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Stable lead isotopes in environmental health with emphasis on human investigations

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ABSTRACT

There has been widespread use of stable lead isotopes in the earth sciences for more than 40 years focussed on the origin and age of rocks and minerals with lesser application in environmental investigations where the emphasis has been directed typically to the source of lead in environmental media such as air, water and soils.
In contrast, the number of environmental health investigations focussed on humans (and primates) is limited in spite of the demonstrated utility of the approach in pioneering studies in the early 1970's. This paper reviews the status of lead isotopes in human investigations especially over the past 2 decades, the period over which most activity has taken place. Following a brief introduction to the method, examples are provided illustrating the use of lead isotopes in a wide spectrum of activities including sources and pathways of lead in diverse environments from urban to mining communities, various applications associated with pregnancy, the contribution of bone lead to blood lead including in the elderly, the half-life of lead in blood, and lead in bones and other media. A brief outline of critical research on non-human primates is also given. The lead isotope method is a powerful technique for tracing lead and could be employed more widely in human investigations.

1. Introduction

There has been widespread use of lead isotopes in the earth sciences for more than 40 years focussed on the origin and age of rocks and minerals such as the pioneering work of Patterson (1956) to determine the age of the earth using lead isotopes in iron meteorites. There has been lesser application in environmental investigations where the emphasis has been directed typically to the source of lead in environmental media such as air, water and soils.

In contrast, the number of environmental health investigations focussed on humans (and primates) is limited in spite of the demonstrated utility of the approach in the pioneering studies of Rabinowitz and colleagues (1973, 1974, 1976a,b, 1977, 1980) and Manton (1973) in the 1970's. Possible reasons for this are the cost and expertise required for the analyses, the reluctance of researchers to work on biological samples, and limited collaboration between the medical fraternity and other disciplines.

As the use of stable lead isotopes in environmental sciences has been recently reviewed (Komárek et al., 2008), this review will be restricted to investigations in "modern-day" humans. This review examines investigations related to modern human health issues rather than those encompassing, for example, lead isotope investigations of archaeological flavour in attempting to establish population issues within communities using media such as teeth and bones (e.g. Patterson et al., 1991; Manea-krichten et al., 1991; Budd et al.,

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1998, 2000, 2004; Farmer et al., 2006). Likewise, only where directly relevant will studies using stable lead isotopes in animal experiments be briefly mentioned.

2. The lead isotope method

The lead isotope method makes use of the variations, arising from radioactive decay throughout geological time, in abundances of three of four lead isotopes and relative concentrations of Pb, Th and U and the time when the ore was formed. Lead has four naturally-occurring isotopes three of which are the stable end products of radioactive decay of uranium and thorium. For example, ^{206}Pb is derived by radioactive decay from ^{238}U, ^{207}Pb from ^{235}U, and ^{208}Pb from ^{232}Th. The other low abundance isotope, ^{204}Pb (approximately 1%), has no known radioactive parent and is used as a reference isotope. The data are presented as ratios of abundance of one to the other, such as ^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, and ^{206}Pb/^{204}Pb, or any combinations of these. In the earlier days of use of Pb isotopes, because of the difficulty in measurement of the low abundance ^{204}Pb isotope, the data were reported as ^{206}Pb/^{207}Pb ratios.

Hence lead mineral accumulations (mines, deposits) of different geological age have different isotope ratios. For example, the geologically-ancient so-called massive sulphide Pb–Zn–Ag Broken Hill and Mt Isa deposits in Australia formed about 1700–1800 million years ago and have a ^{206}Pb/^{204}Pb ratio of 16.0 or 16.1 respectively whereas geologically-younger deposits of similar composition in eastern Australia and western Tasmania formed 400 to 500 million years ago have a ^{206}Pb/^{204}Pb ratio of about 18.1.

3. Analytical methods

Current methods for lead isotope analysis employ either thermal ionisation mass spectrometry (TIMS) or inductively coupled plasma mass spectrometry (ICP-MS). Although the high temperature conditions in the plasma of the ICP-MS theoretically allows analysis without chemical separation, under real conditions, to obtain high-precision data, it is necessary to undertake a limited sample treatment (Chillrud et al., 2005).

3.1. *TIMS*

Thermal ionisation mass spectrometry requires good separation of lead from other elements which may inhibit the ionisation of lead in the mass spectrometer and avoid interference from some ions with the same mass/charge ratio as some lead isotopes. Although lead levels in the environment have dropped since the lead was removed from gasoline, the processing blank is still a major concern in the design of chemical separation procedures. The following details are for the CSIRO Radiogenic Isotope laboratories in Sydney for blood samples. All reagents used are ultrapure and containers are either Teflon of polypropylene. Under best conditions, all processing is done in Class 350 clean rooms with further handling in Class 100 laminar flow clean workbench stations.

Approximately 0.3–0.5 g of blood is digested with concentrated nitric acid/hydrogen peroxide and the lead separated from other elements on a column of lead selective resin. A small amount of ^{202}Pb is added to determine the lead concentration in the sample at the same time as measurement of the isotope ratios (the isotope dilution method). The procedural blank is about 50 pg (50×10^{-12} g) which has an insignificant effect on the measured ratios.

The sample is dissolved in water and a small volume is evaporated on to a cleaned rhenium filament along with silica gel/phosphoric acid to enhance ionisation. The filaments are placed in a VG Sector 354 multi-collector thermal ionisation mass spectrometer and 250 lead isotope ratios are measured in static mode. From replicates of the NIST standard SRM 981 and natural samples, a precision of better than ±0.05% (2σ) can be obtained. To enable comparison between laboratories, the isotope ratios are normalized to those of the NIST standard SRM 981.

3.2. *ICP-MS*

Inductively coupled plasma mass spectrometry, especially multi-collector sector field ICP-MS (MC-ICP-MS), has gained increasing popularity in recent years for lead isotope and other isotopic analyses. The ICP-MS instruments include those with quadrupole (ICP-QMS), sector (or sector field) (ICP-SFMS) and time-of-flight mass analysers (ICP-TOF-MS). The advantages of ICP methods are simplified sample preparation methods, higher sample throughput, and higher sensitivity compared with TIMS. In low resolution modes, MC-ICP-MS yields isotope ratio precision of $<$0.05%. Although often promoted as providing higher throughput with similar precision to TIMS, constant mass fractionation and with minimal sample preparation, MC-ICP-MS has yet to replace TIMS (Walczyk, 2004).

For more details on ICP-MS analysis including precision, accuracy, and QA/QC issues the reader is directed to Komárek et al. (2008).

In this review, the reported measurement of the isotope ratios has been by TIMS unless stated otherwise.

4. Examples of use of lead isotopes in environmental health

For Pb isotopes to be successfully employed in investigations a number of conditions need to be satisfied which include (i) knowledge (data) of relevant potential sources, (ii) the sources need to be isotopically distinct (i.e. the isotopic separation between the sources needs to be significantly larger than the observed variability within a source), with the larger the separation the more advantageous to obtain meaningful results, and (iii) isotopic data with precision significantly higher than differences between sources.

A more detailed discussion of changing isotopic compositions associated with globalisation is provided in the Summary and throughout the text but it is sufficient at this stage to mention that the use of lead isotopes has seen limited application in human studies in the US because of overlapping sources especially from paint samples, and difficulties in