

# Holocene Pb isotope evolution: the record of the anthropogenic activity in the last 6,000 years

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**ABSTRACT** *The objective of this contribution is to build a Pb isotope standard curve during the last 6,000 years based on reported data worldwide. The history of Pb isotope signature has been investigated by analyzing the isotope composition of Pb in suspended particulate matter (aerosols), sediments, water, ice and soil. The  $^{206}\text{Pb}/^{207}\text{Pb}$  natural background values are about 1.199 between 12,000 and 2,600 years, as observed in sediments (Europe and North America) and ice caps (Europe and Antarctica). The depression of the  $^{206}\text{Pb}/^{207}\text{Pb}$  values at about 2,500 years (1.176 to 1.184) may be explained due to an intensive mining activity during the time of the Roman Empire. During the Medieval period (1,700–1,200 years ago)  $^{206}\text{Pb}/^{207}\text{Pb}$  values increased whereas, at the same time, the worldwide Pb production decreased after the fall of Rome, and the values of  $^{206}\text{Pb}/^{207}\text{Pb}$  recorded in sediments are about 1.176.*

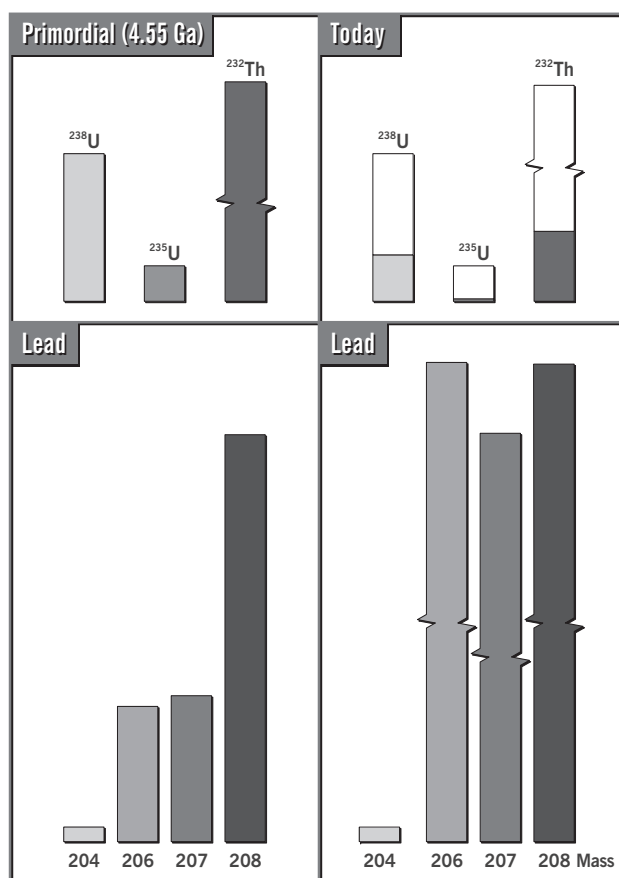
*The Pb isotope curves in sediments and ice caps for the industrial revolution period recorded in Europe, North America and Antarctica present different patterns. In general way, the Pb isotope curve for the last 200 years records the initial period of industrialization, when coal was the main source of energy ( $^{206}\text{Pb}/^{207}\text{Pb}$  values about 1.125), followed by the Pb-enriched gasoline ( $^{206}\text{Pb}/^{207}\text{Pb}$  values about 1.190–1.195), and as last period, occurred after the fall in the use of gasoline Pb additives ( $^{206}\text{Pb}/^{207}\text{Pb}$  values about 1.240).*

## Introduction

Over the last 6,000 years, natural and anthropogenic Pb has been introduced into the global environment through atmospheric transport. Prior to the industrial revolution, anthropogenic lead was emitted solely as a by-product of mining and smelting of lead, silver, and copper ores. By the mid-18th century, combustion of Pb-containing coal became the primary source of industrial lead emissions to the atmosphere. Since the 1920s, automobile exhaust, with Pb-containing gasoline additives (alkyllead), has overwhelmed all other sources of anthropogenic Pb emitted into the environment. More than 95% of present-day lead deposited in the environment is of anthropogenic origin (Marcantonio *et al.* 2002).

Attempts to identify pollution sources have included the use of elemental values, but total Pb concentrations alone may be insufficient for separating pollution from natural background. This is because background Pb concentration is often highly variable due to natural processes (Helland *et al.* 2002). In contrast, Pb isotope abundances (Fig. 1) are not affected to any measurable extent by physical or chemical processes in terrestrial environment. Given the significant isotopic differences in Pb emissions, researchers have been able to use historical records of anthropogenic Pb isotope variations to trace the changing sources of pollutant Pb in continental environment through time.

Pb is one of the high priority contaminants in surface water and occurs naturally as four stable isotopes. Pb is known to adsorb strongly to particles and typically follow organic particles draining out of the soil. In the last decades Pb isotopic analysis has been used successfully to trace elements in recent sediments back to their source, distinguishing between sources, tracing elements along their route from source to burial, and assessing the effect of remedial actions taken to reduce emissions from a specific polluter (Marcoantonio *et al.* 2002). In addition, establishing reference sites is a critical factor in determining the baseline of ecosystems and the information on contaminant background concentrations subsidizes the remediation of impacted areas. Thus, it would be important the construction of a Pb isotope chronological standard curve applicable to these environments over the last millennia. This contribution aims to make a tentative Holocene



**Figure 1** –  $^{208}\text{Pb}$ ,  $^{207}\text{Pb}$  and  $^{206}\text{Pb}$  isotopes had increasing abundances during the geological history of the Earth as result of the  $^{232}\text{Th}$ ,  $^{235}\text{U}$  and  $^{238}\text{U}$  decay, respectively

Pb isotope curve (using reported data) and also intends to encourage future research on Holocene deposits with the objective to obtain the Pb isotopes curve for the South America continent.

## Pb isotopes in aerosol, water, sediments, ice and soil

The anthropogenic Pb is distributed through the atmosphere and subsequently enters the terrestrial and marine environments by wet and dry deposition. The history of anthropogenic Pb emissions has been investigated by analyzing the isotope composition of Pb in suspended particulate matter (aerosols), sediments, water, ice and soil. The time of residence of Pb isotopes in the atmosphere is of about 2 weeks (Verón *et al.* 1992); the residence time of Pb in deep water vary between 50 to 200 years. Further, the geographic distribution of Pb isotopes in sedimentary deposits worldwide is not a simple response to local sources.

Studies of airborne particulates have shown that atmospheric Pb is dominated by long-range, transported anthropogenic Pb. The sources of the anthropogenic Pb differ between regions, as exemplified in the northern Canadian and Greenland High Arctic (Outridge *et al.* 2002), US and part of Canadian territory (Sturges and Barrie 1989), and Europe (Luck and Othman 2002). About 85% of the global industrial emissions are introduced into the atmosphere in the Northern Hemisphere. It has been shown, however, that the characteristic time for the inter-hemisphere exchange is about one year. Since the mean residence time of Pb rich aerosols in the atmosphere is about two weeks, thus Northern Hemisphere emissions are taken to have a negligible influence on the Southern Hemisphere.

Pb isotope vertical profiles in recent sediment cores have been used for various purposes, such as stratigraphic interpretation of paleoenvironment and recent pollution history. There has been of increasing interest in the application of radiogenic isotopic tracers (Nd, Pb and Sr) in marine deposits to oceanographic problems, and to the cycling of these elements in seawater (Hemming and McLennan 2001). These tracers are largely derived from continental sources and must ultimately enter the ocean by rivers or in the form of wind-blown dusts. In estuarine marshes, such a global atmospheric signal should be recorded, despite local input (industry, shipping and dense human population), which could obscure the atmospheric signal. By contrast, local mantle-derived inputs are evident in hydrothermal Fe-Mn deposits located near active spreading ridges. River and anthropogenic inputs, and biological and geochemical cycling may influence the concentration of metals in estuarine and coastal seawater to a much greater extent than that occurring in open-ocean water and deep-sea turbidites. The mechanism for dispersal of these metals, and their inputs into receiving systems such as sediments, have been the subject of numerous studies and, in such research, it is often necessary to attempt to evaluate the impact of local, point source releases against background levels due to regional or global contamination (Bollhöfer and Rosman 2000).

Continental Pb contamination may originate from diffuse sources, such as vehicle exhaust emission, or from point sources, such as metal smelters or mine waste tips. The Pb isotope data from natural environmental archives are useful not only for assessing background concentration and temporal

trends, but can also potentially be used to identify source regions. Unfortunately, data from many regions are sparse and individual sites are often used to characterize and reconstruct depositional trends over vast areas. At local scale Pb isotope studies have been applied in the investigation of contaminant Pb sources and behavior within specific environments with, for example, applications in the studies of streams and groundwater, soils and rivers. Various investigations have confirmed the advantages of the use of Pb isotopes to probe the anthropogenic inputs *versus* natural origins of this toxic heavy metal in well-preserved snow and ice archives of atmosphere constituents. Most investigations have been devoted to the Greenland icecap, high-altitude alpine regions, and in Antarctic snow (Planchon *et al.* 2003).

In stratigraphic studies, the most commonly used chronological tool is the down-core oxygen isotope variations measured in foraminifera and calibrated according to the standard SPECMAP curve. In coastal and continental environment, there is no such toll due the lack of foraminifera. A similar approach could be applied using ostracoda, when they are present. Consequently, in such environment, dating is generally obtained by radiochronology ( $^{14}\text{C}$ ,  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ , etc). However,  $^{14}\text{C}$  measurements provide only discrete data, while  $^{137}\text{Cs}$  and  $^{210}\text{Pb}$  are best applied in the last century (Hong *et al.* 1994, Planchon *et al.* 2003).

### Prior industrial revolution Pb record

The history of anthropogenic Pb emission has been investigated by analyzing the isotope composition of Pb in sediments and ice to evaluate prior industrial revolution Pb record (Fig. 2a). The natural background corresponds to sections displaying high  $^{206}\text{Pb}/^{207}\text{Pb}$  between 12,000 and 2,600 years. A continuous atmospheric Pb signature from 12,000 years has been observed in peat bog (in Swiss, Rosman *et al.* 2000) and the average for  $^{206}\text{Pb}/^{207}\text{Pb}$  values is 1.199. The Pb isotopic composition has been reported in Holocene estuarine marshes (in France, Monna *et al.* 2000) dated at  $6,053 \pm 172$  years ( $^{14}\text{C}$  age), with background  $^{206}\text{Pb}/^{207}\text{Pb}$  values about 1.20–1.19.

During the time of the Roman Empire, due to an intensive mining activity, large quantities of heavy metals were emitted into the atmosphere. Metal pollution dating to ancient times was recorded in various types of environment such as polar ice, ombrotrophic peat bogs and lake sediments

(Niagru 1989). The Pb isotope contamination in Greenland icecap was dated at 2,500 years ago ( $^{210}\text{Pb}$  age, Hong *et al.* 1994) and at 2,600 years ago ( $^{210}\text{Pb}$  age, Renberg *et al.* 2000) in lake sediments of Sweden. The depression of the  $^{206}\text{Pb}/^{207}\text{Pb}$  values occurred from the background values of 1.199-1.206 to values from 1.176 to 1.184 and may be explained by the influence of ore Pb signature exploited at that time. The main lead deposit in operation was the Rio Tinto deposit in Spain, which  $^{206}\text{Pb}/^{207}\text{Pb}$  values from 1.162 to 1.168.

During the Medieval period (1,700-1,200 years ago)  $^{206}\text{Pb}/^{207}\text{Pb}$  values increased whereas, at the same time, the worldwide Pb production decreased after the fall of Rome (ca. 2,000 years ago), and the values of  $^{206}\text{Pb}/^{207}\text{Pb}$  recorded in sediments is about 1.176. From 1,200 years ago the  $^{206}\text{Pb}/^{207}\text{Pb}$  values (about 1.172) can be associated to the increase of the Pb signature related to the production of mining Pb ores in Europe. The more important mining areas during this period were located in Germany (Harz Mountains and Rammelsberg mines) and in England (Derbyshire mine), which  $^{206}\text{Pb}/^{207}\text{Pb}$  values are 1.180, 1.164-1.168, and 1.171-1.187, respectively (Alfonso *et al.* 2001).

## Industrial revolution Pb isotope record

Pb isotopes have proven to be powerful tracers of the origin and provenance of soils, lake sediments, coasts estuarine sediments and ice in distinguishing the Pb isotope signatures contamination resulted of the industrial revolution (Fig. 2b). Since the economic development occurred in specific periods and with distinct characteristics in countries and continents, the Pb isotopes record of this period of time is geographic- and time-dependent. In this way, the Holocene Pb isotope curve recorded in several continental masses presents different patterns. Actually, it is possible to have this approach in three continental areas: Europe, North America and Antarctica. In general way, the Pb isotope curve to the last 200 years records the initial period of industrialization, when coal was the main source of energy, followed by the Pb-enriched gasoline, and as last period, occurred the fall in the use of gasoline Pb additives.

In Europe, several investigations have confirmed variation of the Pb signatures in the last two centuries. Pb isotopes results of ice and sediments (Rosman *et al.* 2000, Monna *et al.* 2000) show  $^{207}\text{Pb}/^{206}\text{Pb}$  decreased from 1.18 in the earliest core (200 years B.P.) to 1.17 by the mid twentieth century.

The rate of decline then increases significantly until 1969 probably reflecting the increasing Pb emission from automobile exhausts following the introduction of leaded gasoline in the mid 1920s. Deposits from the late 1800s have high  $^{206}\text{Pb}/^{207}\text{Pb}=1.200$  values (Rosman *et al.* 2000) interpreted as regional background and inputs of coal and wood burning. The following lowered Pb ratios (about 1.142) indicate an influence of industrial and domestic emissions, and the uppermost sediments record the leaded gasoline  $^{206}\text{Pb}/^{207}\text{Pb}$  values of 1.069-1.094.

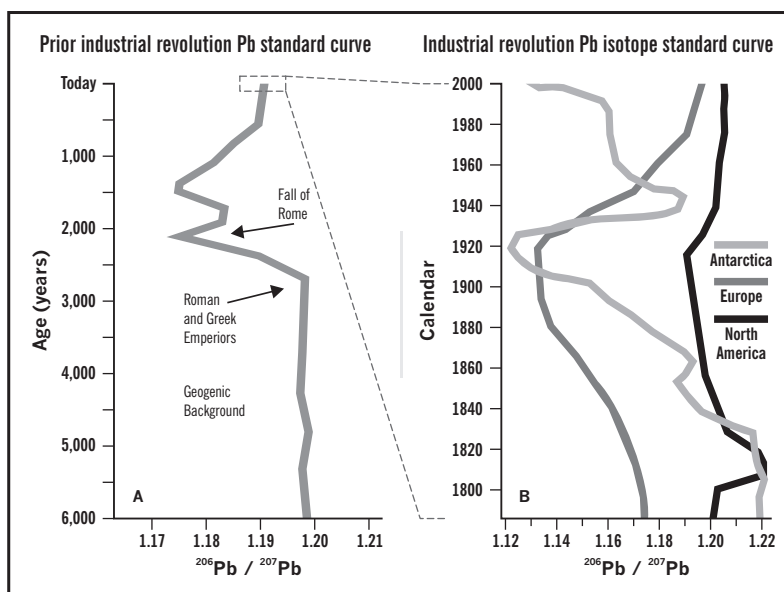
In North America, the history of anthropogenic Pb emission has been investigated by analyzing the isotope composition of Pb in sediments, corals and ice. The Pb isotope recorded in Chesapeake Bay (east of U.S.) demonstrated that the anthropogenic Pb isotope in the bay is derived from regional industrial emissions that vary through time (Marcantonio *et al.* 2002). Over the past century, there is an excellent temporal agreement between anthropogenic  $^{206}\text{Pb}/^{207}\text{Pb}$  isotope ratios of this bay and those determinate in a dated coral in Bermuda, almost 2,000 km away. This correlation is used to argue that these Pb signature contain a regional industrial atmospheric Pb isotope signal that is representative of the mid-Atlantic region of U.S. Anthropogenic Pb is found in sediments deposited as early as approximately 1800 and the background (sediments older than 200 years) is characterized by the  $^{206}\text{Pb}/^{207}\text{Pb}=1.205-1.210$ . From about 1880 to 1930, the Pb signal is probably derived from burning of coal ( $^{206}\text{Pb}/^{207}\text{Pb}=1.125$ , Niagru 1990). After this period, and up until about the 1980s, the signal is overwhelmed by the Pb derived from the combustion of leaded gasoline ( $^{206}\text{Pb}/^{207}\text{Pb}=1.190-1.195$ , Niagru 1990).

In Antarctica, initial investigations indicate the  $^{206}\text{Pb}/^{207}\text{Pb}$  value of 1.196 for regional background in ice dated at 22.6 kyr, corresponding to the last glacial maximum. In addition, one hundred fifty-year record of Pb isotopes in Antarctic snow, covering the period between ~1840 and 1990, shows evidence of pollution for this metal as early as 1880s (Rosman *et al.* 1994). Observed Pb isotope signature at the beginning of the 20<sup>th</sup> century show  $^{206}\text{Pb}/^{207}\text{Pb}$  values ranging from 1.165 to 1.209. There is a  $^{206}\text{Pb}/^{207}\text{Pb}$  peak (1.174) about 1834 interpreted as a result of Mount Erebus volcanic contribution. About 1890, the  $^{206}\text{Pb}/^{207}\text{Pb}$  presented a significantly decrease to 1.200, which may be linked to Australian contribution (Pb-contaminating aerosols emitted during Pb mining, smelting, or coal combustion), or whaling and sealing activities very significant in

the southern ocean at that time. The  $^{206}\text{Pb}/^{207}\text{Pb}$  values from 1.145 to 1.200, during the 1940s and 1950s, suggest that there has been a weakening in anthropogenic inputs of Pb to the remote Antarctica (probably linked to the decrease in ship traffic around the southern tip of South America due to the opening of canal of Panama in 1914). There is a clear decrease from the early 1960s to the early 1980s in  $^{206}\text{Pb}/^{207}\text{Pb}$  values as consequence of the very large rise in the use of leaded gasoline in the Southern Hemisphere continents during that period, combined with the continuous increase in nonferrous metal production in South America, South Africa and Australia.

### Holocene Pb isotopes studies in South America

Pb isotope studies in South America on Holocene sediments are rare. Most of the reports are about Pb concentrations in rivers and estuaries. Two studies using Pb isotope signatures of aerosols have been reported: the first study (Bollhöfer and Rosman 2000) reports aerosols Pb signatures from Brazil (9 samples), Argentina (3 samples) and Chile (9 samples) and show  $^{206}\text{Pb}/^{207}\text{Pb}$  values from 1.147 to 1.177. Studies on the Pb isotope composition of the São Paulo (Aily 2001) city atmosphere collected daily during fourteen months (August, 1999-September, 2000) indicated  $^{206}\text{Pb}/^{207}\text{Pb}$  values from 1.142 to 1.273. The values are related to contribution of Pb-containing gasoline additives and industrial activities. In addition, investigations on Pb isotopes analysis in mining waste (galena massive vein hosted in Neoproterozoic carbonates; Tassinari *et al.* 1990) and river channel sediments in a transect downstream from the mine dump, readily identified the mines as a highly pollutant (Morales 1997). Ongoing investigations using Pb isotopes in aerosols (Brasilia-Brazil, Gioia *et al.* 2003) and Holocene deposits (Rio de Janeiro-Brazil, Gerales *et al.* 2006) will contribute to a better understanding on this subject in South America.



**Figure 2** – A tentative Holocene Pb isotope standard curve based on reported data worldwide. (A) Prior industrial revolution and (B) during the industrial revolution

### Concluding remarks

Pb isotopes have been used to characterize historical records of anthropogenic activities and to trace the changing sources of pollutant Pb in continental environment through time. As Pb is one of the high priority contaminants in surface water, it is important the construction of a Pb isotope chronological standard curve applicable to these environments over the last millennia. In this way, Holocene Pb isotope curve may be divided in the following periods:

- 1) The natural background displays  $^{206}\text{Pb}/^{207}\text{Pb}$  values about 1.199 between 12,000 and 2,600 years, as observed in sediments (Europe and North America) and ice caps (Europe and Antarctica).
- 2) The depression of the  $^{206}\text{Pb}/^{207}\text{Pb}$  values at 2,600 years ago occurred from the background values of 1.199-1.206 to values from 1.176 to 1.184 and may be explained by the influence of the Pb ore (Rio Tinto deposit) signature during the time of the Roman Empire due to an intensive mining activity.
- 3) During the Medieval period (1,700-1,200 years ago)  $^{206}\text{Pb}/^{207}\text{Pb}$  values increased whereas, at the same time, the worldwide Pb production decreased after the fall of Rome, and the values of  $^{206}\text{Pb}/^{207}\text{Pb}$  recorded in sediments is about 1.176.

4) The Pb isotopes record of the industrial revolution period is geographic- and time-dependent. The Pb isotope curves for this period recorded in Europe, North America and Antarctica present different patterns. In general way, the Pb isotope curves for the last 200 years record the initial period of industrialization, when coal was the main source of energy ( $^{206}\text{Pb}/^{207}\text{Pb}$  values about 1,200), followed by the Pb-enriched gasoline ( $^{206}\text{Pb}/^{207}\text{Pb}$  values about 1,170), and as last period, occurred after the fall in the use of gasoline Pb additives.

## References

- Aily C. 2001 *Caracterização isotópica de Pb na atmosfera: um exemplo da cidade de São Paulo*. MSc Dissertation. São Paulo: Instituto de Geociências, Universidade de São Paulo. 76p.
- Alfonso S., Grousset F., Massé L., Tastet J.-P. 2001. A European lead isotope signal recorded from 6000 to 300 years BP in coastal marshes (SW France). *Atmos. Environ.*, **35**(21):3595-3605.
- Bollhöfer A., Rosman K.J.R. 2000. Isotopic source signatures for atmospheric lead: the Southern Hemisphere. *Geochim. Cosmochim. Acta*, **64**(19):3251-3262.
- Geraldès M.C., Paula A.H., Godoy J.M., Valeriano C.M. 2006. Pb isotope signatures of sediments from Guanabara Bay, SE Brazil: evidence for multiple anthropogenic sources. *J. Geochem. Explor.*, **88**(1-3):384-388.
- Gioia S.M.C.L., Pimentel M.M., Guimarães E.M., Campos J.E.L., Dantas E.L., Maruoka M.T.S. 2003 Atmospheric deposition and sources of anthropogenic lead in sediments from a recent lake in Brasília, Central Brazil. *IV South American Symposium on Isotope Geology, Short Papers*, **1**:434-437.
- Helland A., Åberg G., Skei J. 2002. Source dependent behaviour of lead and organic matter in the Glomma estuary, SE Norway: evidence from isotope ratios. *Mar. Chem.*, **78**(2-3):149-169.
- Hemming S.R., McLennan S.M. 2001. Pb isotope compositions of modern deep sea turbidites. *Earth Planet. Sc. Lett.*, **184**(2):489-503.
- Hong S., Candelone J.P., Patterson C.C., Boutron C.F. 1994. Greenland ice evidence of hemispheric lead pollution two millennia ago by Greek and Roman civilizations. *Science*, **265**:1841-1843.
- Luck J.M., Othman D.B. 2002. Trace element and Pb isotope variability during rainy events in the NW Mediterranean: constraints on anthropogenic and natural sources. *Chem. Geol.*, **182**(2-4):443-460.
- Marcantonio F., Zimmerman A., Xu Y., Canuel E. 2002. A Pb isotope record of mid-Atlantic US atmospheric Pb emissions in Chesapeake Bay sediments. *Mar. Chem.*, **77**(2-3):123-132.
- Monna F., Clauer N., Toukeridis T., Lancelot J.R. 2000. Influence of anthropogenic activity on the lead isotope signature of Thau Lake sediments (southern France): origin and temporal evolution. *Applied Chemistry*, **15**(9):1291-1305.
- Moraes, R.P. 1997. *Transporte de chumbo e metais pesados no rio Ribeira de Iguape, São paulo, Brasil*. MSc Dissertation. Campinas: Instituto de Geociências, Universidade de Campinas. 126p.
- Nriagu J.O. 1989. A global assessment of natural sources of atmospheric trace metals. *Nature*, **338**:47-49.
- Nriagu J.O. 1990. The rise and fall of leaded gasoline. *Sci. Total Environ.*, **92**:13-28.
- Outridge P.M., Hermanson M.H., Lockhart W.L. 2002. Regional variations in atmospheric deposition and sources of anthropogenic lead in lake sediments across the Canadian Arctic. *Geochim. Cosmochim. Acta*, **66**(20):3521-3531.
- Planchon F.A.M., Van de Velde K., Rosman K.J.R., Wolff E.W., Ferrari C.P., Boutron C.F. 2003. One hundred fifty-year record of lead isotopes in Antarctic snow from Coats Land. *Geochim. Cosmochim. Acta*, **67**(4):693-708.
- Renberg I., Brännvall M.-L., Bindler R., Emteryd O. 2000. Atmospheric lead pollution history during four millennia (2000 BC to 2000 AD) in Sweden. *Ambio*, **29**(3):150-156.
- Rosman K.J.R., Chisholm W., Boutron C.F., Candelone J.-P., Patterson C.C. 1994. Anthropogenic lead isotopes in Antarctica. *Geophys. Res. Lett.*, **21**(24):2669-2672.
- Rosman K.J.R., Ly C., Van de Veld K., Boutron C.F. 2000. A two century record of lead isotopes in high altitude Alpine snow and ice. *Earth Planet. Sc. Lett.*, **176**(3-4):413-424.
- Sturges W.T., Barrie L.A. 1989. The use of stable lead 206/207 isotope ratios and elemental composition to discriminate the origins of lead in aerosols at a rural site in eastern Canada. *Atmos. Environ.*, **23**(8):1645-1657.
- Tassinari C.C.G., Barbour A.P., Daitx E.C., Sato, K. 1990. Aplicação dos isótopos de Pb e Sr na determinação da natureza das fontes das mineralizações de Chumbo do vale do Ribeira, SP e PR. In: XXXVI Congresso Brasileiro de Geologia. *Anais...*, Natal-RN, v. 3, p. 1255-1266.
- Véron A., Flament P., Bertho M.L., Alleman L., Flegel R., Hamelin B. 1999. Isotopic evidence of pollutant lead sources in Northwestern France. *Atmos. Environ.*, **33**(20):3377-3388.

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