

LEAD ISOTOPES AS TRACERS OF CORROSION IN WATER PIPELINES AT LA SPEZIA, ITALY

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ABSTRACT

In the 1940's-1950's Pb isotopes were used for determining the age of the Earth and the whole solar system. Afterwards, Pb isotopes were applied to investigate the dispersion of anthropogenic Pb in the environment as well as in archeology, to assess the origin of the metals used in the manufacturing of coins and other objects. Recently, we have used Pb isotopes as tracers of corrosion in water pipelines. The study was carried out on the ACAM aqueduct of La Spezia, which transports and distributes throughout this municipality the groundwater extracted from several boreholes drilled in the alluvial aquifer of the Lower Magra Basin. The main pipeline of this aqueduct was built in 1917 using pipe units made up of cast iron and Pb as sealing material. However, Pb is also contained in significant amounts in galvanized iron (i.e., Fe with Zn coatings), which is typically used for domestic pipelines. In order to establish which one of these two possible sources contributes Pb to the Fe(III)-oxy-hydroxides representing the corrosion products, Pb isotopes were analyzed in the cast iron of the main pipeline and related Pb seals, in the domestic pipes of galvanized iron and in the corrosion products as well.

Analytical results indicate that the Pb contained in Fe(III)-oxy-hydroxides is totally contributed by corrosion of domestic pipes, whereas no Pb is derived from the main pipeline of the ACAM aqueduct. This conclusion is not surprising, considering that Fe(III)-oxy-hydroxides are rich in Zn, which evidently comes from corrosion of the Zn-coated domestic pipes. In fact, Fe (with an atomic fraction of 0.865) and Zn (with an atomic fraction of 0.106) constitute together 97% of the corrosion products. To corroborate these conclusions, the corrosion processes affecting the galvanized-iron domestic pipelines were simulated by means of the EQ3/6 software package. Concentrations of trace elements in the aqueous solution undergo a very slight increase during the progressive dissolution of the solid reactant, whereas elements released through this process enter almost entirely an Fe(III)-rich solid mixture of oxy-hydroxides, which represents the only precipitating secondary solid phase. Its chemical composition approaches progressively that of the starting material, suggesting that corrosion of the galvanized-iron domestic pipelines is a sort of quasi-isochemical dissolution-precipitation process. A further consequence of the results outlined above is that not only Pb, but also all the metals contained into the Fe(III)-oxy-hydroxides (Fe, Zn, Cu, Cr, Pb, Ni, Mn, in order of decreasing importance) come from corrosion of the domestic pipelines. Further researches are needed to establish the ultimate causes governing corrosion (stagnation of water in the domestic pipelines, bacterial mediation of relevant redox reactions, etc.).

Keywords: Corrosion, Water pipelines, Pb isotopes, Reaction path modelling, EQ3/6.

1. INTRODUCTION

In the 1940's-1950's Pb isotopes were used by famous geochemists, such as E.K. Gerling, Arthur Holmes, Fritz G. Houtermans and Clair Cameron Patterson, in different attempts to date the Earth. Finally, in 1956, Clair Cameron Patterson [1] obtained an isochron age for the solar system (obviously including our planet) of 4.55 ± 0.07 billion years, which was confirmed by numerous researches carried out afterwards, apart from a smaller error range of ± 0.02 billion years (Dalrymple [2]).

Clair Cameron Patterson together with his coworkers and pupils also studied the dispersion of anthropogenic Pb in the environment, which begun ~4500 year ago, attaining worrying levels since the 1920's, when tetraethyl Pb was introduced as antiknock additive in gasoline. Owing to the importance of this topic, Pb isotopes have been used more and more for environmental purposes, especially since the 1960's.

The isotope composition of Pb has been applied also in archaeology, to establish the provenance of metals utilized for manufacturing coins and other objects. Thanks to these researches, chiefly performed by the so-called Oxford Group, comprising Gale, Stos-Gale and coworkers, a database of the Pb isotope ratios of ore deposits (especially those of Cu and Pb) in the Mediterranean area has been implemented (see website <http://www.brettscaife.net/lead/data/index.html>).

Starting from the knowledge acquired in these different discipline, we have recently used Pb isotopes to trace corrosion processes in water pipelines, namely to establish the provenance of Pb contained in the deposits of Fe(III) oxy-hydroxides formed through these corrosion phenomena.

The subject of our investigation is the ACAM aqueduct, which transports and distributes throughout La Spezia municipality the groundwater collected from several wells drilled in the alluvial aquifer of the Lower Magra Basin. The main pipeline of the ACAM aqueduct was constructed in 1917, using pipe units made up of cast iron whereas Pb was utilized to seal the connections between different pipe units. However, Pb is also contained, in comparatively small but not negligible amounts, in the pipes of galvanized iron (i.e., Fe with Zn coatings), which are typically used for domestic networks. In contrast, there is no galvanized iron in the ACAM aqueduct, whose secondary pipelines are made up of high-density polyethylene.

It must be underscored that the ACAM aqueduct of La Spezia has always guaranteed, and guarantees at present, a supply of high-quality water. In addition, since its construction, no problem due to presence of Pb or other undesired metals has never arisen. Recently, in the tap water of a few houses, high turbidity levels have been reported, with correspondingly low turbidity values at the end-points of the ACAM aqueduct. In spite of this evidence, it was decided to strengthen it, discriminating the provenance of metals from either the private domestic network or the ACAM aqueduct by means of the isotope fingerprint of Pb contained in trace amounts in the deposits of Fe(III) oxy-hydroxides. Therefore, Pb is taken into consideration, in the case under study, as tracer of the turbidity phenomenon, and not because the presence of Pb in drinking water poses a problem. As a matter of fact, dissolved Pb in the drinking water distributed in the western part of La Spezia urban area was measured through isotope dilution in the laboratory of the Institute of Geosciences and Earth Resources of CNR (IGG-CNR) and resulted to be in the range 0.07 - 0.14 $\mu\text{g/L}$ (while in the past, in some cases, high concentrations of lead have been found at the tap of the domestic network). Summing up, the question to be answered in this study is: where does Pb (which is contained in trace amounts in the deposits of Fe(III) oxy-hydroxides) come from? Does it derive from corrosion/erosion of either the cast-iron pipelines of the ACAM aqueduct or the galvanized-iron pipelines of the domestic network?

2. SAMPLING OF SOLID MATERIALS AND ISOTOPE ANALYSIS OF LEAD

To answer these questions, the following solid materials were sampled: (i) Cast iron from the main pipeline of the ACAM aqueduct; this sample is labelled Cast Iron. (ii) Lead used to seal the connections between different units of the main pipeline of the ACAM aqueduct; this sample is labelled Lead. (iii) Piece of domestic pipe in galvanized iron from a house situated in the eastern part of La Spezia urban area; the domestic network of this house is fed by the main pipeline of the ACAM aqueduct; the sample was collected immediately downstream of the flow-meter and was split in two portions: an inner part rich in Zn (labeled Domestic Pipe + Zn) and an overall sample (labeled Domestic Pipe). (iv) deposits of Fe(III) oxy-hydroxides separated from the tap water of the house; this sample is labeled Fe(OH)₃.

For each one of these solid materials, Pb was separated from the matrix through ionic exchange, in the laboratory of IGG-CNR in Pisa, in a class 100 Clean Room. The Pb-bearing eluates were then charged on rhenium wire filaments after drying and re-dissolution in H₃PO₄, using tetraethyl orthosilicate (TEOS) as activator. Afterwards, the isotopic composition of Pb was determined through a thermal ionization multi-collector mass spectrometer Finnigan Mat 262, following a standard procedure (Agostini et al. [3]). To correct results for isotopic fractionation occurring during measurement, the international standard NIST SRM 981 was measured after each sample. The following Pb isotope ratios were adopted for this standard (Todt et al. [4]): ²⁰⁸Pb/²⁰⁴Pb = 36.7054; ²⁰⁷Pb/²⁰⁴Pb = 15.4925; ²⁰⁶Pb/²⁰⁴Pb = 16.9373.

3. RESULTS

Comparison of Pb isotope ratios for the solid materials of interest with available data for Sardinian and Tuscan ore deposits suggests that these solids, or at least the Pb they contain, come from Sardinia (Figs. 1 and 2).

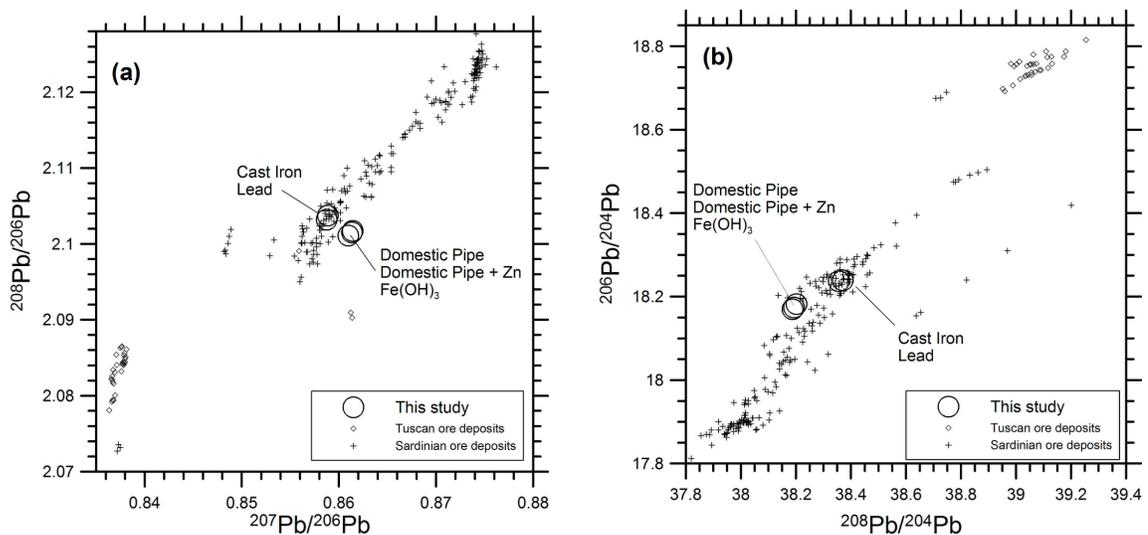


Figure 1. Correlation plots of (a) $^{208}\text{Pb}/^{206}\text{Pb}$ vs. $^{207}\text{Pb}/^{206}\text{Pb}$ and (b) $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ for the solid samples of interest, also showing available data for ore deposits of Sardinia and Tuscany, from <http://www.brettscaife.net/lead/data/index.html>.

In addition and even more important, it is clearly evident the similarity between samples labelled Lead and Cast Iron, on the one hand, and samples coded Domestic Pipe, Domestic Pipe + Zn, and Fe(OH)₃, on the other hand (Fig. 2). In fact, the two first samples and the other three samples belong to two totally distinct groups, irrespective of analytical errors. Consequently, these data prove, without question, that the Pb contained in the Fe(III) oxy-hydroxides (sample Fe(OH)₃) derives in toto from corrosion of domestic pipelines, represented by samples Domestic Pipe and Domestic Pipe + Zn, whereas there is no contribution from the main pipeline of the ACAM aqueduct, which is represented by samples Lead and Cast Iron.

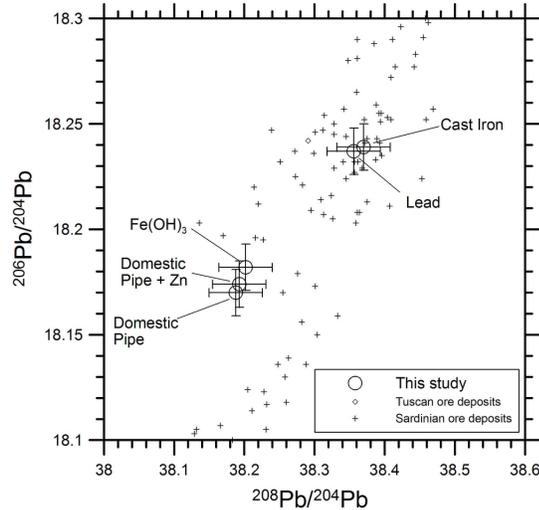


Figure 2. Detail of the correlation diagram $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ highlighting differences between the two groups of analyzed solid samples (error bars refer to two standard deviations).

Let us now consider the chemical composition of the Fe(III) oxy-hydroxides representing the product of the corrosion process affecting the domestic pipes made up of galvanized iron (as indicated by Pb isotopes), by means of the pie chart of Fig. 3. Iron (with an atomic fraction of 0.865) together with Zn (with an atomic fraction of 0.106) made up 97% of this material. The high content of Zn in these Fe(III) oxy-hydroxides evidently represents a further proof of the generation of these materials through corrosion of the domestic pipelines, which are in fact constituted by Fe with Zn coatings.

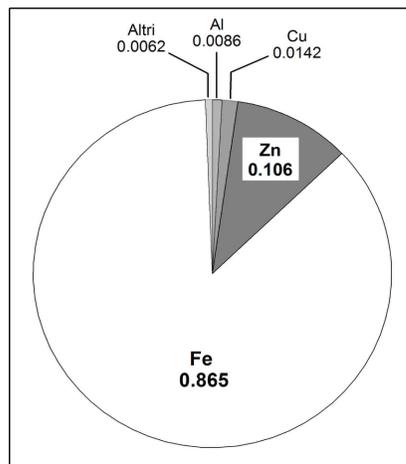


Figure 3. Pie chart showing the chemical composition of the Fe(III) oxy-hydroxides produced through corrosion of the domestic pipes made up of galvanized iron.

4. MODELLING OF CORROSION

Reaction path modelling (a powerful geochemical tool proposed by Helgeson, [5]) of both the corrosion process affecting the domestic pipelines and the consequent formation of the Fe(III) oxy-hydroxides deposits is needed to move from the qualitative perception of these phenomena to their quantitative understanding. Therefore, reaction path modelling was carried out by means of the software package EQ3/6, version 8.0 (Wolery and Jarek, [6]), in stoichiometric mode, that is referring to the reaction progress variable, irrespective of the kinetics of relevant processes. The system was considered closed with respect to precipitating secondary solid phases, i.e., the Fe(III) oxy-hydroxides in the case of interest.

The initial composition of the aqueous solution was computed by means of the EQ3 code referring to the average chemistry of the ACAM aqueduct water (Brozzo and Marini, [7]) and imposing an Eh value of 795 mV, to reproduce the strongly oxidising conditions determined by addition of sodium hypochlorite, whose concentration was assumed to be 2 $\mu\text{mol/kg}$, corresponding to 0.1 ppm. This appears to be a reasonable value based on several determinations carried out on the ACAM aqueduct water.

The working hypothesis (which is what we want to demonstrate or reject through the reaction path modelling exercise, although it can be considered very likely based on previous discussion) is that Fe(III) oxy-hydroxides of sample Fe(OH)₃ are totally produced through corrosion of the domestic pipelines made of galvanized iron. In other words, the phenomenon of interest is a quasi-isochemical dissolution /precipitation process, i.e., with close-to-complete conservation of the considered chemical elements in the solid phases. Starting from these premises, the chemical composition of the Fe(III) oxy-hydroxides (i.e., the reaction product) was used to define the stoichiometry of the galvanized-iron pipe (i.e., the reactant) and inserted as a so-called “special reactant” in the input file of the EQ6 code. We recall that a “special reactant”, sensu EQ6, is any material of known chemical composition and unknown thermodynamic and kinetic properties (Wolery and Jarek, [6]).

Reaction path modelling was extended up to a maximum value of 0.01 moles of the reaction progress variable, corresponding to 572 mg of destroyed pipe, keeping a constant temperature of 12.2°C. Eh remained in the 795-779 mV, in line with the presence of excess hypochlorite, as recalled above.

The concentrations of all trace elements coming from dissolution of galvanized iron experience limited changes for increasing values of the reaction progress variable. Most of these elements, in fact, enter a solid mixture of oxy-hydroxides (dominated by the Fe(III) end-member, as expected), which is the only secondary solid phase. Its composition gradually approaches that of the starting material (Fig. 4), in agreement with our working hypothesis, namely the quasi-isochemical dissolution /precipitation of galvanized iron, which is what we wanted to demonstrate.

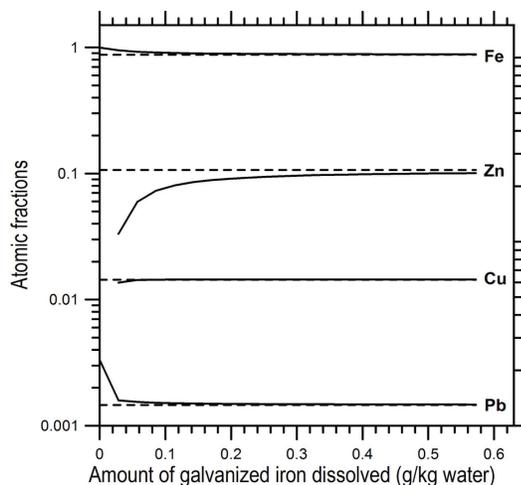


Figure 4. Changes in the composition of the solid mixture of oxy-hydroxides (solid lines) precipitating during the progressive dissolution of galvanized iron (dashed lines), constituting the domestic pipelines, in tap water at 12.2°C under oxidizing redox conditions (Eh 795-779 mV).

5. CONCLUSIONS

The Pb isotope ratios measured on the solid samples collected during this study highlight that:

- (i) the Pb contained in small amounts in the Fe(III) oxy-hydroxides present in tap water is totally contributed by corrosion of galvanized-iron pipelines constituting the domestic network of the house which is affected by turbidity phenomena;
- (ii) no Pb is contributed through dissolution of the metals (cast iron and lead) which were used long ago to realize the main pipeline of the ACAM aqueduct connecting the groundwater extraction area, within the alluvial aquifer of the Lower Magra Basin, and La Spezia town.

Consequently, not only Pb, but also all the metals contained in the Fe(III) oxy-hydroxides (Fe, Zn, Cu, Cr, Pb, Ni, Mn, etc.) are released through corrosion of the galvanized-iron private pipelines of the house which is affected by turbidity phenomena, downstream of the end-point of the ACAM aqueduct. Although the factor or the factors governing galvanized-iron corrosion cannot be established based on available data (stagnation of drinking water in the domestic pipelines constituted by metals of low durability, possible bacteria mediation of the redox process, etc.), there is no doubt on the provenance of Pb, and consequently of other metals as well, from the private network.

This conclusion based on Pb isotopes is confirmed by the strong atomic fraction of Zn in the Fe(III) oxy-hydroxides, which are chiefly made up of Fe, 86.5%, and Zn, 10.6 %, jointly constituting over 97% of the material of interest.

Corrosion of the domestic pipelines of galvanized iron (a material which is not present in this part of ACAM hydraulic network, whose secondary pipelines are made up of high-density polyethylene) can be considered as a quasi-isochemical dissolution /precipitation process, that is with close-to-complete conservation of relevant metals (Fe, Zn, Cu, Pb, ...) in the solid phases, as shown by a reaction path modelling exercise carried out by means of the software package EQ3/6.

Although this work represents a first attempt to study the corrosion of drinking water pipelines through the use of powerful geochemical techniques, such as reaction path modelling and Pb isotopes,

results are very interesting and encouraging as they allow one to understand some characteristics of the phenomena of interest with a good detail.

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REFERENCES

- [1] Patterson, C.C., Age of meteorites and the Earth. *Geochim. Cosmochim. Acta*, vol. 10, pp. 230-237, 1956.
 - [2] Dalrymple, G.B., *The Age of the Earth*, California, Stanford University Press, 1991.
 - [3] Agostini, S., S. Bruni, S. Tonarini, 2005 Lead Isotope Analyses. Internal Report. Institute of Geosciences and Earth Resources of C.N.R., Pisa, pp. 8, 2005
 - [4] Todt, W., R.A. Cliff, A. Hanser, A.W. Hofmann, Re-calibration of NBS lead standards using a ²⁰²Pb-²⁰⁵Pb double spike. *Terra Abstracts*, vol. 5, issue 1, p. 396, 1993.
 - [5] Helgeson, H.C., Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions: I. Thermodynamic relations, *Geochim. Cosmochim. Acta*, vol. 32, pp. 853-877, 1968.
 - [6] Wolery, T.W., R.L. Jarek, Software user's manual EQ3/6, Version 8.0. Sandia National Laboratories – U.S. Dept. of Energy Report, 2003.
 - [7] Brozzo, G., L. Marini, *Atlante degli acquiferi della Liguria - Volume IV: L'acquifero alluvionale della bassa valle del Fiume Magra*, Pacini, Pisa, pp. 85, 2009.
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