions to Antarctica.

### 5.2. Glacial–interglacial changes in Pb isotopic compositions

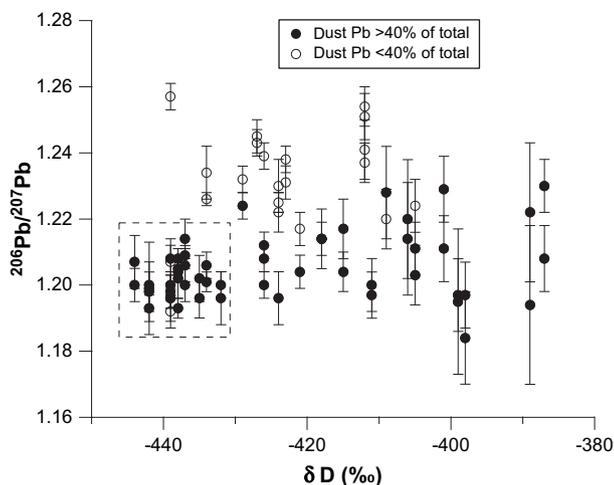
Variability in the Pb isotopic composition of Antarctic dust is primarily dependent on dust concentrations that, in turn, are related to changes in climate. While the observed Pb isotopic composition results from a combination of volcanic and dust signatures, the overwhelming influence of dust sources during glacial maxima and other cold climatic periods ensures the predominance of dust-Pb signatures which are in correspondence with the isotopic signature of Southern South American PSAs. These periods of high dust concentration are characterized by  $\delta\text{D}$  values less than  $-435\text{‰}$  which is the value corresponding to a sharp increase in dust concentration with decreasing temperature.

The climatic periods characterized by low dust concentrations cannot be distinguished from those corresponding to high dust concentrations on the basis of Pb isotopic compositions. Low dust concentrations occurred during either warm (interglacial or interstadial) temperatures or intermediate/cool (glacial) temperatures for which  $\delta\text{D} > -435\text{‰}$ . Lambert et al. (2008) also observed that the relation between dust and climate is much less sensitive at intermediate and warm temperatures and linked this relation to the



**Fig. 3.** Lead isotopic compositions in pre-industrial Antarctic ice from EPICA Dome C (this work), Coats Land (Planchon et al., 2003), Law Dome (Vallelonga et al., 2002a,b) and Taylor Dome (Matsumoto and Hinkley, 2001). The dotted line indicates a least-squares regression fit for all locations [ $(^{206}\text{Pb}/^{207}\text{Pb}) = 1.009 \times (^{208}\text{Pb}/^{207}\text{Pb}) - 1.285$ ;  $r^2 = 0.63$ ] but is not intended to accurately represent the locations of volcanic (radiogenic) and dust (less radiogenic) mixing-line end-members. All uncertainties are 95% confidence intervals.

movement of westerly atmospheric circulation patterns and reduced extent of Antarctic sea ice. As shown in Fig. 4 and discussed in this section, average  $^{206}\text{Pb}/^{207}\text{Pb}$  values in samples with  $\delta\text{D} > -435\text{‰}$  are statistically indistinguishable from samples corresponding to cold climate phases. The samples corresponding to warmer temperatures have a greater average value and more variability:  $^{206}\text{Pb}/^{207}\text{Pb}$  values average  $1.201 \pm 0.011$  for samples with  $\delta\text{D} < -435\text{‰}$  and  $1.217 \pm 0.034$  for samples with  $\delta\text{D} > -435\text{‰}$  ( $2\sigma$  uncertainties). The greater  $^{206}\text{Pb}/^{207}\text{Pb}$  average observed in samples deposited during warmer temperatures is due to the radiogenic character of volcanic Pb, the inputs of which can be quantified via the sample Pb/Ba ratio. Of the samples corresponding to warm or intermediate climate phases ( $\delta\text{D} > -435\text{‰}$ ), those with



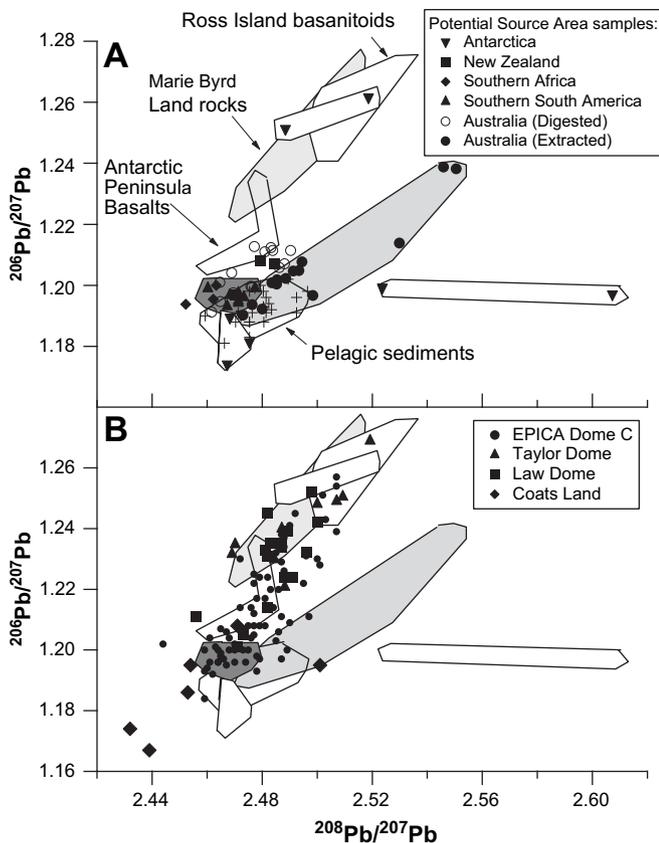
**Fig. 4.** Comparison of  $^{206}\text{Pb}/^{207}\text{Pb}$  isotope ratios with  $\delta\text{D}$  values in EPICA Dome C ice core. Empty circles indicate samples that contain less than 40% dust Pb (Pb/Ba > 0.075). Samples from colder climatic periods (located within the dotted lines) display less variability in  $^{206}\text{Pb}/^{207}\text{Pb}$  compared to samples from warmer periods. The sample with  $\delta\text{D} = -439\text{‰}$  and  $^{206}\text{Pb}/^{207}\text{Pb} = 1.257$  corresponds to an identified volcanic deposition event. The  $\delta\text{D}$  data are from Jouzel et al. (2007). All uncertainties are 95% confidence intervals.

dust-Pb inputs greater than 40% have similar  $^{206}\text{Pb}/^{207}\text{Pb}$  values ( $1.205 \pm 0.020$ ) to the samples from cold climate phases – these samples are represented by filled circles in Fig. 4. The wider ranges of  $^{206}\text{Pb}/^{207}\text{Pb}$  values observed during warmer climate periods suggests greater variability in dust sources at those times. As may be expected, the  $^{206}\text{Pb}/^{207}\text{Pb}$  signature of samples containing mostly (>60%) volcanic Pb is consistently radiogenic irrespective of temperature. While glacial–interglacial variations in the composition of Antarctic dust sources have been suggested by Delmonte et al. (2008) and Lambert et al. (2008), among others, the influence of volcanic Pb during interglacial climate phases inhibits the identification of such variations using Pb isotope signatures.

### 5.3. Sources of dust Pb in Antarctica

As has been recently summarized by Delmonte et al. (2008), ongoing geochemical, geophysical and modelling research suggests Southern South America to be the predominant source of Antarctic dust during glacial climate phases. Lead isotopic signatures in Antarctic ice and PSAs support this contention, based upon the correspondence between the non-radiogenic end-member of isotopic signatures in EDC samples ( $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.19$  and  $^{208}\text{Pb}/^{207}\text{Pb} \sim 2.46$ ) and the Pb isotopic compositions identified in Southern South American samples. While Pb isotopic signatures of some other PSAs do overlap with those of Southern South America, each of these regions can be discounted from consideration as the predominant source of dust supplied to Antarctica: the digested Australian PSA samples can be excluded from consideration because they correspond to coarse-grained particles (predominantly silicates) which are unlikely to be successfully transported to Antarctica. This is confirmed by dust particle sizes in EDC, which have a mode around  $2 \mu\text{m}$  in diameter (Lambert et al., 2008). South African PSAs occupy a restricted range with low  $^{208}\text{Pb}/^{207}\text{Pb}$  values < 2.46 (indicating Th-depleted basement rock) that cannot uniquely account for the range of Pb isotopic compositions observed in EDC ice ( $^{208}\text{Pb}/^{207}\text{Pb}$  values from 2.44 to 2.49). Similarly, the limited surface area and likely limited scale of dust production would exclude New Zealand from being the predominant source of Antarctic dust (Delmonte et al., 2004), before PSA isotopic signatures are considered. In the case of New Zealand, all samples fall within the field defined by Southern South American PSAs as well as Australia coarse-grained particles, so these sources cannot be distinguished isotopically. The widespread distribution of Pb isotopic signatures in PSAs corresponding to local Antarctic dust sources is discussed in Section 5.5.

While the aforementioned arguments have been applied to compensate for the superposition of Pb isotopic signatures in PSAs from SSA, New Zealand and Southern Africa, there is an ongoing need to accurately quantify the dust fluxes from each region as well as to determine representative Pb isotopic signatures. Only three samples have been measured to represent Southern Africa or New Zealand, which are of utility as an indicative signature but should not be considered a conclusive description of the diverse geologies of these regions (Mackie et al., 2008, p. 16). In a similar fashion, the Southern South American PSA samples analysed here do not represent recently identified regions of dust production such as the Puna-Altiplano Plateau reported by Gaiero (2007) and so may not be considered representative of all dust sources within that continent. The discrepancy in Pb isotopic signatures between the Southern South American PSA samples reported here and South Atlantic Ocean pelagic sediments (Chow and Patterson, 1962) is another indication that further work is required to reliably characterize PSA sources in Southern South America. Mixing of PSAs from different regions should also be considered: for example Marx et al. (2005) showed that substantial quantities of dust deflated



**Fig. 5.** A: lead isotopic compositions in PSA samples from the Southern Hemisphere (this work) and other proxies of dust and volcanic Pb signatures. Also shown are South Atlantic and South Pacific Ocean pelagic sediments (Chow and Patterson, 1962), Ross Island basanitoids (Sun and Hanson, 1975), Marie Byrd Land rocks (Hart et al., 1997) and Antarctic Peninsula basalts (Hole et al., 1993). Error bars for the PSA samples reported here are smaller than the image symbols shown. B: lead isotopic compositions of Antarctic firn and ice core samples from Fig. 3 compared to the PSA fields shown in Fig. 5a.

from Australia are transported to New Zealand and so may mix with dust deflated from New Zealand, or alter the signature of PSA samples collected from New Zealand. Recent modelling (Li et al., 2008) also indicates some level of mixing of continental dust sources in the Southern Hemisphere. Ultimately, attempts should be made to compare regional PSAs with aerosols collected in remote locations of the Southern Ocean as well as Antarctica, to more accurately characterize the dust transported to Antarctica.

#### 5.4. Australian dust in Antarctica

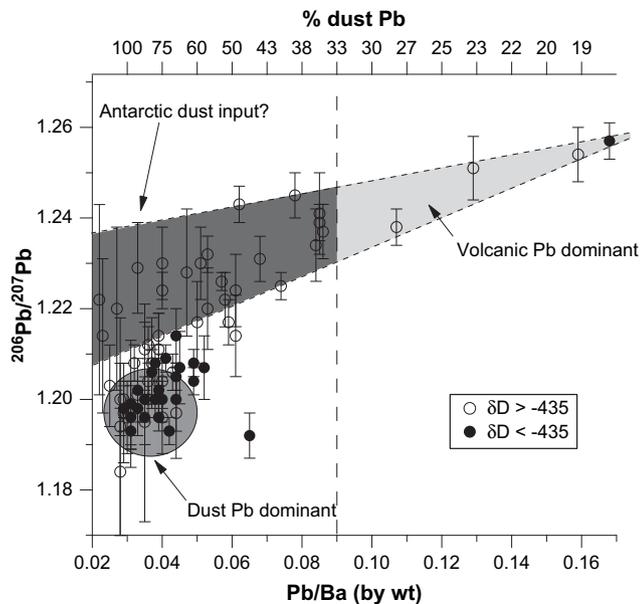
Recent geochemical and modelling studies indicate that Eastern Australia may be a non-trivial source of dust deposition during interglacial climate phases. Revel-Rolland et al. (2006) showed that Sr and Nd isotopic compositions of Eastern Australian PSA samples are similar to Sr and Nd signatures in interglacial ice from Vostok and EDC, while modelling by Li et al. (2008) also indicates the importance of Australia as a source of dust to Antarctica as well as the Pacific Ocean and Eastern sector of the Southern Ocean. The fine fraction of Australian PSAs (here determined by chemical solubility rather than size-filtering) available to weathering and aeolian deflation are characterized by radiogenic  $^{208}\text{Pb}/^{207}\text{Pb}$  ratios that are offset from the bulk of the Pb signatures identified in EDC ice. The orientation of the majority of EDC samples (66 of 74) away from the Australian PSA field suggests that Australian dust is not the main

component of dust deposited in Antarctic ice. Some Australian PSAs overlap with Southern South American PSAs as well as signatures in some EDC samples, allowing the possibility of Australian dust as a minor component, but as discussed in Section 5.1 this possibility cannot be quantified with the available analytical precision because these samples cannot be distinguished isotopically from the bulk of EDC samples. Of those EDC samples that display an isotopic composition overlapping with the Australian PSA field (8 of 74), five of these correspond to interglacials (Holocene: 6.93, 14.91, 15.61, 15.63 ky BP and Eemian: 114.14 ky BP) and three correspond to the LGM (19.66, 21.97, 29.09 ky BP), precluding any systematic climate-related influence. Given the relative similarity of Australian and Southern South American PSA signatures, greater analytical precision will be required to allow Pb isotope-based elucidation of Australian dust inputs to central Antarctica during the most recent glacial cycles.

#### 5.5. Local sources of dust in Antarctica

The Pb isotopic signatures observed in Antarctic PSAs cover a broad range and can be categorized in three types previously described in Section 4.3 – radiogenic (McMurdo province), relatively unradiogenic (NVL) and Th-rich (Pearse valley). As noted in Section 5.3, relatively few samples are available to define these PSA fields so more extensive sampling will be required to corroborate our findings. While EDC samples show no influence from the Th-rich Pearse valley signature, which would be readily observed by an enhanced  $^{208}\text{Pb}/^{207}\text{Pb}$  ratio, the influence of the relatively unradiogenic NVL signatures in the samples cannot be dismissed on isotopic arguments alone. While Delmonte et al. (2004) noted that “geochemical and atmospheric circulation parameters support the contention that dust from the Antarctic Dry Valleys is unlikely to be deflated in sufficient quantity, or transported efficiently enough, to account for a substantial proportion of the dust flux observed in central Eastern Antarctica”, evidence exists for minor contributions of dust from local Antarctic sources to central Antarctica (Lanci et al., 2008). The distribution and geochemical characteristics of this Antarctic PSA source with such an unusually unradiogenic Pb signature demand further investigation.

An evaluation of  $^{206}\text{Pb}/^{207}\text{Pb}$  and Pb/Ba ratios in the EDC samples does indicate that dust of local Antarctic origin could be present as a minor component. This data is presented in Fig. 6, with the Pb/Ba value used to indicate the ratio of total Pb to dust Pb (which can be calculated from Ba concentrations) and the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio indicating Southern South American dust sources (low values  $\sim 1.20$ ) or McMurdo-province volcanic Pb sources (values  $> 1.24$ ). The trend of the data is toward greater  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios with increasing Pb/Ba ratio, which supports the model advanced by Hinkley (2007) in which radiogenic volcanic Pb is entrained in Antarctic snow as a physically distinct matrix to dust particles which contain also Ba, Al and other major and minor elements of the upper crust. Samples containing Pb/Ba ratios  $> 0.09$ , which corresponds to a dust-Pb fraction of 33%, always feature radiogenic Pb signatures  $> 1.23$  while a broader range of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios was found in samples with lower Pb/Ba ratios. A concentration of samples around crustal Pb/Ba ratios of 0.025–0.045 and  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios of 1.19–1.21 indicate the predominant source of dust Pb to EDC, which is compatible with PSA signatures from Southern South America. The EDC samples which indicate a  $>50\%$  input from such a local Antarctic dust source correspond to interglacial periods (10.27, 12.82, 114.12, 122.81 ky BP) or other phases of minimal dust flux (38.16, 102.25, 198.89 ky BP) at EDC. Only one of the samples featuring a  $>50\%$  contribution from local Antarctic dust corresponds to a period of enhanced dust flux, in this case MIS 4.2 (53.83 ky BP). It is not possible to apply a similar evaluation to samples from Taylor Dome or Law Dome because they



**Fig. 6.** Comparison of  $^{206}\text{Pb}/^{207}\text{Pb}$  isotope ratios with Pb/Ba ratios in EPICA Dome C ice core. The samples are differentiated by temperature from colder (filled circles) to warmer (empty circles) climate phases, based on the  $\delta\text{D}$  value below which Pb and Ba concentrations were observed to increase rapidly ( $-435\%$ ). Samples with greater Pb/Ba and  $^{206}\text{Pb}/^{207}\text{Pb}$  values reflect a dominant volcanic Pb source. Samples in the grey circle, with lower Pb/Ba and  $^{206}\text{Pb}/^{207}\text{Pb}$  values, reflect a dominant dust-Pb source. The dotted vertical line corresponds to a Pb/Ba ratio of 0.09, at which point dust Pb accounts for only 33% of total Pb in the ice samples. The presence of samples with low Pb/Ba but high  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios suggests a possible local Antarctic dust source. All uncertainties are 95% confidence intervals.

often display Pb/Ba ratios greater than 0.09 and so their isotopic signatures are dominated by volcanic Pb.

EDC samples with Pb/Ba ratios of 0.02–0.04 have dust-dominated compositions, but some samples within this Pb/Ba range also feature radiogenic  $^{206}\text{Pb}/^{207}\text{Pb}$  signatures that can only be explained by local Antarctic dust sources such as that characterized by the McMurdo-province PSA samples. This supports the findings of Lanci et al. (2008) who used isothermal remanent magnetization to identify highly magnetic dust, such as those from local Antarctic soils or volcanic terrains, in EDC ice during interglacial phases. It is important to distinguish between the two Antarctic, radiogenic Pb signatures discussed here: the first originates directly from quiescent degassing of volcanoes (Antarctic or Ocean Islands), while the second is a dust source (or sources) of radiogenic nature located within Antarctica, in the Antarctic Peninsula – Transantarctic Mountains – Victoria Land area. The deposition mechanism of Pb produced from quiescent volcanism could consist of direct deposition on surface snow and/or adsorption onto dust particles that are then deposited on surface snow. Variable amounts of adsorption of quiescently degassed Pb may explain the different proportions of volcanic and dust Pb found in EDC ice within each distinct climate phase.

## 6. Conclusions

Lead isotopic data presented here support the contention that Southern South America is an important source of dust deposited in Antarctic ice and indicate that during interglacial periods and other times of minimal dust flux, Antarctica may be a non-negligible dust source. These data suggest that Australian PSAs are not a major component of Antarctic dust but do not allow a quantifiable evaluation, due to the partial overlap of Australian and Southern South

American PSA signatures as well as the persistent influence of volcanic Pb. Partial overlaps exist for the Pb isotopic signatures of Southern South American, Australian, Southern African and New Zealand PSAs, demanding better evaluations of those sampling locations that can be considered credible dust sources. Three different geochemical signatures can be observed in Antarctic PSA samples, which can be related to the McMurdo volcanic province, a Th-rich source associated with Pearce Valley and Enderby Land, and a relatively unradiogenic source from Northern Victoria Land that has not been previously observed. Improved analytical precision of Pb isotopes in Antarctic ice will be required to study variations in Pb isotopic compositions during interglacials and to further investigate climate-related variations in Pb isotopes. The location of a drilling site in Antarctica with minimal isotopic interference from volcanism would also allow improved evaluation of Antarctic dust provenance by Pb isotopes.

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## Appendix. Supplementary information

Supplementary information related to this article can be found at doi: 10.1016/j.quascirev.2009.06.019.

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