Lead isotope ratios as a tracer for contaminated waters from uranium mining and milling

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Abstract. The elevated uranium concentrations of the ores of the Witwatersrand and the great age of the deposits have resulted in the development of extremely radiogenic lead isotope ratios. These ratios are reflected in the wastes and effluents generated by mining activities and may be used for the identification and tracing of Witwatersrand-sourced contamination. Fine sediments act as accumulators of heavy metals in the streams and rivers downstream of mining activities. Analysis of the lead isotopic compositions of these sediments can be used to identify and apportion the sources of this contamination.

Introduction

Gold has been mined in the Witwatersrand of South Africa since the late 19th Century. The gold ores contain appreciable (up to 5.8%) concentrations of uranium, which was economically extracted starting in the early 1950s. This production made South Africa the world's 4th largest producer of uranium (Cole, 1988). This study looks at lead isotope ratios in the Wonderfonteinspruit catchment (see Fig. 1), which has its source in the mining areas of the West Rand, west of Johannesburg and flows south-west through the Far West Rand mines, finally discharging into the Mooi River, where it becomes a significant source of domestic water for the city of Potchefstroom (population ~300 000). The upper portion of the catchment (around Krugersdorp and Randfontein) is referred to as the upper Wonderfonteinspruit, while the lower portion (downstream of Carletonville) is referred to as the lower Wonderfonteinspruit. Between these two sections of the river it flows in a pipeline, which has been constructed to prevent water entering the mine workings below the stream bed. The work formed part of a larger study of the contamination of this catchment by mining activities, which found that uranium contamination posed a significant risk to water users, while uranium and

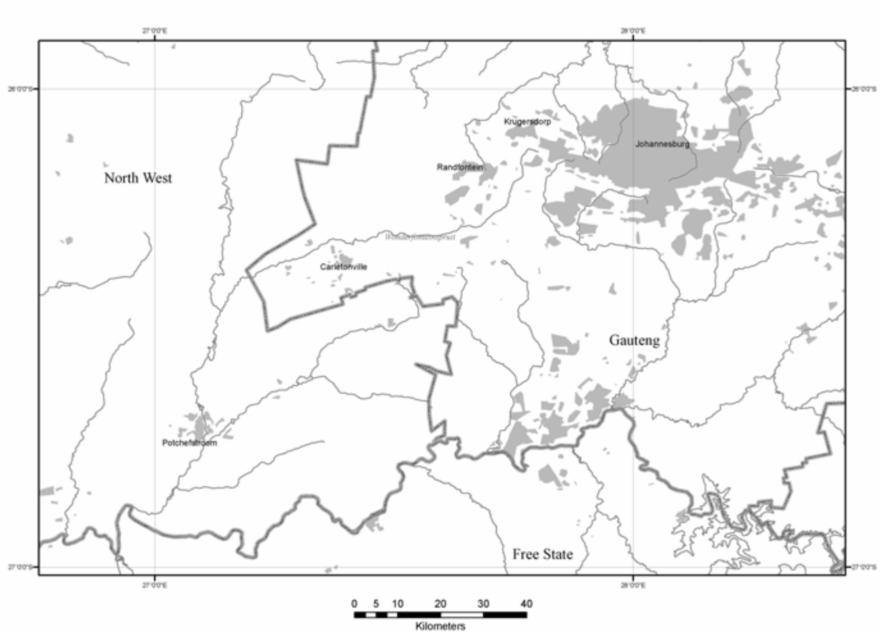

Fig. 1. Location of the Wonderfonteinspruit in the Gauteng and North West Provinces of South Africa.

other heavy metal contamination of stream sediments constitute a potential long term risk to downstream communities (Coetzee 2005).

Isotope ratio measurements may be applied for the tracing and, in some cases, apportionment of water and contaminant sources in mining areas. Eglington et al. (2001) present an approach to the use of different stable isotope systems for the tracing of acid mine drainage. In uranium mining districts, the radiogenic isotopes of lead (the daughter isotopes of uranium and thorium) provide a powerful tool for the tracing of waters and contaminant streams, as their evolution over geological time in a uranium rich orebody produces isotopic signatures which are distinct from normal environmental lead.

Radiogenic and common lead

Environmental lead is known to vary significantly in isotopic composition. Naturally occurring lead comprises four stable isotopes, with mass numbers 204, 206, 207 and 208. These have different origins, ^{204}Pb having been produced only during cosmogenesis, and ^{206}Pb, ^{207}Pb and ^{208}Pb being formed in the radioactive decay of ^{238}U, ^{235}U and ^{232}Th respectively. These three isotopes produced during radioactive decay are referred to as radiogenic isotopes, while ^{204}Pb is referred to as common lead.

These decays are governed by the decay law, which can be written for each isotopic system as:

$$\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}} = \left(\frac{^{206}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_i + \frac{^{238}\mathrm{U}}{^{204}\mathrm{Pb}}(e^{\lambda_{238_U}t} - 1)$$

$$\frac{^{207}\mathrm{Pb}}{^{204}\mathrm{Pb}} = \left(\frac{^{207}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_i + \frac{^{235}\mathrm{U}}{^{204}\mathrm{Pb}}(e^{\lambda_{235_U}t} - 1)$$

$$\frac{^{208}\mathrm{Pb}}{^{204}\mathrm{Pb}} = \left(\frac{^{208}\mathrm{Pb}}{^{204}\mathrm{Pb}}\right)_i + \frac{^{232}\mathrm{Th}}{^{204}\mathrm{Pb}}(e^{\lambda_{232_{Th}}t} - 1)$$

Where t is the period elapsed since the system became closed w.r.t. uranium, thorium and lead, the R_i's represent the initial isotopic ratio (*i.e.* the ratio at the time of formation) and λ_X is the decay constant of the respective parent nuclide. In the case of rocks, these relationships can be used to determine the age of formation of a mineral grain or rock.

These relationships show that lead isotopic ratios will change over time depending on the uranium and thorium concentrations of the material and time. The half lives of all three of the parent nuclides is sufficiently long (10^8-10^{10} years) that no significant change will take place during the historical scale time periods generally investigated during environmental studies, while the small relative mass differences between isotopes (At mass ~206, a 1 a.m.u. mass difference amounts to less than one half of a percent of the atomic mass, compared to differences of several percent seen in the light stable isotopes) result in no significant fractionation by normal environmental processes. Thus, while lead, and many other metal, concentrations may change significantly due to different environmental processes, the isotope ratios of lead remain constant, being influenced only by mixing of lead from different sources.

Isotopic evolution of lead in the Earth's crust

A number of models of the isotopic evolution of lead in the crust have been proposed. These will be discussed in detail in any text on isotope geochemistry. One commonly used is that of Stacey and Kramers (1975). In this model, it is assumed that the isotopic composition of lead in the earth's crust has evolved over time in response to the decay of uranium and thorium. The values calculated by the model for ^{206}Pb, ^{207}Pb and ^{208}Pb, all normalised to ^{204}Pb are presented on Fig. 2 and Fig. 3.

For environmental fingerprinting, it is not always practical to use these ratios, which are commonly used for geochronology, due to the difficulty in analysing ^{204}Pb at low levels of lead and the uncertainty introduced by the measurement of large ratios. For this reason, ^{207}Pb is used as a normalising isotope. The Stacey-Kramers curve is shown using this convention on Fig. 4.

In isotope geochemistry, this model is used as a dating tool, with lead being extracted from the crustal reservoir at a certain time and then describing a new trajectory on the curves depending on the new $^{238}U/^{204}Pb$ and $^{232}Th/^{204}Pb$ ratios (μ and ω). In the case of sulphides in mineral deposits, particularly galena in lead deposits, a negligibly small concentration of uranium and thorium will be included in the sulphides, meaning that μ and ω are very small. Isotope ratios from mineral deposits will therefore plot on or close to the crustal evolution curve, at a position relating to the age of the deposit. Uranium and/or thorium rich deposits will however have much higher values of μ and ω, and will therefore grow to a point significantly removed from the crustal evolution curve.

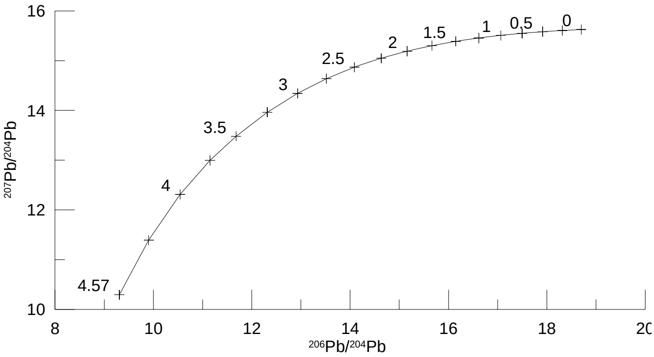

Fig. 2. Stacey-Kramers crustal isotopic evolution curve for lead $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$, showing the evolution of these ratios over time (tick marks indicate different times in the earth's history in billions of years).

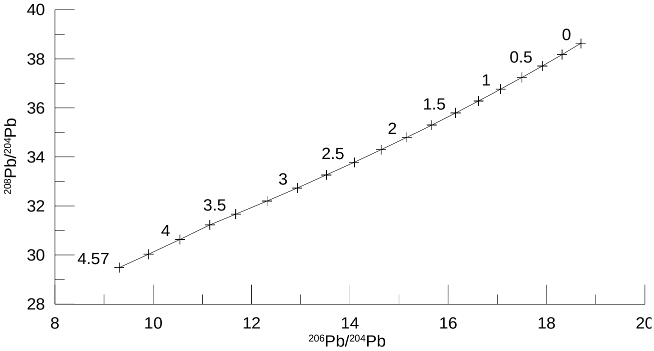

Fig. 3. Stacey Stacey-Kramers crustal isotopic evolution curve for lead $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$, showing the evolution of these ratios over time (tick marks indicate different times in the earth's history in billions of years).

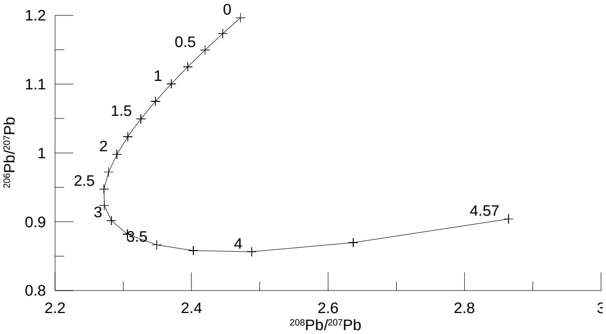

Fig. 4. Stacey Stacey-Kramers crustal isotopic evolution curve for lead $^{208}Pb/^{207}Pb$ and $^{206}Pb/^{207}Pb$, showing the evolution of these ratios over time (tick marks indicate different times in the earth's history in billions of years).

Sampling and analysis

Sampling

Samples of mine tailings were collected from two source areas where active discharge of mine water is taking place. These were selected to represent the orebodies mined in the West Rand and Far West Rand gold fields. At the time of sampling, no method for the direct analysis of lead isotope ratios in water, which often contains a very low lead concentration, was available in the laboratory used. River sediments downstream of the relevant mines were therefore used for the analyses, these having been shown to concentrate heavy metals dissolved in the water column by precipitation and adsorption (Wade et al. 2002; Coetzee et al. 2002). Samples were collected in uncontaminated areas to provide background isotopic compositions (Unfortunately, it is not possible to sample the Wonderfonteinspruit upstream of mining activities, as these have been developed in the source area of the river). Since leaded petrol is still extensively used in South Africa, the isotopic composition of South African leaded petrol has also been included.

Analysis

Samples were dissolved in a mixture of concentrated HF and HNO_3, the resulting solution dried down and redissolved in 0.6N HBr. Lead was separated from this solution by passing it through quartz glass columns using an anion exchange resin. The samples were loaded in a silica gel bed on rhenium filaments and analysed by thermal ionisation mass spectrometry on a Finnigan MAT261 mass spectrometer. Chemical separations were undertaken in clean air, using double distilled reagents.

Results and discussion

Lead isotope data determined on river sediments from the Wonderfonteinspruit are presented on Table 1 and Fig. 5.

Two distinct mixing trends can be seen in these data. These are defined by the source and background end-members. Data from the two sections of the river plot along these trends, indicating that the lead in these samples constitutes a mixture between lead from these end-members, that the source of lead contamination in the samples can be determined from the individual sample and that the contribu-

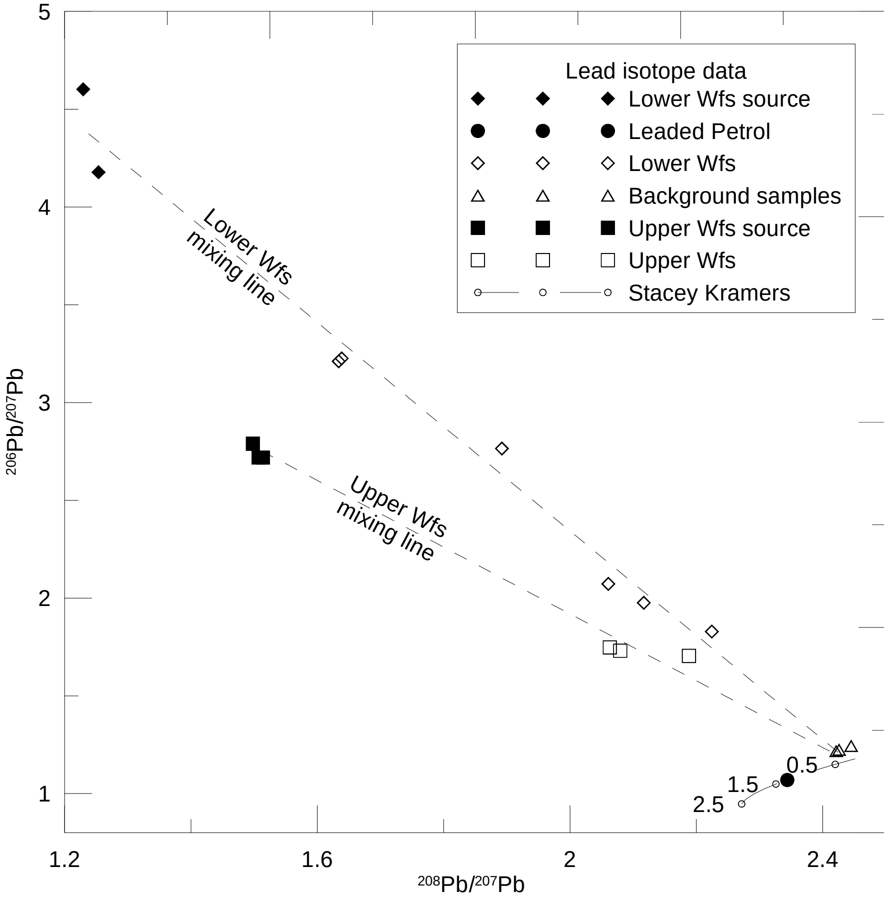

Fig. 5. Lead isotope data determined on river sediments from the Wonderfonteinspruit (Wfs).

tion of the source, relative to the background lead can be determined.

The data show that there is little downstream transport of lead from the upper to the lower catchment, as the data collected from sediments in the lower part of the catchment plot along a distinct mixing line and do not appear to contain a significant component of “Upper Wfs source” lead. This can be attributed to the relatively low solubility of lead and may not apply to the more soluble components of the waste stream.

Another notable feature of the data is the extremely uranogenic lead isotope ratios determined on samples from the vicinity of the gold/uranium mines. These ratios result from the extremely high initial uranium/lead ratios and the great age of the deposits.

Table 1. Lead isotope data determined on river sediments from the Wonderfonteinspruit.

Sample Number	Sample source	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{207}Pb$
1-12	Background (mean of 12 analyses)	19.088	15.792	38.495	2.438	1.209
13	Lower Wfs	76.144	23.716	38.748	1.634	3.211
14	Lower Wfs	76.025	23.571	38.621	1.639	3.225
15	Lower Wfs	57.300	20.726	39.217	1.892	2.765
16	Lower Wfs	31.030	17.852	36.961	2.070	1.738
17	Lower Wfs	38.296	18.477	38.074	2.061	2.073
18	Lower Wfs	35.716	18.078	38.267	2.117	1.976
19	Lower Wfs	31.946	17.469	38.857	2.224	1.829
20	Lower Wfs source	137.595	31.804	39.872	1.254	4.178
21	Lower Wfs source	155.115	33.709	41.442	1.229	4.602
22	Upper Wfs	30.882	17.843	37.103	2.079	1.731
23	Upper Wfs	31.226	17.862	36.848	2.063	1.748
24	Upper Wfs	29.551	17.339	37.943	2.188	1.704
25	Upper Wfs source	66.810	24.071	36.441	1.514	2.718
26	Upper Wfs source	65.489	24.091	36.311	1.507	2.718
27	Upper Wfs source	67.860	24.328	36.441	1.498	2.789
	S.A. Leaded Petrol (mean of 5 analyses)	16.547	15.467	36.255	1.070	2.344

Conclusions

Lead isotope ratios may be used to “fingerprint” the lead contained in a variety of environmental samples. Where more than one lead source, for example lead from a mine discharge and background environmental lead, is present, mixing relationships, such as binary mixing lines may be used to apportion the contribution of the different sources.

In the case of uranium mines or mines exploiting ores with significantly elevated uranium concentrations, particularly where the deposits are geologically old, the highly radiogenic lead isotope ratios provide an excellent fingerprinting tool. This has been successfully applied in a case study of a river draining two Witwatersrand mining districts. Using lead isotope ratios, it is possible to identify and separate waste streams from the two districts.

References

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