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The Graphical Presentation of Lead Isotope Data for

Environmental Source Apportionment

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Abstract

Lead isotope ratios are widely used to identify original sources of Pb in the environment. Such source apportionment depends on the ability to distinguish potential sources on the basis of their isotopic composition. However, almost all terrestrial Pb is co-linear in some of the plots i.e. ^{206}Pb/^{208}Pb $v.$ ^{206}Pb/^{207}Pb and ^{206}Pb/^{204}Pb $v.$ ^{206}Pb/^{207}Pb commonly presented in the literature. These diagrams are unable to distinguish more than two sources of environmental Pb. Linear trends in such plots are an inevitable consequence of the co-linearity of terrestrial leads and should not be taken necessarily to indicate simple binary mixing of sources. A more reliable test for multiple source mixing can be obtained from plots involving ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb and therefore requires measurements of the minor ^{204}Pb isotope.

Keywords

1. Introduction

Lead isotope data have been widely used to constrain the sources of Pb in the environment (e.g. Chow & Earl, 1972; Chow, 1975; Bacon et al, 1992; Sugden et al, 1993) and particularly to demonstrate the anthropogenic input from leaded gasoline (e.g. Chow & Johnstone, 1965) and Pb mining activity (e.g. Gulson et al., 2004). A recent review (Komárek et al, 2008) demonstrates the efficacy of isotopic analyses in tracing the sources of Pb pollution. Often, environmental samples have been geared towards identification of gasoline as the dominant source of Pb and this can be readily achieved with $^{206}Pb/^{207}Pb$ data. With the demise of leaded gasoline, more subtle source apportionment should prove possible and several studies have already demonstrated the value of high-precision Pb isotope data in such studies (e.g. Weiss et al., 1999; Shotyk et al., 2001; Kamenov, 2008; Kamenov et al., 2009). Environmental samples often show simple linear trends in diagrams that compare isotopic ratios of Pb e.g., $^{206}Pb/^{208}Pb$ *versus* $^{206}Pb/^{207}Pb$. Such trends could be interpreted as simple mixtures of two discrete Pb sources. In this paper, I demonstrate that such interpretations may not always be reliable because, for the diagrams commonly used, *all* likely sources of Pb are co-linear.

Inductively coupled plasma mass spectrometry (ICP-MS) is a favoured method for Pb isotope analysis in environmental science (e.g. Farmer et al, 1996; Halicz et al, 1996). Quadrupole (Q) ICP-MS systems are relatively inexpensive and fairly precise Pb isotope ratio measurements are possible with quite short counting times. While thermal ionisation mass spectrometry and multiple-collector ICP-MS are usually preferred in geological applications of Pb isotopes for ultimate analytical precision,

the data readily obtainable from modern Q-ICP-MS instruments are widely considered fit-to-purpose for environmental source apportionment studies.

One problem with Q-ICP-MS is that ^{204}Pb is not readily analysed. First, ^{204}Pb is only about 1% of total Pb. A method that is able to achieve 0.1% precision on ^{206}Pb/^{207}Pb would only offer about 0.5% precision on ^{207}Pb/^{204}Pb if counting statistics was the limiting factor. Second, ^{204}Pb is also isobaric with ^{204}Hg and relatively low resolution Q-ICP-MS instruments are unlikely to resolve the interference successfully. Rather than apply a large correction for isobaric ^{204}Hg, many environmental studies do not present ^{204}Pb data and effect source apportionment using the ratios ^{206}Pb/^{207}Pb and ^{206}Pb/^{208}Pb.

2. Graphical presentation of environmental Pb isotope data

2.1 The ^{206}Pb/^{207}Pb *versus* ^{206}Pb/^{208}Pb plot

A popular plot in environmental studies is ^{206}Pb/^{207}Pb *versus* ^{206}Pb/^{208}Pb. This plot is almost never used in the geological literature where authors usually have much higher precision data with reliable ^{204}Pb data. Even when only the major three isotopes are available e.g. high spatial resolution ion microprobe studies (Saal et al, 2005), geologists would tend to plot ^{207}Pb/^{206}Pb *versus* ^{208}Pb/^{206}Pb because the curvature of binary mixing trajectories in ratio-ratio plots depends on the relative abundance of the denominators of each ratio in the two end-members. Making ^{206}Pb the denominator of each ratio ensures that all binary mixing lines are linear – though in practice the relative variations in natural Pb isotope abundance are likely to be so small that inverting the ratios would not induce significant non-linearity.

The problem with the $^{206}Pb/^{207}Pb$ *versus* $^{206}Pb/^{208}Pb$ plot is that geological sources of Pb are very restricted in their position on this diagram (Fig. 1). Stacey & Kramers (1975) compiled the Pb isotope compositions of conformable Pb ore deposits throughout the world of different geological ages from 3.23 Ga to present day. Their original purpose was to model Pb isotope evolution of the Earth through geological time, but the data offer a useful perspective on potential sources of Pb in the environment, which ultimately will have geological origins in Pb ore deposits.

All the ore deposits presented by Stacey & Kramers (1975) are co-linear in the $^{206}Pb/^{207}Pb$ *versus* $^{206}Pb/^{208}Pb$ plot (Fig. 1). Additionally, of 2336 mid-ocean ridge basalt (MORB) plotted in Figure 1 (taken from the PetDB database - http://www.petdb.org/), only 1 sample falls off the Pb ore trend and, in view of the extreme composition of this sample, one must suspect this to be an analytical artefact. Several hundred other basalts derived from the Earth's mantle (from the Georoc database http://georoc.mpch-mainz.gwdg.de/georoc/) all plot on the same linear array (not shown for clarity of presentation). According to the model curve used by Stacey and Kramers (1975) to fit the Pb ore data, the only expected sources of terrestrial Pb not to be co-linear would be any Pb that separated from U in the first few hundred million years after the formation of the solar system. During this period terrestrial Pb evolved from the initial solar system composition (assumed to be equivalent to that of the low U/Pb mineral troilite from the Canyon Diablo meteorite) towards the sub-3.3 Ga ore deposits. In short, most terrestrial Pb is co-linear in this diagram. Hence, this is not a suitable diagram to reveal multiple sources of Pb. It will always yield the same linear trend irrespective of the number of sources of Pb. Only extremely high

U/Pb sources are expected to evolve away from this trend and these, by virtue of the long U half-lives, will contribute negligible Pb to mixtures.

2.2 The ^{206}Pb/^{204}Pb *versus* ^{206}Pb/^{207}Pb plot

Introducing ^{204}Pb data does not necessarily overcome the highlighted problem if there is an injudicious choice of the diagram used to present the data. A plot of ^{206}Pb/^{204}Pb *versus* ^{206}Pb/^{207}Pb (Fig. 2) which is occasionally used in environmental studies (e.g. Bacon et al. 1996) has similar characteristics. Again, the Pb ores are co-linear and the MORB extend the correlation – only meteoritic samples and the early stages of the model Pb isotope evolution curve lie off the main correlation. Again, this is not an appropriate diagram with which to identify multiple sources of terrestrial Pb and any number of mixing sources will yield a correlation that could be misinterpreted as reflecting binary mixing. Of course, any studies that use this diagram to propose binary mixing would be able to test that assertion with other plots e.g. ^{207}Pb/^{204}Pb *versus* ^{206}Pb/^{204}Pb. It should be emphasized that, in the study we have identified that used the ^{206}Pb/^{204}Pb *versus* ^{206}Pb/^{207}Pb plot (Bacon et al., 1996), the interpretation of two dominant Pb sources is, indeed, supported by a strong linear correlation in ^{206}Pb/^{204}Pb *versus* ^{208}Pb/^{204}Pb space.

3. An environmental example

To illustrate the possible effect of not including the minor ^{204}Pb isotope in the ratios used to identify potential sources of Pb, I have plotted data from a compilation of Northern Hemisphere atmospheric lead data (Bollhöfer & Rosman, 2001) in diagrams of ^{208}Pb/^{204}Pb *versus* ^{206}Pb/^{204}Pb (Fig. 3a) and ^{206}Pb/^{208}Pb *versus* ^{206}Pb/^{207}Pb (Fig. 3b). As identified by the original authors, these aerosols are likely to include Pb from a

variety of sources. In ^{208}Pb/^{204}Pb *versus* ^{206}Pb/^{204}Pb space this is clearly indicated by a divergence from a linear correlation especially for the more radiogenic samples. At least three distinct sources of Pb are indicated. However, in ^{206}Pb/^{208}Pb *versus* ^{206}Pb/^{207}Pb space a much stronger linear correlation is observed (r = 0.965). Notably, the samples with high ^{206}Pb/^{204}Pb for given ^{208}Pb/^{204}Pb i.e. those with high ^{206}Pb/^{208}Pb (Fig. 3a) are not readily identified as deviating from the overall best fit correlation in ^{206}Pb/^{208}Pb *versus* ^{206}Pb/^{207}Pb space. Thus, without data for ^{204}Pb, it would not be possible thoroughly to evaluate the sources of Pb contributing to these Northern Hemisphere aerosols.

4. Conclusion

In summary, the approach used in many studies of source apportionment using Pb isotopes is potentially flawed because it will not reliably reveal more than two sources. The most extreme sources may be identified but any contribution from intermediate composition sources will not be obvious. A more reliable test for multiple source mixing can be obtained from plots involving ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb and therefore requires measurements of the minor ^{204}Pb isotope.

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Figure Captions

Fig, 1. $^{206}Pb/^{207}Pb$ *versus* $^{206}Pb/^{208}Pb$ plot showing MORB (open circles), conformable Pb ore deposits (solid circles) and Canyon Diablo meteorite troilite (solid triangle). Solid line is the two-stage Pb isotope growth curve used by Stacey & Kramers (1975) to model the conformable ore data. Cross marks indicate age points every 300 Ma (4.30-3.70 Ga) and every 250 Ma (0-3.70 Ga) as tabulated in the original paper (Table 9).

Fig. 2. $^{206}Pb/^{204}Pb$ *versus* $^{206}Pb/^{208}Pb$ plot, symbols as Fig. 1.

Fig. 3. (a) $^{208}Pb/^{204}Pb$ *versus* $^{206}Pb/^{204}Pb$ and (b) $^{206}Pb/^{208}Pb$ *versus* $^{206}Pb/^{207}Pb$ for Northern Hemisphere atmospheric aerosols (Bollhöfer & Rosman, 2001). Only plotted are data for which individual analyses were presented by Bollhöfer & Rosman (2001). Sites for which ranges of Pb isotope composition were presented are omitted to avoid the possibility of plotting pairs of ratios that do not correspond to the same sample.
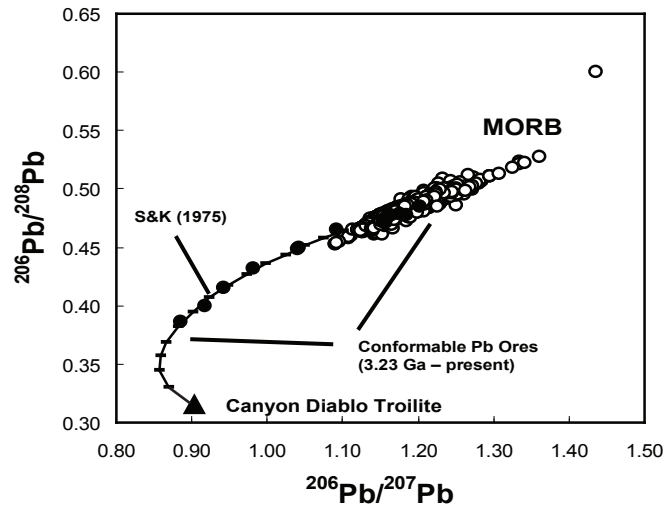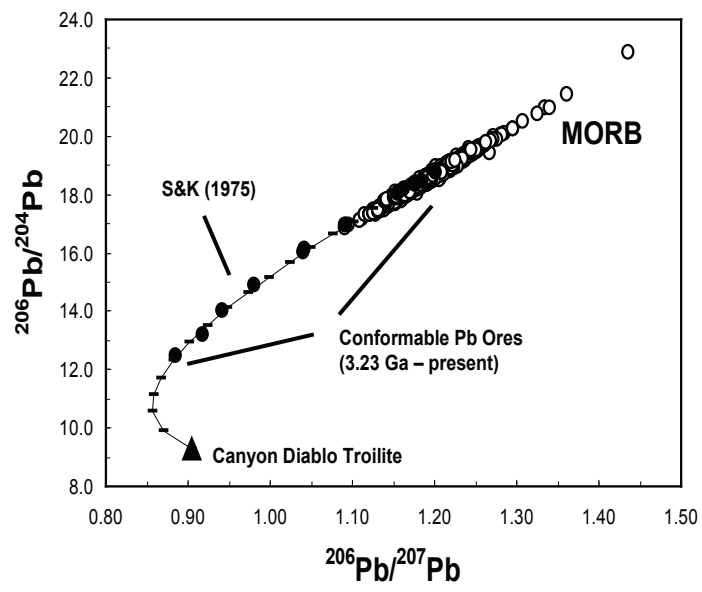
Figure 1

Figure 2

Figure 3