Archaeology & History in Lebanon Issue Eighteen : Autumn 2003, p. 115-119.

Gaël Le Roux[1]
Alain Véron[2]
Christophe Morhange[2]

Geochemical Evidences of Early Anthropogenic Activity in Harbour Sediments from Sidon

Introduction

Sediment accumulated in the sea coast of Saïda (the ancient city of Sidon) record more than 5000 years of palaeoenvironmental changes (Morhange *et al.*, 2000). In a previous article (Le Roux *et al.*, 2002), we showed that ancient metallurgical activities could be evidenced in these sediments thanks to lead isotope imprints. Indeed there are four stable isotopes of lead, three of which are radiogenic end-members of U-Th natural radioactive decay chains (^{232}Th - ^{208}Pb, ^{235}U - ^{207}Pb, ^{238}U - ^{206}Pb). Depending on the age and the initial content of U-Th, various lead, silver and copper ores will display different isotopic signatures. Therefore it is possible to distinguish lead from different ores as well as to evidence anthropogenic activities with isotopic ratios. The use of such isotopic imprints for archaeology and palaeoenvironmental records has been well described (Gale and Stos-Gale, 1982; Hosler and MacFarlane, 1996; Shotyk *et al.*, 1998; Weiss *et al.*, 1999). Unfortunately no precise age dating was available for this study. Here, we present these new radiocarbon ages that allow a better constrain on the contamination of the sediments in Antiquity at this location.

Methods

Sediment samples were collected in the northern harbour of Saïda (BH IX core). Subsamples were taken from the core on the field and sealed in clean plastic bags to avoid external contamination. Samples were then freeze-dried, and powdered in an agate mortar at CEREGE (Aix en Provence). For each sample, 50-70mg of sediments were digested at 120°C with an HNO_{-3}-HCl-HF mixture in acid cleaned Teflon beakers. After evaporation, aliquots were dissolved in an HBr (0,5N) solution. Lead was separated using anionic Agl-X8 resin (50µl). Isotope ratios for lead were determined by standard thermal ionisation mass spectrometry (Hamelin et al., 1990) on a Finnigan MAT 262 at CEREGE. Mass fractionation was corrected using repeated measurements of NBS SRM 981 standard. Pb concentrations were measured by isotopic dilution method using a ^{208}Pb spike solution.

Conventional ^{14}C age dating was obtained on molluscs by liquid scintillation counting at Lyon and calibrated (Stuiver and Braziunas, 1993).

1 Institute of Environmental Geochemistry, University of Heidelberg.

2 CEREGE, UMR CNRS6635, Université Aix-Marseille III.

Results

Lead isotope ratios, concentration, lead fluxes and age dating are presented in Figure 1 along with the lithology of the core (Espic *et al.*, 2002). We can distinguish three different trends for lead geochemistry along the core profile:

- Below 4m, concentrations are lower than 20 ppm and $^{206}Pb/^{207}Pb$ ratios are about 1,207.
- At a depth of about 3,7m deep, the 206Pb/207Pb ratios shift (1,190) and we observe an increase in concentration that is clearly evidenced at 2,7m deep (60ppm).
- While concentrations do not change significantly, the $^{206}Pb/^{207}Pb$ ratios shift to less radiogenic values (1.174) at the top of the core. This signature is similar to modern anthropogenic imprints as shown in recent Mediterranean sediments (Ferrand *et al.*, 1999).

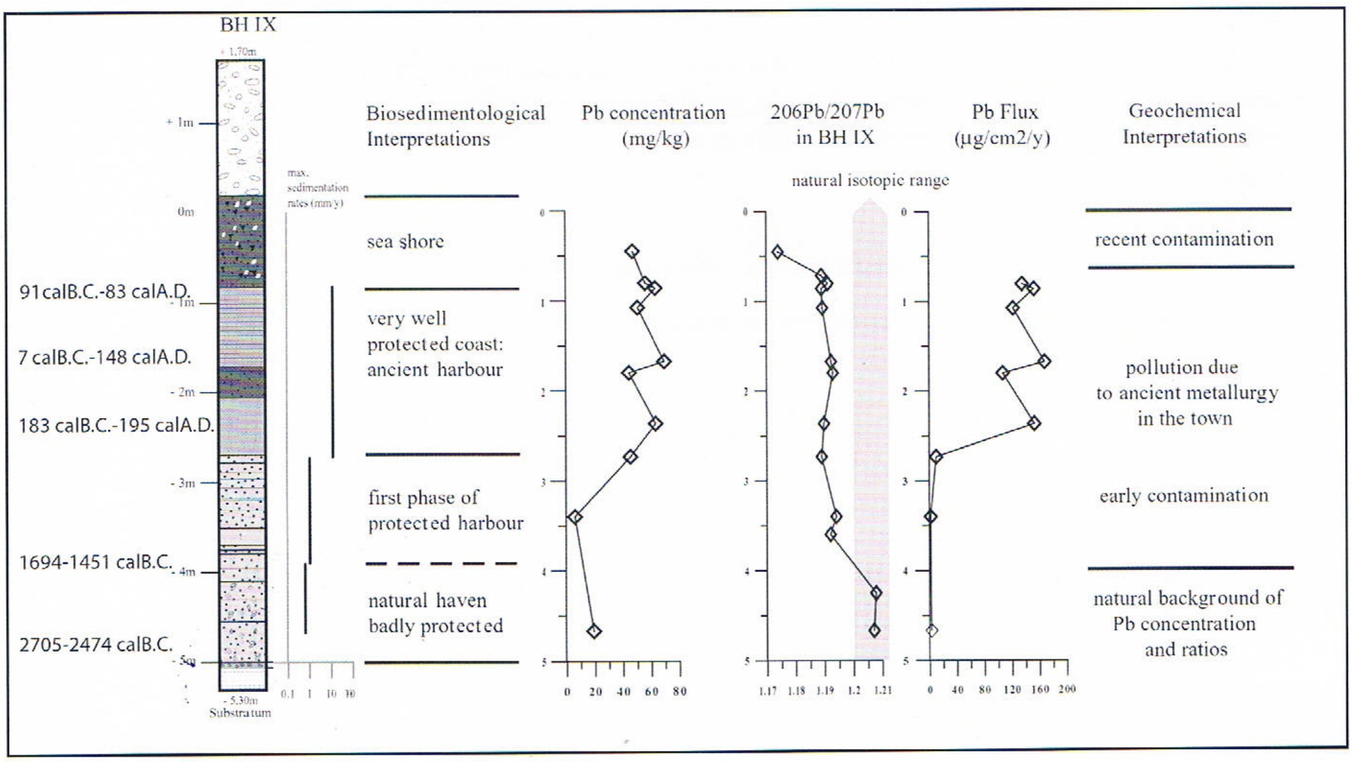
Variations in lead isotope ratios and concentrations cannot be related to the natural variability of deposited sediments since isotopic shifts are observed in core sections where no mineralogical and/or chemical changes occur. Thus we can exclude sedimentological variations as a factor to explain lead trends. Moreover carbonate content in this profile is quite constant (around 40%) and could not explain the variations in lead concentrations by dilution of the detritic sediments with biogenic components.

As shown by Espic *et al.*(2002), establishment of the harbour is followed by a sedimentological change. This is confirmed by ^{14}C dating that shows an increase in sediment deposition rates after the construction of the harbour. Also, anthropogenic indicators such as lead display increasing flux deposition during this period (Fig. 1) as we would expect from a lead concentration increase.

Discussion

The Northern Harbour area could be considered as a final collector for streaming from the town and ship wastes. As a result, sediment accumulation is likely to record anthropogenic activity of the city. The ^{14}C ages and fast sediment accumulation indicate that the well protected harbour was clearly established during the late Greek and Roman period.

1 **Lithological and Pb chemistry profiles of the BHIX core.**



Geochemical analysis shows that during this period, Pb input was important (>100µg/cm^2/y) and similar to that in modern contaminated harbours (Buckley *et al.*, 1995; Croudace and Cundy, 1995). While the $^{206}Pb/^{207}Pb$ ratios do confirm the raise of anthropogenic activities during the 183BC-195AD period, we also have evidence of an early shift at 2.8m deep in the core with no clear changes in lead concentration. Lead isotope signatures are better indicators of anthropogenic activities than concentration alone owing to dilution processes. Here, this early shift in the $^{206}Pb/^{207}Pb$ ratios very likely indicates an early human settlement before the clear and well-defined foundation of the harbour. Based on ^{14}C dating uncertainties, we can infer that this activity could precede the harbour establishment by about 1500±200 years. This is a unique finding that deserves further investigation.

The measured lead concentration (Pb_{meas}) is a mixture of natural (Pb_{nat}) and anthropogenic (Pb_{anth}) lead. In an attempt to use Pb isotopes as fingerprints of metals used in Sidon, we shall calculate anthropogenic lead imprint. This can be done by a simple mass balance calculation assuming constant concentration and isotopic signature for natural deposits

(i.e.: [Pb]=19,01ppm, $^{206}Pb/^{207}Pb$=1,207).

Then the anthropogenic imprint can be calculated

$$(^{206}Pb/^{207}Pb)_{anth} = \frac{(^{206}Pb/^{207}Pb)_{meas} \times [Pb]_{meas} - (^{206}Pb/^{207}Pb)_{nat} \times [Pb]_{nat}}{[Pb]_{meas} - [Pb]_{nat}}$$

as follow for the $^{206}Pb/^{207}Pb$:

Calculated anthropogenic signatures are presented in figure 2 along with lead isotope imprints of representative mines during Antiquity. Some of these mines are exclusively Pb mines but others are multimetallic mines.

In a previous paper (Le Roux *et al.*, 2002), we assumed that lead contamination originated not only from lead-silver metallurgy but also from bronze (copper alloy with tin and/or arsenic and lead traces) in the city. In the absence of ^{14}C age dating, we made the hypothesis that copper ores or alloys (in particularly from Cyprus) were not the major sources of lead in the harbour. With this new dating, it appears that lead pollution dates from the Hellenistic and Roman periods, in perfect agreement with other environmental and archaeological findings (Nriagu, 1983; Rosman *et al.*, 1997). According to this new evidence, lead metallurgy itself is expected to be the major source for pollutant lead input to the harbour. This is the reason why we reported lead mines from the Roman period (Nriagu, 1983) in figure 2.

There is an ongoing discussion on the usefulness and the interpretation of lead isotope imprints in archaeological artefacts, particularly for the Bronze Age metal trade (Budd *et al.*, 1995a; Budd *et al.*, 1995b; Gale, 2001; Knapp, 2000). Here, we emphasize that lead isotope signatures can be interpreted for the Iron Age and the Greek-Roman period, owing to further regional investigations. The quite constant isotopic signature in the Sidon core could be explained by (1) a unique source of lead during Antiquity in Sidon or (2) a mixture of different lead sources that would infer an artificial clustering of lead isotopic ratios in the sediments. It seems rather unlikely that only one region would have provided Sidon with lead (in this case, different mines from Turkey) throughout Antiquity. According to Nriagu (1983), half of the lead production originated from Spain during the Roman period. This finding along with the well known trade links between the Levant and Spain, a mixture between lead from the Rio Tinto and the Carthaginian mines, is more likely to explain lead imprints in Sidon's harbour. However, Taurus or Sardinia mines cannot be totally excluded from this trade.

Because the early contamination (around 1500 B.C.) is only defined by a lead isotopes shift and not an increase in lead concentrations, its origin cannot be so well constrained. At this period, lead was not as widely used as it was during the Roman Period and we can assume that the contamination was coming from lead contained in copper ores. A Cypriot origin for these ores ($^{206}Pb/^{207}Pb$=~1,19) is possible in view of the lead isotopes results.

Conclusions and Perspectives

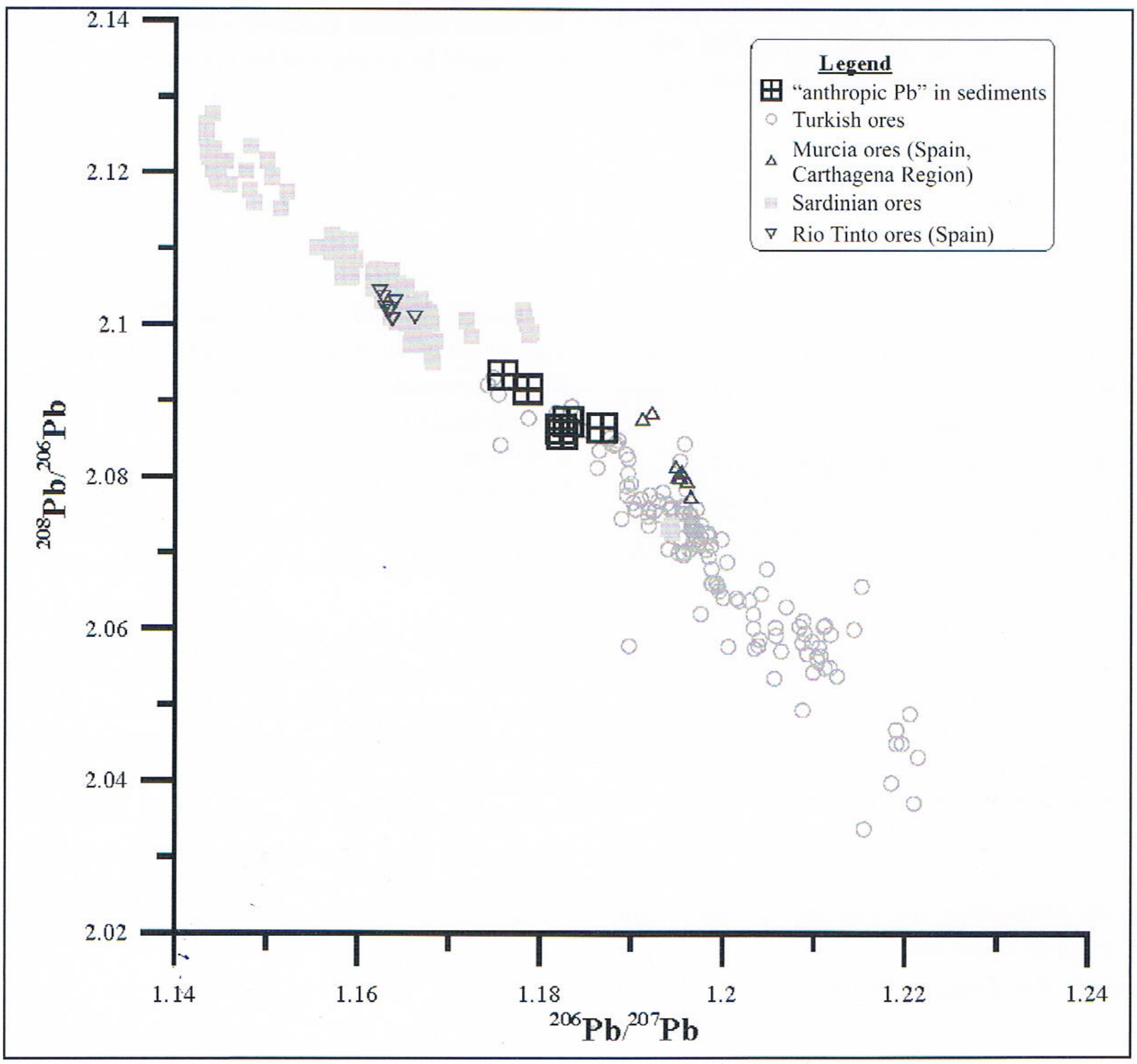
New age dating on a sediment core analysed for lead geochemistry allowed us to better refine our interpretations on the metallurgic history of Sidon. The major lead pollution input occurred during the Roman period as characterized by an increase in lead input and a shift in isotopic signatures. Meanwhile, lead isotopes also did evidence early anthropogenic activity (1500 ± 200 years prior the establishment of the harbour) in the absence of clear archaeological artefacts. These geochemical indications deserve further investigations in this region.

Based on lead isotope ratios, the most plausible cause for pollutant lead input during the Hellenistic-Roman periods is lead metallurgy itself with the use of lead ores from various origins including Spanish mines from the Rio Tinto region and Carthagena (Fig. 2).

With a view to better characterize Bronze and Iron Age metallurgy, other metals (copper, tin, silver) will be measured in these sediments.

This isotopic approach shall be refined owing to further investigations of other ancient harbours within the same archaeological context such as Tyre.

2 "Anthropic" isotopic signatures of the ancient sediments, and signatures of different ores used during Antiquity (data from different sources especially the Isotrace Laboratory, Oxford and the Smithsonian Center for Materials Research and Education, Washington; for the complete references, please contact the first author). Because of the heterogeneity of Sardinian and Turkish field ores and to keep the complexity of ore isotopic signatures, no isotopic fields are drawn.



Acknowledgements

The authors wish to acknowledge Kathia Espic for the sedimentological interpretations on the core.

References

Buckley D. E., Smith J. N. and **Winters G. V.** (1995), "Accumulation of contaminant metals in marine sediments of Halifax Harbour, Nova Scotia: environmental factors and historical trends". *Applied Geochemistry* 10, pp. 175-195.

Budd P., Pollard A. M., Scaife B. and **Thomas R. G.** (1995a), "Lead isotope Analysis and Oxhide Ingots: A Final Comment". *Journal of Mediterranean Archaeology* 8(1), pp. 70-75.

Budd P., Pollard A. M., Scaife B. and **Thomas R. G.** (1995b), "Oxhide Ingots, Recycling and The Mediterranean Metals Trade". *Journal of Mediterranean Archaeology* 8(1), pp. 1-32.

Croudace I. W. and **Cundy A. B.** (1995), "Heavy metal and hydrocarbon pollution in recent sediments from Southampton Water, southern England: a geochemical and isotopic study" *Environmental Science & Technology* 29, pp. 1288-1296.

Espic K., Morhange C., Bourcier M., Bruzzi C., Carbonel P., Nammour T. and **Doumet-Serhal C.** (2002), "Les Ports antiques de Sidon: nouvelles données paléoenvironnementales". *Archaeology & History in Lebanon (*15), pp. 28-36.

Ferrand J.-L., Hamelin B. and **Monaco A.** (1999), "Isotopic tracing of anthropogenic Pb inventories and sedimentary fluxes in the Gulf of Lions (NW Mediterranean sea)". *Continental Shelf Research* 19, pp. 23-47.

Gale N. H. (2001), "Archaeology, science-based archaeology and the Mediterranean Bronze Age metals trade: a contribution to the debate'. *European Journal of Archaeology* 4(1), pp. 113-130.

Gale N. H. and **Stos-Gale Z. A.** (1982), "Bronze Age Copper Sources in the Mediterranean: A New Approach". *Science* 216 (4541), pp. 11-19.

Hamelin B., Grousset F. and **Sholkovitz E. R.** (1990), "Pb isotopes in superficial pelagic sediments from the North Atlantic". *Geochimica et Cosmochimicà Acta* 54, pp. 37-47.

Hosler D. and **MacFarlane A.** (1996), "Copper sources, metal production, and metals trade in late postclassic Mesoamerica". *Science* (273), pp. 1819-1824.

Knapp A. B. (2000), "Archaeology, science-based archaeology and the Mediterranean Bronze Age Metals Trade". *European Journal of Archaeology* 3(1), pp. 31-56.

Le Roux G., Véron A. and **Morhange C.** (2002), "Caractérisation géochimique de l´anthropisation dans le port antique de Sidon". *Archaeology & History in Lebanon* (15), pp. 37-41.

Morhange C., Dubuquoy O., Prunet N., Ribes E., de Beaulieu J.-L., Bourcier M., Carbonel P., Oberlin C. and **Doumet-Serhal C.** (2000), "Etude paléo-environnementale du port antique de Sidon. Premiers résultats du progamme CEDRE". *Méditerranée* 1-2, pp. 91-99.

Nriagu J. O. (1983), *Lead and Lead Poisening in Antiquity.* New-York.

Rosman K. J. R., Chisholm W., Hong S., Candelone J.-P. and **Boutron C. F.** (1997), "Lead from Carthaginian and Roman Spanish Mines Isotopically Identified in Greenland Ice Dated from 600 B.C. to 300 A.D." *Environmental Science & Technology* 31 (12), pp. 3413-3416.

Shotyk W., Weiss D., Appleby P. G., Cheburkin A. K., Frei R., Gloor M., Kramers J. D., Reese S. and **Van Der Knaap W. O.** (1998) "History of atmospheric Lead Deposition since 12,730, 14C yr BP from a Peat Bog, Jura Moutains, Switzerland". *Science* 281, pp. 1635-1640.

Stuiver M. and **Braziunas T. F.** (1993), "Modelling atmospheric 14C influences and 14C ages of marine samples to 10000 BC". *Radiocarbon* 35(1), pp. 137-189.

Weiss D., Shotyk W. and Kempf O. (1999) "Archives of Atmospheric Lead Pollution". *Naturwissenschaften* (86), pp. 262-275.