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Supporting information for:

Lead isotopes in marine surface sediments reveal historical use of leaded fuel

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This supporting information contains more information on Pb isotopes and examples for the use of the formulas for calculating the percentage of Pb from leaded gasoline.

1. Lead Isotopes

Pb has four stable isotopes ^{204}Pb (1.4%), ^{206}Pb (24%), ^{207}Pb (23%) and ^{208}Pb (52%). ^{204}Pb is the only non-radiogenic isotope, as the other isotopes are produced by the radioactive decay of ^{238}U to ^{206}Pb (decay half-time of parent isotope $t_{1/2}$=4.466x10^{9} years), ^{235}U to ^{207}Pb ($t_{1/2}$=0.704x10^{9} years), and ^{232}Th to ^{208}Pb ($t_{1/2}$=1.401x10^{10} years). The difference in ratios between the radiogenic Pb isotopes from different locations is a function of the start composition and decays of the original ore U, Th and Pb content, hence the isotope ratios can be attributed to the geological formation time of Pb in the different mines.

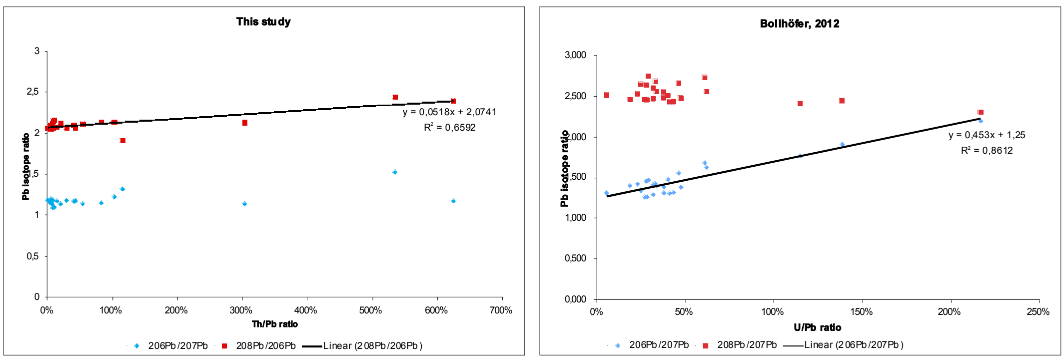

Figure SI-1: ^{208}Pb/^{206}Pb isotope ratio (red squares) vs. Th/Pb in this study and ^{206}Pb/^{207}Pb isotope ratio (blue diamonds) vs. U/Pb in Bollhöfer (2012).[1] The linear regression between ^{208}Pb/^{206}Pb and Th/Pb (left) and ^{206}Pb/^{207}Pb and U/Pb (right) are indicated; whereas no correlation (r^2<0.25) was found for ^{208}Pb vs. U and ^{206}Pb vs. Th, respectively left and right.

For two samples we find a high Th to Pb ratio (Gh1 and Gr3, figure 1 left), and in both cases, the $^{208}Pb/^{206}Pb$ isotope ratio is >2.4 (average of the remaining 21 samples is 2.09; ranging from 1.91 – 2.16). In a recent study,[1] influence of radioactive U mining residues on $^{206}Pb/^{207}Pb$ ratios showed that sediment ratio of U/Pb was correlated to the $^{206}Pb/^{207}Pb$ ratio (figure 1 right), indicating a continuous generation of ^{206}Pb. The high Th/Pb ratios for Gh1, Gr3 is hypothesized to be the same situation, but with lower, perhaps natural sources of ^{232}Th than in mining areas.

2. Example calculations for Australia

Using the gasoline ratios from table 2, and the background isotope ratio values from AU1 on isotope ratios of AU2 and AU3, all from table 3, the calculation of the numbers in table 4 is given below.

Extract of table 2

Continent	Country	208/206Pb	206/207Pb
Oceania	Australia	2.202	1.060

Extract of table 3, gray columns calculated based on the ^{204}Pb-ratios

Station	ID	$^{206/204}Pb$	$^{207/204}Pb$	$^{208/204}Pb$	$^{208/206}Pb$	$^{206/207}Pb$
Lake Conjola	Au1	18.294	15.615	38.472	2,103	1,172
Sydney	Au2	16.960	15.485	36.473	2,151	1,095
Sydney	Au3	17.086	15.497	36.908	2,160	1,103

Calculation based on $^{206}Pb/^{207}Pb$ alone (equation 1)

(1)

$$X_{AU2} = \frac{1.095_s - 1.172_b}{1.060_g - 1.172_b} \times 100\% = 68{,}9\%$$

$$X_{AU3} = \frac{1.103_s - 1.172_b}{1.060_g - 1.172_b} \times 100\% = 61{,}7\%$$

Calculation based on Pythagoras and both $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ (equation 2):

$$X^{v}_{sample} = \frac{\sqrt{\left[\left({}^{206}Pb/{}^{207}Pb\right)_s - \left({}^{206}Pb/{}^{207}Pb\right)_b\right]^2 + \left[\left({}^{208}Pb/{}^{206}Pb\right)_s - \left({}^{208}Pb/{}^{206}Pb\right)_b\right]^2}}{\sqrt{\left[\left({}^{206}Pb/{}^{207}Pb\right)_g - \left({}^{206}Pb/{}^{207}Pb\right)_b\right]^2 + \left[\left({}^{208}Pb/{}^{206}Pb\right)_g - \left({}^{208}Pb/{}^{206}Pb\right)_b\right]^2}} \times 100\% \quad (2)$$

$$X^{v}_{AU2} = \frac{\sqrt{[1.095_s - 1.172_b]^2 + [2.151_s - 2.103_b]^2}}{\sqrt{[1.060_g - 1.172_b]^2 + [2.202_g - 2.103_b]^2}} \times 100\% = 60.9\%$$

$$X^{v}_{AU3} = \frac{\sqrt{[1.103_s - 1.172_b]^2 + [2.160_s - 2.103_b]^2}}{\sqrt{[1.060_g - 1.172_b]^2 + [2.202_g - 2.103_b]^2}} \times 100\% = 60.1\%$$

The "goodness of fit" (GOF, equation 3) are calculated as ratio of the height between sample and background $^{208}Pb/^{207}Pb$ ratio, to the height a' of the sample projected onto the background – gasoline ratio vector (figure 6):

$$GOF = \frac{\left[\left({}^{208}Pb/{}^{206}Pb\right)_s - \left({}^{208}Pb/{}^{206}Pb\right)_b\right]}{\left[\left({}^{208}Pb/{}^{206}Pb\right)_g - \left({}^{208}Pb/{}^{206}Pb\right)_b\right] \times \frac{\left({}^{206}Pb/{}^{207}Pb\right)_s - \left({}^{206}Pb/{}^{207}Pb\right)_b}{\left({}^{206}Pb/{}^{207}Pb\right)_g - \left({}^{206}Pb/{}^{207}Pb\right)_b}} \times 100\% \tag{3}$$

$$GOF_{AU2} = \frac{[2.202_s - 2.103_b]}{[2.202_g - 2.103_b] \times \frac{1.095_s - 1.172_b}{1.060_g - 1.172_b}} \times 100\% = 71\%$$

$$GOF_{AU3} = \frac{[2.202_s - 2.103_b]}{[2.202_g - 2.103_b] \times \frac{1.103_s - 1.172_b}{1.060_g - 1.172_b}} \times 100\% = 94\%$$

In this case, the GOF for AU2 indicates, that the $^{208}Pb/^{206}Pb$ point is below the expected level from the $^{206}Pb/^{207}Pb$ ratio (figure 6). The difference between AU2 and AU3 is very small for the vectors approach, also compared to the simple one-isotope approach, but the GOF suggest that there might be another source of Pb-isotopes than leaded gasoline.

Reference

1. A. Bollhöfer and K. J. R. Rosman, *Applied Geochemistry*, 2012, **27**, 171-185.