

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

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

**This is the author's manuscript**

*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/1950396> since 2024-01-04T15:17:45Z

*Published version:*

DOI:10.1016/j.chemosphere.2020.126858

*Terms of use:*

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(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  
4 Stefano Bertinetti,<sup>1</sup> Francisco Ardini,<sup>1</sup> Alessia Vecchio<sup>1</sup>, Laura Caiazza<sup>2,3</sup> and Marco Grotti<sup>1,\*</sup>

5  
6 <sup>1</sup> Department of Chemistry and Industrial Chemistry, University of Genoa, Via Dodecaneso 31, 16146, Genoa, Italy

7 <sup>2</sup> Department of Chemistry Ugo Schiff, University of Florence, Via della Lastruccia 3, 50019, Sesto Fiorentino, Italy

8 <sup>3</sup> INFN-Florence, Via Sansone 1, 50019, Sesto Fiorentino, Italy

9  
10 **Abstract**

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

25  
26 **Keywords:** lead; isotopic ratios; snow; Antarctica; pollution.

27 \* Corresponding author. Department of Chemistry and Industrial Chemistry, University of Genoa,  
28 Via Dodecaneso, 31 - 16146 Genoa, Italy. E-mail address: grotti@unige.it (M. Grotti). Phone  
29 number: +39 010 3538708.

30 **1. Introduction**

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

50           The first measurements of Pb isotopes in Antarctic snow were performed by Rosman et al.  
51 (1994), who analysed four surface snow blocks collected in 1983-84 along a transect from the  
52 Dumont d'Urville (DDU) station to a site 433 km inland and at the geographic South Pole, and in a  
53 single sample of ancient ice obtained at Dome C. The results highlighted the occurrence of  
54 anthropogenic Pb, even in samples containing  $2.3 \text{ pg g}^{-1}$  Pb, and indicated South America as a  
55 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  
57 presence of significantly less radiogenic Pb in the snow adjacent to the DDU and Amundsen-Scott  
58 stations was ascribed to local contamination. Following various improvements in the analytical  
59 procedures (Chisholm et al., 1995, Vallelonga et al., 2002a), measurements of Pb isotopes were  
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),  
62 Law Dome (Vallelonga et al., 2002b), Coats Land (Planchon et al., 2003), Victoria Land (Van de  
63 Velde et al., 2005), Dome Fuji (Chang et al., 2016) and Dome A (Chang et al., 2016). Additionally,  
64 a composite record of semi-quantitative Pb isotopes data was reported for various sites across  
65 Antarctica (McConnell et al., 2014). Some of these studies (Rosman et al., 1999, Matsumoto and  
66 Hinkley, 2001, Vallelonga et al., 2005, 2010) discussed the Pb isotopic composition of old ice (~1-  
67 200 kyr before present) in relation to natural sources and climate changes. It was found that Pb  
68 isotopic compositions in Antarctic ice varied with changing climate, with lower  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios  
69 (and higher Pb concentration) during the glacial periods than in the Holocene and the other  
70 interglacial climate stages (Rosman et al., 1999, Vallelonga et al., 2005, 2010), although with a high  
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  
73 different proportion of these sources (Vallelonga et al., 2005). For example, Pb from Dome C is  
74 generally less radiogenic than that from Taylor Dome, due to greater proportions of dust. In fact,  
75 dust accounts for 70% of Pb in Dome C ice (Vallelonga et al., 2005), but only a few percent in most  
76 samples from Taylor Dome, where the main source of Pb is represented by emissions from  
77 quiescent volcanoes (Matsumoto and Hinkley, 2001). Concerning the origin of the mineral dust, the  
78 southern part of South America was proposed as the major source of dust in interglacial periods,  
79 although a partial overlap with Australian potential source areas was observed (Vallelonga et al.,  
80 2010). Moreover, local sources were found to be non-trivial contributors (Vallelonga et al., 2010).

81 Other studies focussed on the Pb pollution history, well reconstructed by isotopic  
82 measurements on ice cores and snow dating back to the beginning of the industrial era (Vallelonga  
83 et al., 2002b, Planchon et al., 2003, Van de Velde et al., 2005, McConnell et al., 2014, Chang et al.,  
84 2016). Isotopic evidence of Pb pollution in Antarctica as early as the 1880-90s was first observed at  
85 Law Dome (Vallelonga et al., 2002b), Coats Land (Planchon et al., 2003) and Victoria Land (Van  
86 de Velde et al., 2005), and attributed to mining and smelting of non-ferrous metal ores at Broken  
87 Hill (Australia) and, at a minor extent, to coal combustion. The subsequent pollution events tracked  
88 by Pb isotopic ratios were linked to the rise and fall in the use of alkyl-Pb additives in gasoline in  
89 the Southern Hemisphere, which occurred in the second half of 20th century (Oudijk, 2010). These  
90 events were highlighted by an increase in the concentration and crustal enrichment of Pb (usually  
91 measured as Pb/Ba ratio) in the snow/ice, and a concomitant decrease in the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios, with  
92 marked differences among the sites both in the timings of maxima and in the isotopic values.  
93 Concerning the sources of the anthropogenic Pb due to gasoline consumption, Vallelonga and co-  
94 workers (2002b) observed that the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios measured at Law Dome in samples dated  
95 between 1950 and 1970 are compatible with inputs of alkyl-Pb from Australia and New Zealand,  
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  
98 northern part of South America, such as Brazil. Similar conclusions were reported for Coats Land  
99 (Planchon et al., 2003) and Victoria Land (Van de Velde et al., 2005), explaining the differences  
100 among the sites by the substantial changes in the relative contributions of these two source regions.  
101 More recently, McConnell et al. (2014) analysed a composite record of semi-quantitative  
102  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios across Antarctica (9 ice cores, collectively spanning from 1850-2010), suggesting  
103 that southern Australia was responsible for the introduction of Pb pollution into Antarctica at the  
104 end of the 19th century, remaining a significant source until (at least) 2010. Conversely, Chang et  
105 al. (2016) assigned to northern South America (Chile and Argentina) the origin of the Pb pollution

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

108 In this work, a record of Pb isotope ratios has been obtained by the analysis of 109 snow  
109 samples collected at Dome C and covering the period from 1970 to 2017. The obtained data are  
110 presented and discussed with the aim of: (a) providing updated information on the Pb pollution  
111 trend in the last fifty years (the more recent ones ends at 2010), especially to discriminate between  
112 “steady-state” and “decrease” trends in the last decade; (b) contributing to the source assessment of  
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.

116

## 117 **2. Experimental**

118

### 119 *2.1 Sample collection*

120

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

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

134 Sample dating was assigned on the basis of parallel measurements of non-sea-salt sulphates,  
135 using the well-identified large volcanic depositions from Mt. Pinatubo in 1992 (Castellano et al.,  
136 2005). The corresponding mean annual accumulation is about 8.4 cm yr<sup>-1</sup> and the samples cover  
137 about fifty years (1971-2017).

138

## 139 *2.2 Sample preparation and analysis*

140

141 Lead isotopic analysis of snow samples was performed by ICP-MS using a previously  
142 reported method (Bazzano et al., 2014, Ardini et al., 2018). Briefly, the samples were allowed to  
143 melt in their closed tubes; subsequently, 20.0 g aliquots were acidified with 100 µL of HNO<sub>3</sub> and  
144 100 µL of HF, left to stand for 24 h, and refrozen. Then, the samples were freeze-dried, redissolved  
145 in 200 µL of 0.05% HNO<sub>3</sub> solution and introduced into the ICP-MS spectrometer by using the  
146 heated torch-integrated sample introduction system (Paredes et al., 2009, Grotti et al., 2013).  
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  
149 preparation was carried out under a laminar flow work area. Procedural blanks were concomitantly  
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  
154 NIST SRM 981 standard solution (Pb concentration: 5 µg L<sup>-1</sup>) every three samples and applying the  
155 bracketing external correction method (Vanhaecke et al., 2009). For each sample, twelve replicated  
156 measurements were performed with an integration time of 10 s each one, and raw data were



157 corrected for the detector dead time (determined according to Nelms et al., 2001). Data are  
158 expressed as mean values and 95%-confidence intervals.

159 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).

163

### 164 *2.3. Analytical performances and quality control*

165

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

177

## 178 **3. Results and discussion**

179

### 180 *3.1. Lead concentration*

181

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

183 Antarctic sites and similar periods in Figure 1a. The Pb concentration in the snow samples from

184 Dome C was 8.2 : higher than

185 the mean value of d dated 17th

186 century (McConn

187

188

189

190

191

192

193 (a)

194

195

196

197

198

199

200

201

202 (b)

203

204

205

206

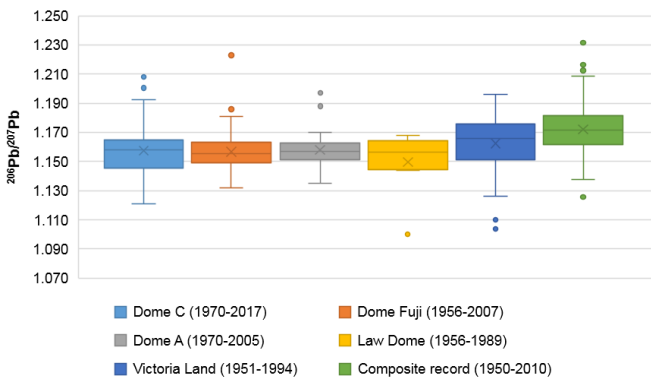
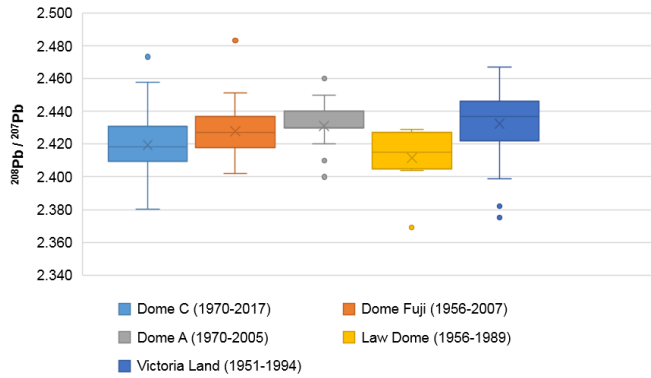
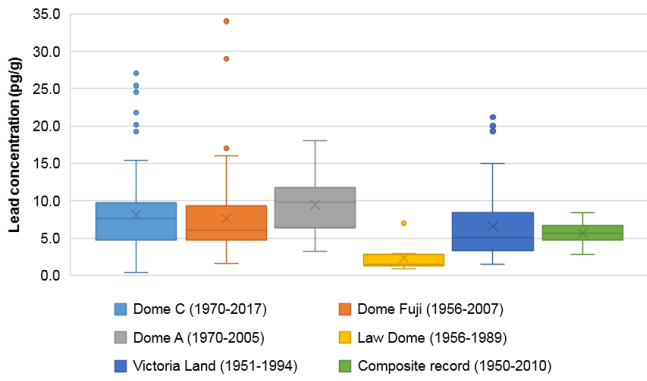
207

208

209

210

211 (c)



212

213 **Figure 1.** (a) Pb concentration, (b)  $^{208}\text{Pb}/^{207}\text{Pb}$  and (c)  $^{206}\text{Pb}/^{207}\text{Pb}$  values in recent snow from  
214 various Antarctic sites: Dome C (this work), Dome Fuji (Chang et al., 2016), Dome A (Chang et al.,  
215 2016), Law Dome (Vallelonga et al., 2002), Victoria Land (Van de Velde et al., 2005) and a  
216 composite Pb record from 16 ice cores across Antarctica (McConnell et al., 2014). See Figure S1  
217 for locations.

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

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  
220 occurring of industrial and mining activities in the Southern Hemisphere caused a significant  
221 increase of Pb inputs to Antarctica since the second half of the 19th century, leading to the values  
222 observed in recent snow. The Pb concentration in Dome C is in a good agreement with values found  
223 in other Antarctic sites, mainly at comparable altitude (see section 3.4), highlighting the  
224 homogeneity of the distribution of atmospheric Pb over Antarctica, as already observed (McConnell  
225 et al., 2014; Chang et al., 2016). The temporal trend of Pb concentration is illustrated in Figure 2.

226

227

228

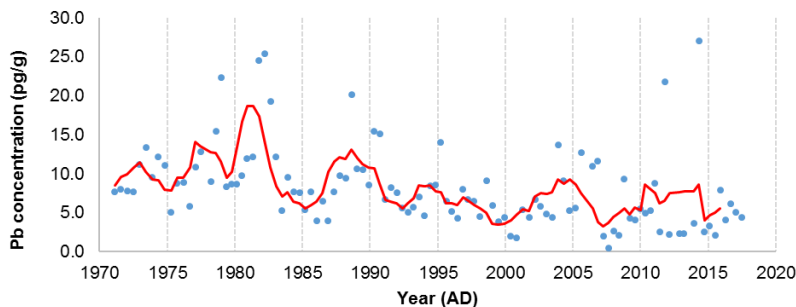
229

230

231

232

233



234 (a)

235

236

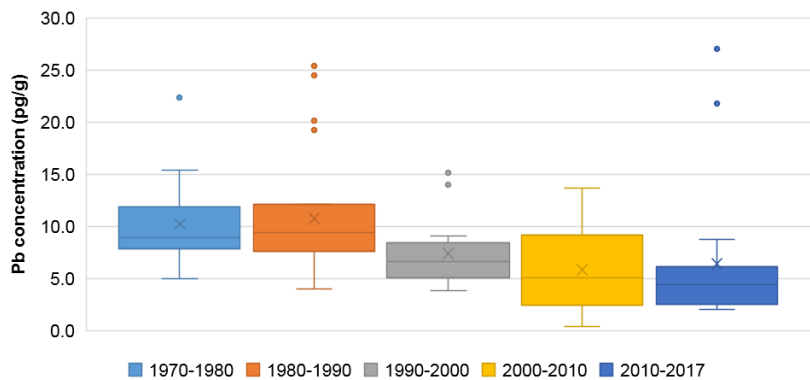
237

238

239

240

241



10

242

243 (b)

244

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

247 The five-point running average shows concentration peaks in the late 1970s and in the early  
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  
252 South America, Australia and local sources (Chang et al., 2016, Li et al., 2008, Van de Velde et al.,  
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  
255 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  
256 with the results by Chang et al. (2016), whereas McConnell et al. (2014) reported a persistent Pb  
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  
260 gasoline in many southernmost countries of the Southern Hemisphere (New Zealand in 1996, Brazil  
261 in 1997, Argentina in 1998, Chile in 2001, Australia in 2002 and South Africa in 2006) and the  
262 reduction of emission of toxic elements from copper (Cu) production activities in Chile (Chang et  
263 al., 2016, McConnell et al., 2014). Nevertheless, the effect of anthropic activities on Antarctica  
264 environment continue to be evident, and even the Pb concentration in the more recent samples (2.1-  
265 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>  
266 in Holocene ice from Dome C (Vallelonga et al., 2010).

267

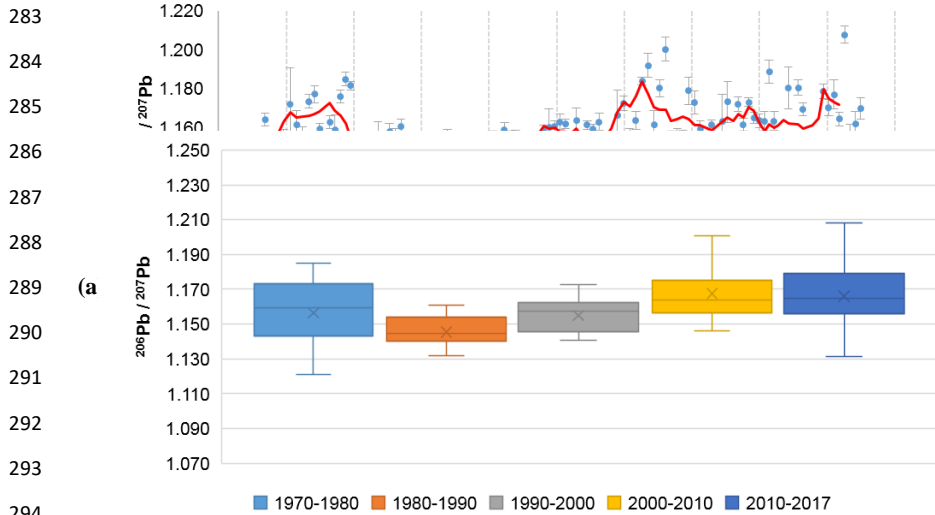
268 3.2. Temporal variation of Pb isotopic ratios

269

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

280 The temporal trend of  $^{206}\text{Pb}/^{207}\text{Pb}$  ratio is displayed in Figure 3a (analogous trend was  
281 obtained for  $^{208}\text{Pb}/^{207}\text{Pb}$ , Figure S2).

282



297

298 (b)

299

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

302 A sharp increase from the beginning to the end of 1970s may be observed, with the ratio  
303 changing from about 1.12 to 1.18. It was followed by an abrupt drop to less radiogenic values  
304 during the 1980s, concomitantly with the Pb concentration peaks in that very period (Figure 2a).  
305 From the end of 1980s, the Pb isotopic ratio raised again reaching the running average of 1.18 and  
306 then it has stabilized at a value of  $1.167 \pm 0.005$  (mean and 95%-confidence interval, n=41) in  
307 2000-2017 (Figure 3b). Similar temporal trends (Figure S3) were recorded at Dome Fuji and Dome  
308 A (Chang et al., 2017), as well as in certain ice cores analysed by McConnell et al. (2014), such as  
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  
312 the consumption of Pb-enriched gasoline in the various regions of the Southern Hemisphere. In fact,  
313 Bollhöfer and Rosman (2000) showed that marked differences existed in the Pb isotopic  
314 composition of the particulate airborne from different cities in the Southern Hemisphere, as a  
315 consequence of the local industrial activities and the different suppliers of the alkyl-Pb additives for  
316 the local gasoline. In particular, the two major alkyl-Pb suppliers were Associated Octel (UK), who  
317 mainly used Pb ores with low isotopic ratios (Broken Hill type ores, Australia,  $^{208}\text{Pb}/^{207}\text{Pb} \approx 2.315$ ,  
318  $^{206}\text{Pb}/^{207}\text{Pb} \approx 1.041$ , Sangster et al., 2000), and Ethyl Corp. (USA) who mainly used Pb ores with  
319 high isotopic ratios (Mississippi Valley type ores, USA,  $^{208}\text{Pb}/^{207}\text{Pb} = 2.528\text{-}2.627$ ,  $^{206}\text{Pb}/^{207}\text{Pb} =$   
320  $1.339\text{-}1.406$ , Sangster et al., 2000). As a consequence, the atmospheric particulate emitted from  
321 cities where the gasoline used was obtained by Broken Hill type ores (the southernmost regions of  
322 the Southern Hemisphere including Argentina, Chile, Australia and New Zealand) was  
323 characterized by lower Pb isotopic ratios than that from cities where the gasoline used was obtained  
324 by Mississippi Valley type ores (the north-central regions of South America, such as Brazil).  
325 Therefore, the abrupt rise of Pb isotope ratios in the first half of 1970s (Figure 3a) can be ascribed  
326 to the quickly increase of the consumption of gasoline in northern South America (mainly Brazil),  
327 characterized by more radiogenic isotopic values. On the other hand, since early 1980s, the

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.  
332 According to Chang et al. (2016), it could be ascribed to the Chilean Cu mining activity. In fact, the  
333 Pb ores of Chilean Andes have relatively high isotope ratios ( $^{208}\text{Pb}/^{207}\text{Pb} = 2.449\text{-}2.469$ ,  $^{206}\text{Pb}/^{207}\text{Pb}$   
334  $= 1.175\text{-}1.189$ ; Puig, 1988) and the relative contribution of the mining activity in South America to  
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  
338 ( $^{208}\text{Pb}/^{207}\text{Pb} = 2.478$ ,  $^{206}\text{Pb}/^{207}\text{Pb} = 1.210$ ; Vallelonga et al., 2005), as suggested by a concomitant  
339 decrease in the total Pb concentration (Figure 2). Finally, the Pb isotopic ratios after 2000 would  
340 seem to indicate that a rather stable situation has been reached, although dispersion of data was  
341 significantly higher compared to the previous decades, thereby indicating more pronounced inter-  
342 annual variations in the atmospheric transport of Pb to Antarctica.

343

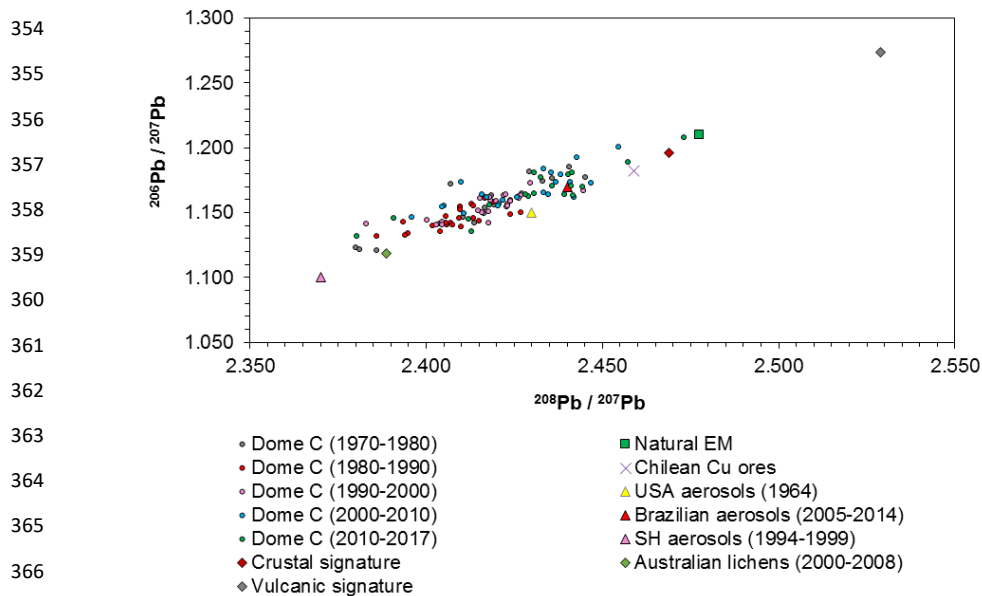
### 344 3.3. Anthropogenic and natural Pb sources

345

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

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





382 2000-2017. For the first decade, van de Velde et al. (2005) used the isotopic signature reported in  
383 gasoline and aerosol in the Los Angeles Basin the early 1970s (Chow and Johnstone, 1965),  
384 considered to be representative of gasoline alkyl-Pb additives consumed in the Southern  
385 Hemisphere between 1951 and 1981. However, these values resulted to be too radiogenic to explain  
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  
388 1980-2000, the mean Pb isotopic signature reported by Bollhoffer and Rosman (2000) for urban  
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  
392 2008 (Wu et al., 2016). In fact, the Pb isotopic signatures of both the Chilean Cu ores and of the  
393 atmospheric particulate collected in Brazilian cities between 2005 and 2014 (average  $^{208}\text{Pb}/^{207}\text{Pb} =$   
394  $2.44$ ,  $^{206}\text{Pb}/^{207}\text{Pb} = 1.17$ ; Mirlean et al., 2005, Gemeiner et al., 2017, Gioia et al., 2017, Khondoker et  
395 al., 2018) were more radiogenic than that measured in the most of the Antarctic snow samples dated  
396 2010-2017 (Figure 4). More likely, these values can be ascribed to inputs from the Australian  
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  
399 of Pb-enriched gasoline in 2002 (Wu et al., 2016), and they could have contributed to lowering the  
400 Pb isotopic ratios of the atmospheric particulate reaching Antarctica, respect to the Chilean Cu ore  
401 or the natural signature. A possible major influence from South Australia was also suggested by  
402 measurements of  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio in surface snow samples collected at Dome C on 2006 and  
403 2010 (Bazzano et al., 2017).

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

408

409

410

411

412

413

414

415

416

417

418

419

420

421

422

423

424

425

426

427

428

429

430

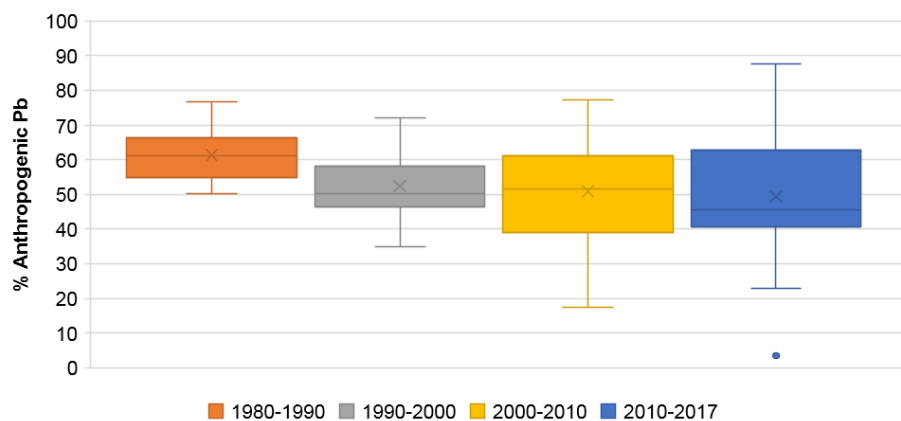
431

432

433

434

435



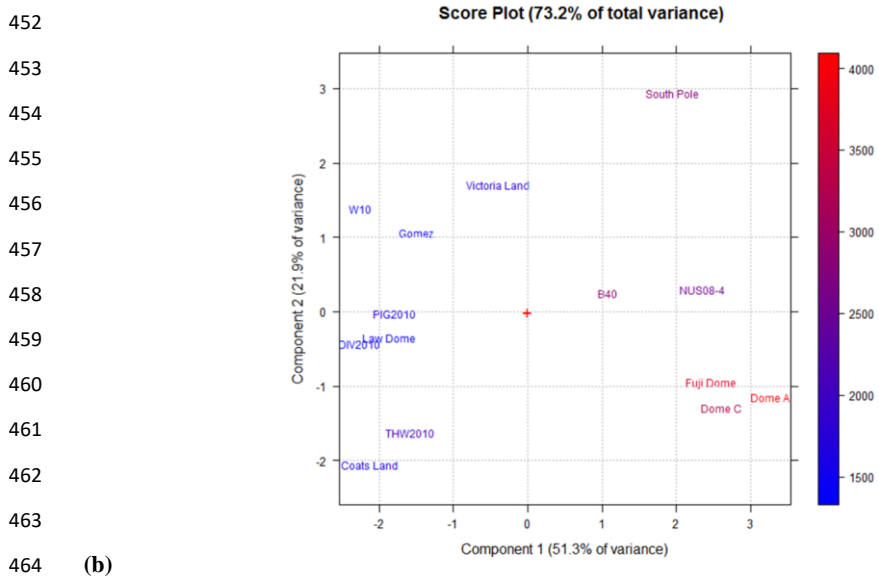
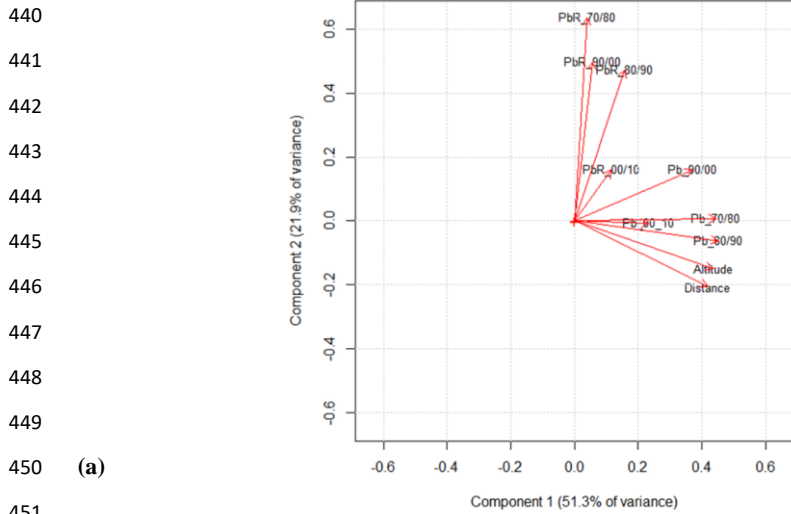
**Figure 5.** Estimated percentages of anthropogenic Pb, grouped by decades.

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 co-workers (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.

### 3.4. Regional variations

Antarctica covers an area of  $14 \times 10^6 \text{ km}^2$ , 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  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios were averaged by grouping the samples by

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



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

467 The loading plot (Figure 6a) shows that Pb concentration, altitude and distance are strongly  
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  
470 correlation of Pb concentration with altitude was statistically significant and decreased with time  
471 (from  $r=0.910$ ,  $p<0.0001$  in 1970-1980 to  $r=0.661$ ,  $p=0.01$  in 2000-2010). Considering the temporal  
472 trend of Pb concentration discussed above (Figure 2b), this would indicate that the effect of the  
473 altitude is stronger when the amount of Pb is high. The correlation with the distance was also  
474 significant ( $r=0.911-0.646$ ,  $p<0.05$ ), except for the 2000-2010 decade. Similarities and differences  
475 among the sites are highlighted in the score plot (Figure 6b). Dome C, Dome A and Dome Fuji,  
476 located on the East Antarctic plateau above 3000 m a.s.l., show a high similarity, although they are  
477 distant about one thousand kilometres from each other. Similarly, the other sites are grouped  
478 according to the altitude and the distance from the coast. For instance, Law Dome and Gomez are  
479 close in the score plot, although they are on opposite sides of the continent. By looking at the score  
480 and loading plots together, it can be deduced that the sites at high altitude are differentiated from the  
481 others because of a higher Pb concentration. This result is in good agreement with the increase in  
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.

485 Finally, Dome C, Dome A, Dome Fuji, Law Dome and Coats Land are characterised by  
486 similar scores on the second PC, mainly affected by the  $^{206}\text{Pb}/^{207}\text{Pb}$  ratios, confirming their similar  
487 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  
491 snow samples from the East Antarctic Plateau, providing new insights into the possible sources and  
492 the temporal trend of Pb atmospheric deposition over the last fifty years. Isotopic data for samples  
493 dated from 1970 to mid-1990s reflected the well-known changes in the consumption of Pb-enriched  
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  
496 decrease of total Pb concentration. According to our estimation, the contribution of anthropogenic  
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  
500 previous measurements of  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio (Bazzano et al., 2017). However, for a better  
501 assessment of the sources of atmospheric Pb to Antarctica, there is still the need of additional  
502 analytical data, including precise measurements of  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios using multi-collector ICP-MS  
503 (Bazzano et al., 2015b) and more detailed isotopic values for Australian and Southern America  
504 potential source areas (Vallelonga et al., 2010). Finally, principal component analysis of data for  
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.

507

508

#### 509 **Acknowledgments**

510 This work has been funded by the Italian National Program of Research in Antarctica  
511 (projects PNRA14\_00091, PNRA16\_00252). The authors wish to thank Giulio Esposito, Andrea  
512 Spolaor, Alessandro Baù, Marco Buttu, Matthias Jaggi, Angelo Domesi and the PNRA logistic staff  
513 for their help in the field work.

514 **References**

515

516 Ardini, F., Bazzano, A., Grotti, M., 2018. Lead isotopic analysis of Antarctic snow by quadrupole  
517 ICP-MS using a total-consumption sample introduction system. J. Anal. At. Spectrom. 33, 2124–  
518 2132. <https://doi.org/10.1039/c8ja00296g>.

519

520 [Ardini, F., Bazzano, A., Grotti, M., 2019. Lead isotopic ratios in the Arctic environment. Environ.](#)  
521 [Chem. In press. <https://doi.org/10.1071/EN19227>.](#)

522

523 Bandura, D.R., Baranov, V.I., Tanner, S.D., 2000. Effect of collisional damping and reactions in a  
524 dynamic reaction cell on the precision of isotope ratio measurements. J. Anal. At. Spectrom. 15,  
525 921-928. <https://doi.org/10.1039/b000285m>.

526

527 Bazzano, A., Grotti, M., 2014. Determination of lead isotope ratios in environmental matrices by  
528 quadrupole ICP-MS working at low sample consumption rates. J. Anal. At. Spectrom. 29, 926–933.  
529 <https://doi.org/10.1039/c3ja50388g>.

530

531 Bazzano, A., Soggia, F., Grotti, M., 2015a. Source identification of atmospheric particle-bound  
532 metals at Terra Nova Bay, Antarctica. Environ. Chem. 12, 245-252.  
533 <https://doi.org/10.1071/en14185>.

534

535 Bazzano, A., Latruwe, K., Grotti, M., Vanhaecke, F., 2015b. Lead isotopic analysis of Antarctic  
536 snow using multi-collector ICP-mass spectrometry. J. Anal. At. Spectrom. 30, 1322–1328.  
537 <https://doi.org/10.1039/c4ja00484a>.

538

ha formattato: Italiano (Italia)

ha formattato: Inglese (Stati Uniti)

ha formattato: Inglese (Stati Uniti)

539 Bazzano, A., Latruwe, K., Grotti, M., Vanhaecke, F., 2017. Determination of the isotopic  
540 composition of sub-ng amounts of Sr in Antarctic snow by multi-collector ICP-mass spectrometry.  
541 J. Anal. At. Spectrom. 32, 1004-1008. <https://doi.org/10.1039/C7JA00062F>.

542  
543 Bollhöfer, A., Rosman, K.J.R., 2000. Isotopic source signatures for atmospheric lead: the Southern  
544 Hemisphere. Geochim. Cosmochim. Acta 64, 3251–3262. [https://doi.org/10.1016/S0016-  
545 7037\(00\)00436-1](https://doi.org/10.1016/S0016-7037(00)00436-1).

546  
547 Bollhöfer, A., Rosman, K.J.R., 2001. Isotopic source signatures for atmospheric lead: the Northern  
548 Hemisphere. Geochim. Cosmochim. Acta 65, 1727–1740. [https://doi.org/10.1016/S0016-  
549 7037\(00\)00630-X](https://doi.org/10.1016/S0016-7037(00)00630-X).

550  
551 Castellano, E., Becagli, S., Hansson, M., Hutterli, M., Petit, J. R., Rampino, M. R., Severi, M.,  
552 Steffensen, J. P., Traversi, R., Udisti, R., 2005. Holocene volcanic history as recorded in the sulfate  
553 stratigraphy of the European Project for Ice Coring in Antarctica Dome C (EDC96) ice core, J.  
554 Geophys. Res. 116, D06114. <https://doi.org/10.1029/2004JD005259>.

555  
556 Chang, C., Han, C., Han, Y., Hur, S.D., Lee, S., Motoyama, H., Hou, S., Hong, S., 2016. Persistent  
557 Pb Pollution in Central East Antarctic Snow: A Retrospective Assessment of Sources and Control  
558 Policy Implications. Environ. Sci. Technol. 50, 12138–12145.  
559 <https://doi.org/10.1021/acs.est.6b03209>.

560  
561 Chisholm, W., Rosman, K.J.R., Boutron, C.F., Candelone, J.P., Hong, S., 1995. Determination of  
562 lead isotopic ratios in Greenland and Antarctic snow and ice at picogram per gram concentrations.  
563 Anal. Chim. Acta 311, 141–151. [https://doi.org/10.1016/0003-2670\(95\)00181-X](https://doi.org/10.1016/0003-2670(95)00181-X).

564

Codice campo modificato



565 Chow, T.J., Johnstone, M.S., 1965. Lead isotopes in gasoline and aerosols of Los Angeles basin,  
566 California. *Science* 147, 502–503. <https://doi.org/10.1126/science.147.3657.502>.

567

568 Cloquet, C., Carignan, J., Libourel, G., 2006. Atmospheric pollutant dispersion around an urban  
569 area using trace metal concentrations and Pb isotopic compositions in epiphytic lichens. *Atmos.*  
570 *Environ.* 40, 574–587. <https://doi.org/10.1016/j.atmosenv.2005.09.073>

571

572 Ellam, R.M., 2010. The graphical presentation of lead isotope data for environmental source  
573 apportionment. *Sci. Tot. Environ.* 408, 3490–3492. <https://doi.org/10.1016/j.scitotenv.2010.03.037>.

574

575 Gemeiner, H., de Araujo Dourado, T., Sulato, E.T., Galhardi, J.A., Gomes, A.C.F., de Almeida, E.c.,  
576 Menegário, A.A., Gastmans, D., Kiang, C.H., 2017. Elemental and isotopic determination of lead  
577 (Pb) in particulate matter in the Brazilian city of Goiânia (GO) using ICP-MS technique. *Environ.*  
578 *Sci. Pollut. Res.* 24, 20616–20625. <https://doi.org/10.1007/s11356-017-9687-9>.

579

580 Gioia, S.M.C.L., Babinski, M., Weiss, D.J., Spiro, B., Kerr, A.A.F.S., Veríssimo, T.G., Ruiz, I.,  
581 Prates, J.C.M., 2017. An isotopic study of atmospheric lead in a megacity after phasing out of  
582 leaded gasoline. *Atmos. Environ.* 149, 70–83. <https://doi.org/10.1016/j.atmosenv.2016.10.049>.

583

584 Grotti, M., Ardini, F., Todoli, J. L., 2013. Total introduction of microsamples in inductively  
585 coupled plasma mass spectrometry by high-temperature evaporation chamber with a sheathing gas  
586 stream. *Anal. Chem. Acta* 767, 14–20. <https://doi.org/10.1016/j.aca.2013.01.017>.

587

588 Grousset, F.E., Biscaye, P.E., 2005. Tracing dust sources and transport patterns using Sr, Nd and Pb  
589 isotopes. *Chem. Geol.* 222, 149–167. <https://doi.org/10.1016/j.chemgeo.2005.05.006>.

590

Codice campo modificato

591 Khondoker, R., Weiss, D., van de Fliedert, T., Rehkämper, M., Kreissig, K., Coles, B.J.,  
592 Strekopytov, S., Humphreys-Williams, E., Dong, S., Bory, A., Bout-Roumazeilles, V., Smichowski,  
593 P., Cid-Agüero, P., Babinski, M., Losno, R., Monna, F., 2018. New constraints on elemental and Pb  
594 and Nd isotope compositions of South American and Southern African aerosol sources to the South  
595 Atlantic Ocean. *Chemie der Erde* 78, 372–384. <https://doi.org/10.1016/j.chemer.2018.05.001>.

Codice campo modificato

596

597 Ikegawa, M., Kimura, M., Honda, K., Akabane, I., Makita, K., Motoyama, H., Fujii, Y., Itokawa,  
598 Y., 1999. Geographical variations of major and trace elements in East Antarctica. *Atmos. Environ.*  
599 33, 1457–1467. [https://doi.org/10.1016/s1352-2310\(98\)00243-x](https://doi.org/10.1016/s1352-2310(98)00243-x).

600

601 Li, F., Ginoux, P., Ramaswamy, V., 2008. Distribution, transport, and deposition of mineral dust in  
602 the Southern Ocean and Antarctica: Contribution of major sources. *J. Geophys. Res. Atmos.* 113,  
603 1–15. <https://doi.org/10.1029/2007JD009190>.

604

605 Matsumoto, A., Hinkley, T. K., 2001. Trace metal suites in Antarctic pre-industrial ice are  
606 consistent with emissions from quiescent degassing of volcanoes worldwide. *Earth Planet. Sci. Lett.*  
607 186, 33–43. [https://doi.org/10.1016/s0012-821x\(01\)00228-x](https://doi.org/10.1016/s0012-821x(01)00228-x).

608

609 McConnell, J.R., Maselli, O.J., Sigl, M., Vallelonga, P., Neumann, T., Anshütz, H., Bales, R.C.,  
610 Curran, M.A.J., Das, S.B., Edwards, R., Kipfstuhl, S., Layman, L., Thomas, E.R., 2014. Antarctic-  
611 wide array of high-resolution ice core records reveals pervasive lead pollution began in 1889 and  
612 persists today. *Scientific Reports* 4, 5848. <https://doi.org/10.1038/srep05848>.

613

614 Mirlean, N., Robinson, D., Kawashita, K., Vignol, M.L., Conceição, R., Chemale, F., 2005.  
615 Identification of local sources of lead in atmospheric deposits in an urban area in Southern Brazil

616 using stable lead isotope ratios. *Atmos. Environ.* 39, 6204–6212.

617 <https://doi.org/10.1016/j.atmosenv.2005.07.002>.

618

619 Morganti, A., Becagli, S., Castellano, E., Severi, M., Traversi, R., Udisti, R., 2007. An improved  
620 flow analysis-ion chromatography method for determination of cationic and anionic species at trace  
621 levels in Antarctic ice cores. *Anal. Chim. Acta* 603, 190-198.

622 <https://doi.org/10.1016/j.aca.2007.09.050>.

623

624 Nelms, S.M., Quérel, C.R., Prohaska, T., Vogl, J., Taylor, P.D.P., 2001. Evaluation of detector dead  
625 time calculation models for ICP-MS. *J. Anal. At. Spectrom.* 29, 333–338.

626 <https://doi.org/10.1039/b007913h>.

627

628 Oudijk, G., 2010. The Rise and Fall of Organometallic Additives in Automotive Gasoline. *Environ.*  
629 *Forensics* 11, 17–49. <https://doi.org/10.1080/15275920903346794>.

630

631 Paredes, E., Grotti, M., Mermet, J. M., Todoli, J. L., 2009. Heated-spray chamber-based low sample  
632 consumption system for inductively coupled plasma spectrometry. *J. Anal. At. Spectrom.* 24, 903–

633 910. <https://doi.org/10.1039/B904002a>.

634

635 Planchon, F.A.M., Van De Velde, K., Rosman, K.J.R., Wolff, E.W., Ferrari, C.P., Boutron, C.F.,  
636 2003. One hundred fifty-year record of lead isotopes in Antarctic snow from Coats Land. *Geochim.*  
637 *Cosmochim. Acta* 67, 693–708. [https://doi.org/10.1016/S0016-7037\(00\)01136-5](https://doi.org/10.1016/S0016-7037(00)01136-5).

638

639 Puig, A., 1988. Geologic and metallogenic significance of the isotopic composition of lead in  
640 galenas of the Chilean Andes. *Econ. Geol.*, 83, 843–858.

641 <https://doi.org/10.2113/gsecongeo.83.4.843>.

Codice campo modificato

642

643 Revel-Rolland, M., De Deckker, P., Delmonte, B., Hesse, P.P., Magee, J.W., Basile-Doelsch, I.,  
644 Grousset, F., Bosch, D., 2006. Eastern Australia: A possible source of dust in East Antarctica  
645 interglacial ice. *Earth Planet. Sci. Lett.* 249, 1–13. <https://doi.org/10.1016/j.epsl.2006.06.028>.

646

647 Rosman, K.J.R., Chisholm, W., Boutron, C.F., Candelone, J.P., Patterson, C.C., 1994.  
648 Anthropogenic lead isotopes in Antarctica. *Geophys. Res. Lett.* 21, 2669–2672.  
649 <https://doi.org/10.1029/94GL02603>.

650

651 Rosman, K.J.R., Chisholm, W., Boutron, C.F., Candelone J.P., 1999. Lead isotopes as tracers of  
652 pollution in snow and ice. *Korean J. Polar Res.* 10, 53–58.

653

654 Sangster, D.F., Outridge, P.M., Davis, W.J., 2000. Stable lead isotope characteristics of lead ore  
655 deposits of environmental significance. *Environ. Rev.* 8, 115–147. <https://doi.org/10.1139/a00-008>.

656

657 Vallelonga, P., Van de Velde, K., Candelone, J.P., Ly, C., Rosman, K.J.R., Boutron, C.F., Morgan,  
658 V.I., Mackey, D.J., 2002a. Recent advances in measurement of Pb isotopes in polar ice and snow at  
659 sub-picogram per gram concentrations using thermal ionisation mass spectrometry. *Anal. Chim.*  
660 *Acta* 453, 1–12. [https://doi.org/10.1016/s0003-2670\(01\)01490-8](https://doi.org/10.1016/s0003-2670(01)01490-8).

661

662 Vallelonga, P., Van de Velde, K., Candelone, J. P., Morgan, V.I., Boutron, C.F., Rosman, K.J.R.,  
663 2002b. The lead pollution history of Law Dome, Antarctica, from isotopic measurements on ice  
664 cores: 1500 AD to 1989 AD. *Earth Planet. Sci. Lett.* 204, 291-306. [https://doi.org/10.1016/s0012-](https://doi.org/10.1016/s0012-821x(02)00983-4)  
665 [821x\(02\)00983-4](https://doi.org/10.1016/s0012-821x(02)00983-4).

666

667 Vallelonga, P., Gabrielli, P., Rosman, K.J.R., Barbante, C., Boutron, C. F., 2005. A 220 kyr record  
668 of Pb isotopes at Dome C Antarctica from analyses of the EPICA ice core. *Geophys. Res. Lett.* 32,  
669 L01706. <https://doi.org/10.1029/2004gl021449>.

670

671 Vallelonga, P., Gabrielli, P., Balliana, E., Wegner, A., Delmonte, B., Turetta, C., Burton, G.,  
672 Vanhaecke, F., Rosman, K.J.R., Hong, S., Boutron, C.F., Cescon, P., Barbante, C., 2010. Lead  
673 isotopic compositions in the EPICA Dome C ice core and Southern Hemisphere Potential Source  
674 Areas. *Quat. Sci. Rev.* 29, 247-255. <https://doi.org/10.1016/j.quascirev.2009.06.019>.

675

676 Van de Velde, K., Vallelonga, P., Candelone, J.P., Rosman, K.J.R., Gaspari, V., Cozzi, G.,  
677 Barbante, C., Udisti, R., Cescon, P., Boutron, C.F., 2005. Pb isotope record over one century in  
678 snow from Victoria Land, Antarctica. *Earth Planet. Sci. Lett.* 232, 95–108.  
679 <https://doi.org/10.1016/j.epsl.2005.01.007>.

680

681 Vanhaecke, F., Balcaen, L., Malinovsky, D., 2009. Use of single-collector and multi-collector ICP-  
682 mass spectrometry for isotopic analysis. *J. Anal. At. Spectrom.* 24, 863-886.  
683 <https://doi.org/10.1039/b903887f>.

684

685 Weiss, D., Shotyk, W., Kempf, O., 1999. Archives of Atmospheric Lead Pollution.  
686 *Naturwissenschaften* 86, 262–275. <https://doi.org/10.1007/s001140050612>.

687

688 Wu, L., Taylor, M.P., Handley, H.K., Gulson, B.L., 2016. Insights into past atmospheric lead  
689 emissions using lead concentrations and isotopic compositions in historic lichens and fungi (1852-  
690 2008) from central and southern Victoria, Australia. *Atmos. Environ.* 139, 46–55.  
691 <https://doi.org/10.1016/j.atmosenv.2016.05.022>.

ha formattato: Italiano (Italia)

Codice campo modificato