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## Isotopic analysis of snow from Dome C indicates changes in the source of atmospheric lead over the last fifty years in East Antarctica

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(Article begins on next page)

1	Sources and recent trend of atmospheric lead over the last fifty years
2	by isotopic measurements on snow from Dome C, East Antarctic Plateau
3	
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## 10 Abstract

Lead (Pb) concentration and Pb isotope ratios have been determined in 109 snow pit samples 11 collected at Dome C, in the East Antarctic Plateau, and corresponding to the period 1971-2017. The 12 Pb concentration was 8.2  $\pm$  1.0 pg g<sup>-1</sup> (mean  $\pm$  95%-confidence interval), with a decreasing trend 13 from early 1990s (the median Pb concentration halved from 9.0 pg g<sup>-1</sup> in 1970-1980 to 4.4 pg g<sup>-1</sup> in 14 2010-2017). The  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{208}\text{Pb}/^{207}\text{Pb}$  ratios were 2.419  $\pm$  0.003 and 1.158  $\pm$  0.003 (mean and 15 95%-confidence interval), respectively. The temporal variations of Pb isotopic composition from 16 17 1970 to mid-1990s reflect the changes in the consumption of Pb-enriched gasoline in the Southern Hemisphere, whereas the subsequent increase of the Pb isotope ratios is ascribed to a shift toward 18 the natural isotopic signature. Accordingly, the anthropogenic Pb decreased from  $61 \pm 3$  % in 1980-19 1990 to  $49 \pm 10$  % in 2010-2017. The measured ratios suggest that Australia has been a significant 20 21 source of anthropogenic Pb to Antarctica, even in recent times. Differences and similarities among Pb content and its isotopic composition in various sites across Antarctica have been explored by 22 principal component analysis, finding that the altitude and the distance from the coast significantly 23 24 affect the Pb content but not its isotopic signature.

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26 Keywords: lead; isotopic ratios; snow; Antarctica; pollution.

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#### 30 1. Introduction

Lead (Pb) is a toxic trace element, whose natural biogeochemical cycle has been strongly 31 affected by anthropogenic activities since ~5000 years ago (Weiss et al., 1999). In particular, Pb has 32 been massively introduced into the atmosphere by mining and smelting activities, as well as by the 33 use of leaded gasoline in the second half of the 1900s, before its phase-out at the end of the century 34 35 (Oudijk, 2010). These anthropogenic inputs overlapped the natural occurrence of Pb, due to rock and soil dusts, ocean salt and volcanic emissions. Lead associated to fine particles can be 36 37 transported over long distances by the atmospheric circulation, reaching the most pristine regions on Earth, like the Arctic and Antarctica. Here, it is accumulated in snow by dry and wet 38 precipitationdeposition, so its determination in well-dated snow and ice samples can provide a 39 proxy of historical changes of both natural and anthropogenic Pb in the atmosphere. In particular, 40 41 the use of Pb isotope ratios for source assessment and to investigate transport pathways have been successfully applied in many polar studies (Ardini et al., 2019). In fact, Pb has four stable isotopes, 42 <sup>204</sup>Pb, <sup>206</sup>Pb, <sup>207</sup>Pb and <sup>208</sup>Pb, and the last three are formed by radioactive decay of <sup>238</sup>U, <sup>235</sup>U and 43 <sup>232</sup>Th, respectively. The relative abundance of Pb isotopes in ores is, therefore, related both to the 44 45 abundance of their parent nuclide at the moment of the ore formation and to the age of the rock. Consequently, there is a relatively large difference between the isotopic composition of Pb from 46 various ore deposits (Sangster et al., 2000), so its isotopic signature can be an efficient tool for 47 48 tracing sources of pollution and the movement of air-masses on a global scale (Bollhöfer and Rosman, 2001, 2000). 49

The first measurements of Pb isotopes in Antarctic snow were performed by Rosman et al. (1994), who analysed four surface snow blocks collected in 1983-84 along a transect from the Dumont d'Urville (DDU) station to a site 433 km inland and at the geographic South Pole, and in a single sample of ancient ice obtained at Dome C. The results highlighted the occurrence of anthropogenic Pb, even in samples containing 2.3 pg g<sup>-1</sup> Pb, and indicated South America as a likely source of the anthropogenic Pb in Antarctic snow dated from the 1980s. Emission from 56 Australia was also proposed as an alternative explanation for a site 33 km from DDU, and the presence of significantly less radiogenic Pb in the snow adjacent to the DDU and Amundsen-Scott 57 stations was ascribed to local contamination. Following various improvements in the analytical 58 procedures (Chisholm et al., 1995, Vallelonga et al., 2002a), measurements of Pb isotopes were 59 60 carried out on ice and snow from various locations, including Dome C (Rosman et al., 1999, 61 Vallelonga et al., 2005, Vallelonga et al., 2010), Taylor Dome (Matsumoto and Hinkley, 2001), Law Dome (Vallelonga et al., 2002b), Coats Land (Planchon et al., 2003), Victoria Land (Van de 62 63 Velde et al., 2005), Dome Fuji (Chang et al., 2016) and Dome A (Chang et al., 2016). Additionally, a composite record of semi-quantitative Pb isotopes data was reported for various sites across 64 65 Antarctica (McConnell et al., 2014). Some of these studies (Rosman et al., 1999, Matsumoto and Hinkley, 2001, Vallelonga et al., 2005, 2010) discussed the Pb isotopic composition of old ice (~1-66 200 kyr before present) in relation to natural sources and climate changes. It was found that Pb 67 isotopic compositions in Antarctic ice varied with changing climate, with lower <sup>206</sup>Pb/<sup>207</sup>Pb ratios 68 (and higher Pb concentration) during the glacial periods than in the Holocene and the other 69 interglacial climate stages (Rosman et al., 1999, Vallelonga et al., 2005, 2010), although with a high 70 71 level of variability (Vallelonga et al., 2010). Mineral dust and volcanism are the natural sources of 72 Pb in this pre-industrial ice, and regional differences in the isotopic signature can be ascribed to different proportion of these sources (Vallelonga et al., 2005). For example, Pb from Dome C is 73 74 generally less radiogenic than that from Taylor Dome, due to greater proportions of dust. In fact, dust accounts for 70% of Pb in Dome C ice (Vallelonga et al., 2005), but only a few percent in most 75 76 samples from Taylor Dome, where the main source of Pb is represented by emissions from quiescent volcanoes (Matsumoto and Hinkley, 2001). Concerning the origin of the mineral dust, the 77 78 southern part of South America was proposed as the major source of dust in interglacial periods, although a partial overlap with Australian potential source areas was observed (Vallelonga et al., 79 2010). Moreover, local sources were found to be non-trivial contributors (Vallelonga et al., 2010). 80

Other studies focussed on the Pb pollution history, well reconstructed by isotopic 81 measurements on ice cores and snow dating back to the beginning of the industrial era (Vallelonga 82 et al., 2002b, Planchon et al., 2003, Van de Velde et al., 2005, McConnell et al., 2014, Chang et al., 83 2016). Isotopic evidence of Pb pollution in Antarctica as early as the 1880-90s was first observed at 84 Law Dome (Vallelonga et al., 2002b), Coats Land (Planchon et al., 2003) and Victoria Land (Van 85 86 de Velde et al., 2005), and attributed to mining and smelting of non-ferrous metal ores at Broken Hill (Australia) and, at a minor extent, to coal combustion. The subsequent pollution events tracked 87 88 by Pb isotopic ratios were linked to the rise and fall in the use of alkyl-Pb additives in gasoline in the Southern Hemisphere, which occurred in the second half of 20th century (Oudijk, 2010). These 89 90 events were highlighted by an increase in the concentration and crustal enrichment of Pb (usually measured as Pb/Ba ratio) in the snow/ice, and a concomitant decrease in the 206Pb/207Pb ratios, with 91 marked differences among the sites both in the timings of maxima and in the isotopic values. 92 Concerning the sources of the anthropogenic Pb due to gasoline consumption, Vallelonga and co-93 workers (2002b) observed that the 206Pb/207Pb ratios measured at Law Dome in samples dated 94 between 1950 and 1970 are compatible with inputs of alkyl-Pb from Australia and New Zealand, 95 96 while the higher Pb isotopic ratios observed in the late 1970s and

97 1980s would suggest increased influence of gasoline Pb emissions from countries in the northern part of South America, such as Brazil. Similar conclusions were reported for Coats Land 98 99 (Planchon et al., 2003) and Victoria Land (Van de Velde et al., 2005), explaining the differences among the sites by the substantial changes in the relative contributions of these two source regions. 100 More recently, McConnell et al. (2014) analysed a composite record of semi-quantitative 101 <sup>206</sup>Pb/<sup>207</sup>Pb ratios across Antarctica (9 ice cores, collectively spanning from 1850-2010), suggesting 102 103 that southern Australia was responsible for the introduction of Pb pollution into Antarctica at the end of the 19th century, remaining a significant source until (at least) 2010. Conversely, Chang et 104 al. (2016) assigned to northern South America (Chile and Argentina) the origin of the Pb pollution 105

in snow samples dated from mid-1980s to mid-1990s, collected at the central East Antarctic plateau(Dome Fuji and Dome A).

In this work, a record of Pb isotope ratios has been obtained by the analysis of 109 snow 108 samples collected at Dome C and covering the period from 1970 to 2017. The obtained data are 109 presented and discussed with the aim of: (a) providing updated information on the Pb pollution 110 111 trend in the last fifty years (the more recent ones ends at 2010), especially to discriminate between "steady-state" and "decrease" trends in the last decade; (b) contributing to the source assessment of 112 113 the atmospheric Pb reaching Antarctica, as a tracer of the mineral dust (Grouset and Biscaye 2005); 114 (c) evaluating the anthropogenic-to-natural Pb ratio and its temporal variation, to be compared to 115 similar estimations for other Antarctic sites.

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## 117 2. Experimental

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119 2.1 Sample collection

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121 The samples were collected in December 2017 at Dome C, East Antarctic Plateau 122 (elevation: 3233 m a.s.l.; 1100 km from the Adelie Land coast; Supporting Information, Figure S1), in a site (75.052° S; 123.580° E) 5-km far from the Italian-French Concordia station, and out from 123 124 its influence according to the prevailing SSW wind direction. A continuous series of 109 snow samples was obtained from the wall of a 4-m-deep pit, by horizontally inserting 50 mL 125 126 polypropylene graduated tubes, at about 3-cm intervals. In order to minimize Pb contamination, the snow pit was hand-dug and, after the digging, the potentially contaminated layer was removed by 127 128 means of a pre-cleaned polypropylene scalpel. Operators wore clean room clothes and the tubes were inserted and removed manually. The sampling tubes had been previously acid-washed (0.05% 129 HNO<sub>3</sub>) and individually checked by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) 130 measurements to exclude any significant Pb contamination. Immediately after the collection, the 131 6

tubes were sealed inside polypropylene bags and stored at -20 °C until analysis. Field blanks wereconcomitantly collected and treated as the samples.

Sample dating was assigned on the basis of parallel measurements of non-sea-salt sulphates,
using the well-identified large volcanic depositions from Mt. Pinatubo in 1992 (Castellano et al.,
2005). The corresponding mean annual accumulation is about 8.4 cm yr<sup>-1</sup> and the samples cover
about fifty years (1971-2017).

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## 139 2.2 Sample preparation and analysis

140

Lead isotopic analysis of snow samples was performed by ICP-MS using a previously 141 reported method (Bazzano et al., 2014, Ardini et al., 2018). Briefly, the samples were allowed to 142 melt in their closed tubes; subsequently, 20.0 g aliquots were acidified with 100  $\mu$ L of HNO<sub>3</sub> and 143 100 µL of HF, left to stand for 24 h, and refrozen. Then, the samples were freeze-dried, redissolved 144 in 200 µL of 0.05% HNO3 solution and introduced into the ICP-MS spectrometer by using the 145 heated torch-integrated sample introduction system (Paredes et al., 2009, Grotti et al., 2013). 146 147 Therefore, the sample volumes were reduced from 20.0 to 0.200 mL, providing a 100-fold 148 preconcentration of Pb. All reagents used were of ultrapure grade quality and the sample preparation was carried out under a laminar flow work area. Procedural blanks were concomitantly 149 150 prepared and analysed exactly as the snow samples, using 20.0 g of ultrapure water. The instrument 151 used (PerkinElmer Elan DRC II) was equipped with a dynamic reaction cell, placed between the ion 152 optics and the mass analyser, which was pressurised with neon to improve the precision by 153 collisional damping (Bandura et al., 2000). Instrumental mass bias was corrected for-by measuring a NIST SRM 981 standard solution (Pb concentration: 5 µg L<sup>-1</sup>) every three samples and applying the 154 155 bracketing external correction method (Vanhaecke et al., 2009). For each sample, twelve replicated measurements were performed with an integration time of 10 s each one, and raw data were 156

157	corrected for the detector dead time (determined according to Neims et al., 2001). Data are		
158	expressed as mean values and 95%-confidence intervals.		
159	9 Lead concentration was estimated by comparing the ion intensity at m/z=208 measured in		
160	each sample to that measured in the bracketing NIST SRM 981 standard solutions.		

161 Sea-salt sulphates were measured by ion chromatography in a parallel sequence of snow 162 samples, at about 3-cm intervals, according to the procedure by Morganti et al. (2007).

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164 2.3. Analytical performances and quality control

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The procedural blank of the procedure was 0.2±0.1 pg g<sup>-1</sup> (n=4), resulting in a method 166 detection limit of 0.3 pg g<sup>-1</sup>, lower than the actual Pb concentration in the samples (Table S1). Field 167 blanks were not significantly different from the procedural ones. Measurements of <sup>208</sup>Pb/<sup>207</sup>Pb and 168 169 <sup>206</sup>Pb/<sup>207</sup>Pb isotopic ratios were characterized by an internal precision in the 0.2-1% range, at the concentration level of the analytical solutions (0.1-3 µg L<sup>-1</sup>). The quality of the Pb isotopic 170 171 measurements was systematically controlled at the beginning and the end of each analytical session, by the analysis of the reference material IRMM CRM 482, for which Pb isotopic data obtained by 172 multi-collector ICP-MS are available (Cloquet et al., 2006). The mean measured values (208Pb/207Pb 173 =  $2.4087 \pm 0.0013$ ,  ${}^{206}Pb/{}^{207}Pb$  =  $1.1305 \pm 0.0005$ , n=26) did not significantly differ from the 174 reference ones ( $^{208}$ Pb/ $^{207}$ Pb = 2.4078 ± 0.0004,  $^{206}$ Pb/ $^{207}$ Pb = 1.1311 ± 0.0001), showing an external 175 176 precision of 0.12% and an accuracy better than 0.05%.

- 177
- 178 3. Results and discussion
- 179
- 180 *3.1. Lead concentration*



#### Lead concentration values are reported in Table S1 and compared to data obtained for other

Figure 1. (a) Pb concentration, (b) <sup>208</sup>Pb/<sup>207</sup>Pb and (c) <sup>206</sup>Pb/<sup>207</sup>Pb values in recent snow from
various Antarctic sites: Dome C (this work), Dome Fuji (Chang et al., 2016), Dome A (Chang et al.,
2016), Law Dome (Vallelonga et al., 2002), Victoria Land (Van de Velde et al., 2005) and a
composite Pb record from 16 ice cores across Antarctica (McConnell et al., 2014). See Figure S1
for locations.

218 In fact, Pb in the pre-industrial ice largely derived from natural sources, such as crustal dust 219 and volcanic activity (Matsumoto and Hinkley, 2001; Vallelonga et al., 2005). However, the occurring of industrial and mining activities in the Southern Hemisphere caused a significant 220 221 increase of Pb inputs to Antarctica since the second half of the 19th century, leading to the values observed in recent snow. The Pb concentration in Dome C is in a good agreement with values found 222 223 in other Antarctic sites, mainly at comparable altitude (see section 3.4), highlighting the homogeneity of the distribution of atmospheric Pb over Antarctica, as already observed (McConnell 224 et al., 2014; Chang et al., 2016). The temporal trend of Pb concentration is illustrated in Figure 2. 225



Commentato [b1]: immagine (a) sopra il testo

- 243 (b)
- 244

Figure 2. Temporal trend of Pb concentration in snow from Dome C. (a) single data and five-point
running average; (b) boxplots of data grouped by decades.

The five-point running average shows concentration peaks in the late 1970s and in the early 247 248 1980s, as well as around 1990, in good agreement with the temporal trend observed at Dome Fuji 249 (Chang et al., 2016). Moreover, the pattern is consistent with that reported for other Antarctic sites, 250 with differences in the peaks position which can be attributed both to variations in the atmospheric 251 processes (transport, deposition) and different contributions of anthropogenic and natural Pb from South America, Australia and local sources (Chang et al., 2016, Li et al., 2008, Van de Velde et al., 252 253 2005). From the early 1990s onward, a gradual decrease in the Pb concentration was observed, as 254 highlighted by grouping data by decades (Figure 2b). For example, the median Pb concentration decreased from 9.0 pg g<sup>-1</sup> in 1970-1980 to 4.4 pg g<sup>-1</sup> in 2010-2017. This trend is in good agreement 255 with the results by Chang et al. (2016), whereas McConnell et al. (2014) reported a persistent Pb 256 257 concentration since 1980s, without a significant decreasing trend until 2010. By considering the 258 global anthropogenic input to Antarctica, the observed decrease over the last decades can be 259 ascribed to the reduction of Pb release into the environment after the ban of the Pb-enriched gasoline in many southernmost countries of the Southern Hemisphere (New Zeeland in 1996, Brazil 260 in 1997, Argentina in 1998, Chile in 2001, Australia in 2002 and South Africa in 2006) and the 261 262 reduction of emission of toxic elements from copper (Cu) production activities in Chile (Chang et al., 2016, McConnell et al., 2014). Nevertheless, the effect of anthropic activities on Antarctica 263 environment continue to be evident, and even the Pb concentration in the more recent samples (2.1-264 7.9 pg g<sup>-1</sup> in 2015-17) is still one order of magnitude higher than the natural background (0.2 pg g<sup>-1</sup> 265 in Holocene ice from Dome C (Vallelonga et al., 2010). 266

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268 3.2. Temporal variation of Pb isotopic ratios

Lead isotopic ratios and their uncertainties are reported in Table S1. Values of <sup>208</sup>Pb/<sup>207</sup>Pb 270 and  ${}^{206}Pb/{}^{207}Pb$  were 2.419 ± 0.003 and 1.158 ± 0.003 (mean and 95%-confidence interval, n=109), 271 respectively. These values are significantly lower than the natural ratios measured at Dome C 272 (2.478 and 1.210, respectively, Vallelonga et al., 2005), thereby highlighting the anthropogenic 273 274 contribution to the Pb deposited in Antarctica over the last 50 years. Data are in good agreement with previous studies (Figure 1b,c). For example, the median value of the <sup>206</sup>Pb/<sup>207</sup>Pb ratio (1.158) 275 276 is very close to those reported for comparable periods at Fuji Dome (1.156, Chang et al., 2016), 277 Dome A (1.157, Chang et al., 2016) and Law Dome (1.157, Vallelonga et al., 2002), and slightly lower than that obtained at Victoria Land (1.166, Van de Velde et al., 2005) and by the analysis of 278 279 the composite record of semi-quantitative values (1.171, McConnell et al., 2014).

The temporal trend of <sup>206</sup>Pb/<sup>207</sup>Pb ratio is displayed in Figure 3a (analogous trend was
 obtained for <sup>208</sup>Pb/<sup>207</sup>Pb, Figure S2).



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## **(b**)

- **Figure 3**. Temporal trend of  ${}^{206}Pb/{}^{207}Pb$  isotopic ratio in snow from Dome C. (a) single data with
- *associated uncertainty and five-point running average; (b) boxplots of data grouped by decades.*

A sharp increase from the beginning to the end of 1970s may be observed, with the ratio 302 changing from about 1.12 to 1.18. It was followed by an abrupt drop to less radiogenic values 303 304 during the 1980s, concomitantly with the Pb concentration peaks in that very period (Figure 2a). From the end of 1980s, the Pb isotopic ratio raised again reaching the running average of 1.18 and 305 then it has stabilized at a value of  $1.167 \pm 0.005$  (mean and 95%-confidence interval, n=41) in 306 307 2000-2017 (Figure 3b). Similar temporal trends (Figure S3) were recorded at Dome Fuji and Dome A (Chang et al., 2017), as well as in certain ice cores analysed by McConnell et al. (2014), such as 308 309 PIG2010 and B40, although the composite record did not show any variation in the ratio between 310 1970 and the end of 1990s.

311 The temporal trend from 1970s to the 2000 can be explained by considering the variations in the consumption of Pb-enriched gasoline in the various regions of the Southern Hemisphere. In fact, 312 Bollhöfer and Rosman (2000) showed that marked differences existed in the Pb isotopic 313 composition of the particulate airborne from different cities in the Southern Hemisphere, as a 314 consequence of the local industrial activities and the different suppliers of the alkyl-Pb additives for 315 the local gasoline. In particular, the two major alkyl-Pb suppliers were Associated Octel (UK), who 316 mainly used Pb ores with low isotopic ratios (Broken Hill type ores, Australia,  $^{208}Pb/^{207}Pb \approx 2.315$ , 317 318  $^{206}$ Pb/ $^{207}$ Pb  $\approx$  1.041, Sangster et al., 2000), and Ethyl Corp. (USA) who mainly used Pb ores with high isotopic ratios (Mississippi Valley type ores, USA, <sup>208</sup>Pb/<sup>207</sup>Pb = 2.528-2.627, <sup>206</sup>Pb/<sup>207</sup>Pb = 319 320 1.339-1.406, Sangster et al., 2000). As a consequence, the atmospheric particulate emitted from cites where the gasoline used was obtained by Broken Hill type ores (the southernmost regions of 321 322 the Southern Hemisphere including Argentina, Chile, Australia and New Zealand) was characterized by lower Pb isotopic ratios than that from cities where the gasoline used was obtained 323 by Mississippi Valley type ores (the north-central regions of South America, such as Brazil). 324 Therefore, the abrupt rise of Pb isotope ratios in the first half of 1970s (Figure 3a) can be ascribed 325 to the quickly increase of the consumption of gasoline in northern South America (mainly Brazil), 326 characterized by more radiogenic isotopic values. On the other hand, since early 1980s, the 327 14 328 consumption of Pb-enriched gasoline in Brazil significantly decreased, while it was unchanged in 329 Argentina and Chile and Australia, where the gasoline (from Broken Hill type ores) was 330 characterised by lower Pb isotopic ratios. This caused a decrease in the isotopic ratios measured in 331 the samples dated 1980-1995. The following rise in the ratios can be explained in different ways. According to Chang et al. (2016), it could be ascribed to the Chilean Cu mining activity. In fact, the 332 Pb ores of Chilean Andes have relatively high isotope ratios  $(^{208}Pb)^{207}Pb = 2.449 - 2.469, ^{206}Pb)^{207}Pb$ 333 = 1.175 - 1.189; Puig, 1988) and the relative contribution of the mining activity in South America to 334 335 the total Pb emission in the atmosphere increased after the phase-out of Pb-enriched gasoline. On 336 the other hand, the increase in the Pb isotopic ratios after mid-1990s could also be due to a decrease 337 of anthropogenic Pb compared to the natural one, which is characterized by more radiogenic values  $(^{208}\text{Pb}/^{207}\text{Pb} = 2.478, ^{206}\text{Pb}/^{207}\text{Pb} = 1.210$ ; Vallelonga et al., 2005), as suggested by a concomitant 338 decrease in the total Pb concentration (Figure 2). Finally, the Pb isotopic ratios after 2000 would 339 seem to indicate that a rather stable situation has been reached, although dispersion of data was 340 significantly higher compared to the previous decades, thereby indicating more pronounced inter-341 annual variations in the atmospheric transport of Pb to Antarctica. 342

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344 3.3. Anthropogenic and natural Pb sources

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346 In order to assess the contribution of possible anthropogenic and natural sources, Pb isotopic data were displayed in a three-isotope plot and compared to reference values (Figure 4). All the 347 measured Pb isotopic ratios are scattered along a straight line ( $R^2 = 0.764$ ), resulting from the 348 mixing of at least two sources. However, the assessment of these sources is not trivial, because of 349 350 the temporal variation mentioned above and the co-linearity of the isotopic data (Ellam, 2010). According to previous studies on Antarctic snow and atmospheric particulate (Van de Velde et al., 351 2005, Bazzano et al., 2015a,b), the measured Pb isotopic ratios may be interpreted according to a 352 two-terms mixing model, with a natural and an anthropogenic end-member. 353

**Commentato [b2]:** Fino a qua non emerge il contributo dell'Australia sui rapporti isotopici, mentre dopo se ne afferma l'importanza.



Figure 4. Three-isotope plot of Pb isotopic ratios in Antarctic snow from Dome C, differentiated by
sample age. Possible natural and anthropogenic sources are also showed (see text for references).

In particular, the natural end-member ( $^{208}Pb/^{207}Pb = 2.478$ ,  $^{206}Pb/^{207}Pb = 1.210$ ) was 371 372 computed by averaging data obtained by the analysis of 30 ice core samples from Dome C and dated 6.9 to 217 kyr before present (Vallelonga et al., 2005). Considering the Pb isotopic signatures 373 of volcanic (208Pb/207Pb = 2.529, 206Pb/207Pb = 1.274; Van de Velde et al., 2005) and crustal 374 (<sup>208</sup>Pb/<sup>207</sup>Pb = 2.469, <sup>206</sup>Pb/<sup>207</sup>Pb = 1.196; Rosman et al., 1999) sources and applying a simple 375 376 binary mixture model, the relative contribution of these sources to the composition of the natural 377 end-member would result 17% and 83%, respectively. This result highlights the major contribution of dust at Dome C compared to other Antarctic sites (e.g. Taylor Dome, see Matsumoto and 378 Hinkley, 2001), as pointed out by Vallelonga et al., (2005). 379

Concerning the anthropogenic end-member, according to the major variations in the sources
discussed above (section 3.2), three periods have been considered: 1970-1980, 1980-2000 and

2000-2017. For the first decade, van de Velde et al. (2005) used the isotopic signature reported in 382 gasoline and aerosol in the Los Angeles Basin the early 1970s (Chow and Johnstone, 1965), 383 384 considered to be representative of gasoline alkyl-Pb additives consumed in the Southern Hemisphere between 1951 and 1981. However, these values resulted to be too radiogenic to explain 385 386 the ratios found in our 1970-1980 samples (Figure 4) and, for the lack of other reference data for 387 that period, we could not set a reliable anthropogenic end-member for those samples. For the period 1980-2000, the mean Pb isotopic signature reported by Bollhoffer and Rosman (2000) for urban 388 389 aerosols in various Southern Hemisphere cities over the period 1994-1999 was used, according to 390 van den Velde et al. (2005). Finally, for the 2000-2017 samples, the anthropogenic signature was 391 deduced from the isotopic composition of Australian lichens and fungi collected between 2000 and 2008 (Wu et al., 2016). In fact, the Pb isotopic signatures of both the Chilean Cu ores and of the 392 atmospheric particulate collected in Brazilian cities between 2005 and 2014 (average <sup>208</sup>Pb/<sup>207</sup>Pb = 393 394 2.44, <sup>206</sup>Pb/<sup>207</sup>Pb =1.17; Mirlean et al., 2005, Gemeiner et al, 2017, Gioia et al., 2017, Khondoker et al., 2018) were more radiogenic than that measured in the most of the Antarctic snow samples dated 395 2010-2017 (Figure 4). More likely, these values can be ascribed to inputs from the Australian 396 397 regions, as suggested by many authors (Revel-Rolland et al., 2006, Li et al., 2008, McConnell et al., 398 2014). In fact, Australian regions have preserved low values of Pb isotopic ratios even after the ban of Pb-enriched gasoline in 2002 (Wu et al., 2016), and they could have contributed to lowering the 399 400 Pb isotopic ratios of the atmospheric particulate reaching Antarctica, respect to the Chilean Cu ore or the natural signature. A possible major influence from South Australia was also suggested by 401 measurements of <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratio in surface snow samples collected at Dome C on 2006 and 402 2010 (Bazzano et al., 2017). 403

Using these natural and anthropogenic end-members, the proportion of anthropogenic Pb deposited at Dome C was computed. The result is illustrated in Figure 5, where data are grouped by decade. The estimated percentage of anthropogenic Pb was  $54 \pm 3$  % (mean  $\pm$  95%-confidence interval, n=89), slightly decreasing from  $61 \pm 3$  % in 1980-1990 to  $49 \pm 10$  % in 2010-2017.



419 *Figure 5. Estimated percentages of anthropogenic Pb, grouped by decades.* 

These data are in good with the estimations by van den Velde et al. (2005), who calculated an anthropogenic Pb contribution of  $\approx 60\%$  in the Hercules Neve (Victoria Land) snow samples dated between 1986 and 1994. On the other hand, our estimation is in contrast with Chang and coworkers (2016), who reported that more than 90% of the Pb in the snow from the Antarctic Plateau (Dome A and Dome Fuji) is of anthropogenic origin.

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427 3.4. Regional variations

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Antarctica covers an area of 14x10<sup>6</sup> km<sup>2</sup>, wider than Europe and U.S. However, its position in the globe, that keeps it in the centre of the atmospheric transport processes, and its morphological characteristics (e.g. a flat plateau covering a large portion of east Antarctica), make it possible to have analogies among places also very far from each other. Using the data by McConnell et al. (2014), Chang et al. (2016), Planchon et al. (2003), Van de Velde et al. (2005), Vallelonga et al. (2002) and this work, the sampling sites were compared by applying a principal component analysis (PCA). Lead concentrations and <sup>206</sup>Pb/<sup>207</sup>Pb ratios were averaged by grouping the samples by 18



decades and the mean values in each decade were considered as variables, along with altitude and
distance from the coast, while the different sites were set as objects. After autoscaling of data, two
principal components (PCs) were obtained, collectively explaining 73.2% of the total variance of

Figure 6. Principal component analysis results: (a) loading plot; (b) score plot. <u>The sites name are</u>
 <u>colored according their altitude in agree with the chromatic scale shown on the side.</u>

The loading plot (Figure 6a) shows that Pb concentration, altitude and distance are strongly 467 468 correlated between each other, directly loading on the first PC, whereas Pb isotopic ratios load on 469 the second PC and are uncorrelated with the total Pb concentration, altitude and distance. The correlation of Pb concentration with altitude was statistically significant and decreased with time 470 471 (from r=0.910, p<0.0001 in 1970-1980 to r=0.661, p=0.01 in 2000-2010). Considering the temporal trend of Pb concentration discussed above (Figure 2b), this would indicate that the effect of the 472 altitude is stronger when the amount of Pb is high. The correlation with the distance was also 473 significant (r=0.911-0.646, p<0.05), except for the 2000-2010 decade. Similarities and differences 474 475 among the sites are highlighted in the score plot (Figure 6b). Dome C, Dome A and Dome Fuji, located on the East Antarctic plateau above 3000 m a.s.l., show a high similarity, although they are 476 distant about one thousand kilometres from each other. Similarly, the other sites are grouped 477 according to the altitude and the distance from the coast. For instance, Law Dome and Gomez are 478 close in the score plot, although they are on opposite sides of the continent. By looking at the score 479 480 and loading plots together, it can be deduced that the sites at high altitude are differentiated from the others because of a higher Pb concentration. This result is in good agreement with the increase in 481 482 the fallout flux of anthropogenic elements in the Antarctic plateau above 3500 m a.s.l. reported by 483 Ikegawa et al. (1999), reflecting the polar stratospheric precipitation or long-range tropospheric 484 transport from the Southern Hemisphere.

Finally, Dome C, Dome A, Dome Fuji, Law Dome and Coats Land are characterised by
similar scores on the second PC, mainly affected by the <sup>206</sup>Pb/<sup>207</sup>Pb ratios, confirming their similar
isotopic composition.

- 488
- 489 Conclusion

**Commentato [b3]:** Law Dome sembra essere diverso dal gruppo DomeC-DomeA-DomeFuji sulla PC2. Ci sarebbe il sito chiamato THW2010, che è simile a Coats Land

490 This study has presented an updated record of Pb concentration and isotopic ratios in snow samples from the East Antarctic Plateau, providing new insights into the possible sources and 491 492 the temporal trend of Pb atmospheric deposition over the last fifty years. Isotopic data for samples dated from 1970 to mid-1990s reflected the well-known changes in the consumption of Pb-enriched 493 494 gasoline in the Southern Hemisphere, whereas the subsequent increase of the Pb isotope ratios is 495 here ascribed to a shift toward the natural isotopic signature, in agreement with the concomitant decrease of total Pb concentration. According to our estimation, the contribution of anthropogenic 496 497 Pb was  $61 \pm 3$  % in 1980-1990 samples (in excellent agreement with van den Velde et al. 2005), 498 and decreased to  $49 \pm 10$  %- in 2010-2017. Moreover, the measured Pb isotopic ratios suggest that 499 Australia has been a significant anthropogenic source over the last fifty years, as indicated by previous measurements of <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratio (Bazzano et al., 2017). However, for a better 500 assessment of the sources of atmospheric Pb to Antarctica, there is still the need of additional 501 analytical data, including precise measurements of <sup>20X</sup>Pb/<sup>204</sup>Pb ratios using multi-collector ICP-MS 502 (Bazzano et al., 2015b) and more detailed isotopic values for Australian and Southern America 503 potential source areas (Vallelonga et al., 2010). Finally, principal component analysis of data for 504 505 various sites across Antarctica highlighted that the altitude and the distance from the coast 506 significantly affect the Pb concentration, but not its isotopic signature.

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## 508

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