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The use of lead isotopes  
for research and  
monitoring the  
environmental impacts  
of uranium mining

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September 2003



# **The use of lead isotopes for research and monitoring the environmental impacts of uranium mining**

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September 2003

Registry File SG2001/0157



**Australian Government**

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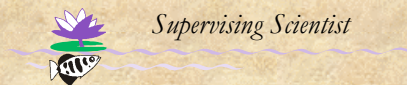


## Powerpoint presentation

# The use of lead isotopes for research and monitoring the environmental impacts of uranium mining

Andreas Bollhöfer

## The use of lead isotopes for research and monitoring the environmental impacts of uranium mining



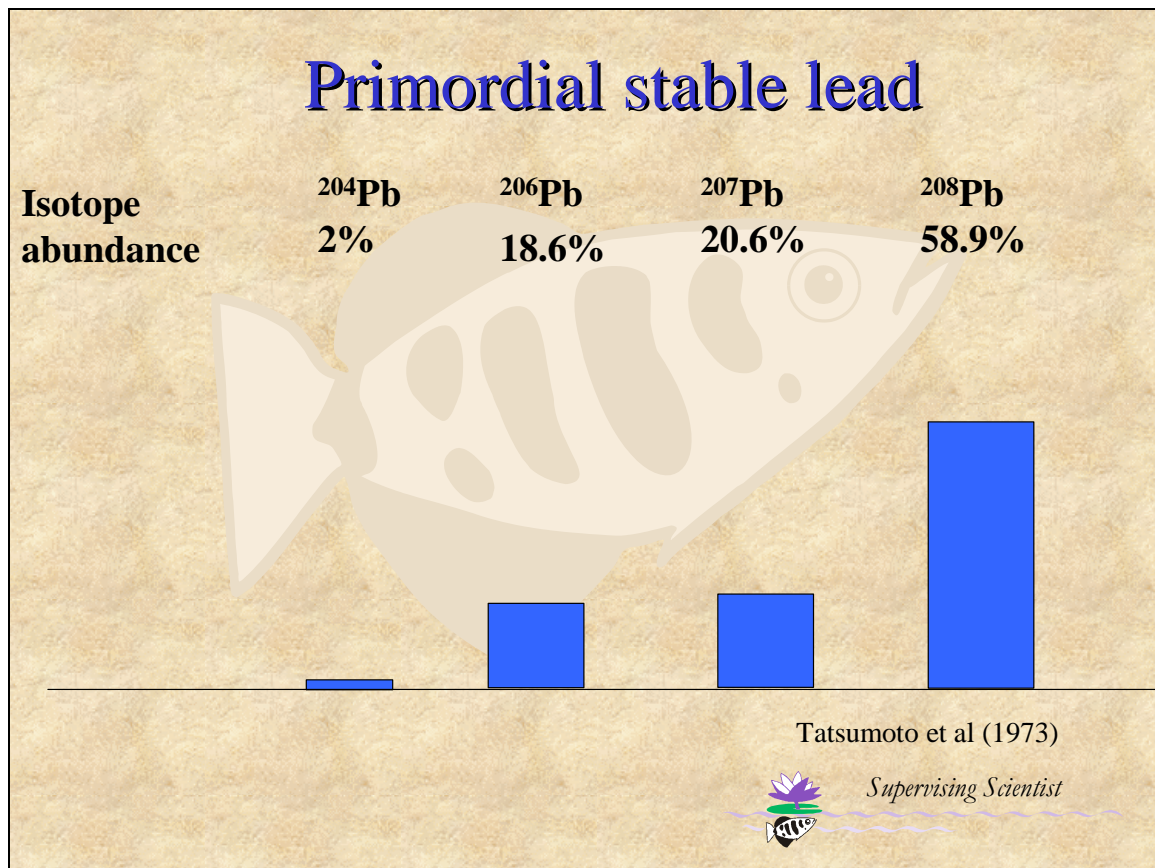
This technique has not been used much at *eriss* yet. In 1996, Gulson et al. studied lead isotopes as seepage indicators around the Ranger tailings dam. Gulson since then works on application of lead isotopes to problems in the environment - especially related to mining - at CSIRO/Macquarie University. This talk is meant to give an overview and explain in easy terms how and why the technique works.

## Overview

- Why does it work ?
- How does it work ?
- Why is it so sensitive ?
- Sources worldwide
- Sources in Kakadu NP

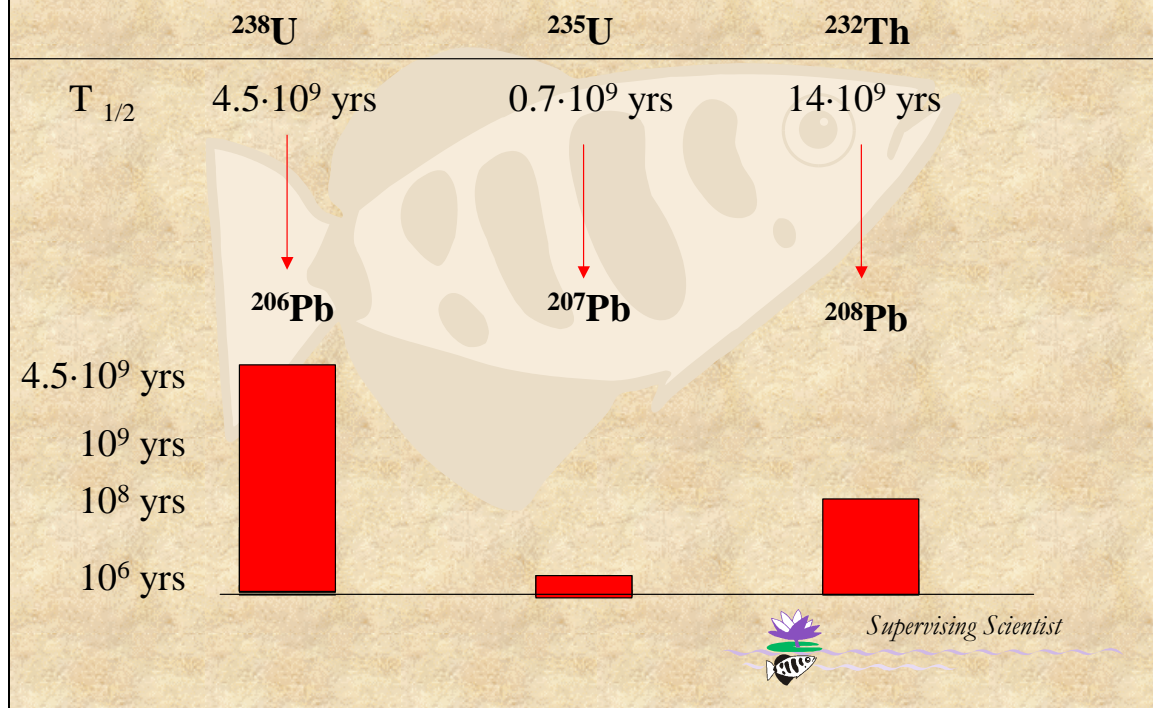
The reason why there are differences in lead isotopic ratios is because we have two different kinds of lead. Primordial lead, which is lead that has been around since the formation of the earth at a fixed isotopic composition. And radiogenic lead, which is produced by the decay of uranium and thorium.





Isotope abundance is the relative abundance of one lead isotope relative to all lead atoms added up, i.e.: 2 % of all lead atoms are the lead isotope 204. The isotopic composition of primordial lead was determined by Tatsumoto et al. (1973) by measuring triolite (a mineral) in iron meteorites of 4.5 Ga for its isotopic composition. The mineral had a negligible U/Th content, therefore there was no radiogenic lead in the mineral produced by their respective decays.

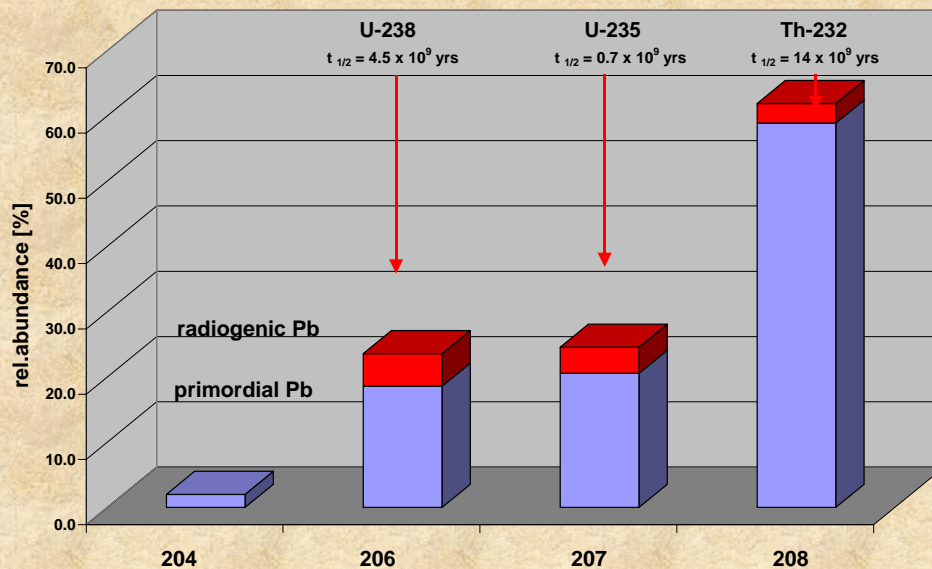
# Radiogenic stable lead




Radiogenic lead is the lead produced by the radioactive decay of uranium and thorium. Despite the shorter half-life of U-235, relatively more Pb-206 is produced by the decay of U-238 as there is 137.88 times more U-238 than U-235. This means, the radiogenic Pb-206/Pb-207 ratio increases with time.

The radiogenic Pb-208/Pb-207 ratio is dependent on the uranium and thorium content of the source rock. Generally, the higher the Th content of the source rock the higher the Pb-208/Pb-207 ratio and vice versa.

# Lead isotope systematics



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The radiogenic lead is produced on top of the primordial Pb. The reason why there are different lead isotope ratios for different sources worldwide (such as alkyllead in leaded petrol, industrial lead etc.) is that the lead used in various industrial processes is produced from lead ore bodies that have formed at different times. In addition, the lead isotopic composition of an ore body depends on the U/Th content of the source rock and the amount of primordial lead.

The lead isotopic composition of the lead ore is a snapshot of the Pb isotopic composition of the source rock at the time of the formation of the lead ore body. Once the ore body has formed, its isotopic composition does not change and it has the lead isotopic composition of the host rock it formed in.

Therefore, old lead ore bodies have relatively low Pb-206/Pb-207 ratios (such as Mt. Isa ore) whereas young lead ore bodies have relatively high lead isotopic ratios (such as Mississippi valley type ores). In uranium ore bodies the amount of radiogenic lead will dominate over the primordial lead.

## Common lead isotope ratios

ratio	Primordial	PDAC (present day average crustal)
206/207	0.90	1.20
208/207	2.86	2.47



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## Advantages of lead isotopes

- heavy isotopes, therefore no chemical or physical fractionation during transport and deposition
  - source tracer
  - fingerprint
- large differences in isotope ratios compared to measurement precision available:

TIMS:  $< 0.1 \%$      $(1.200 \pm 0.001)$

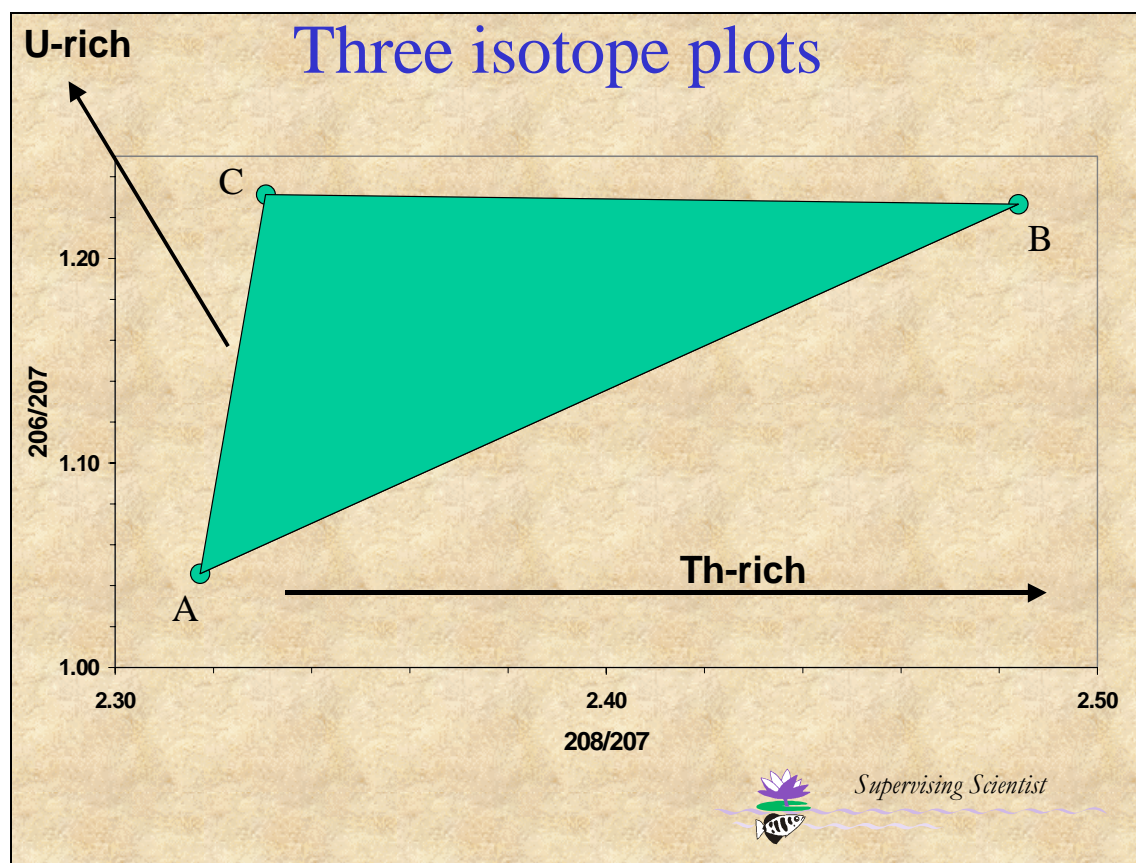
ICPMS:  $< 1 \%$      $(1.20 \pm 0.01)$



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TIMS: Thermal Ionisation Mass Spectrometry

ICPMS: Inductively Coupled Plasma Mass Spectrometry



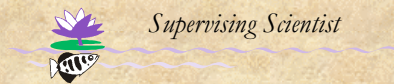
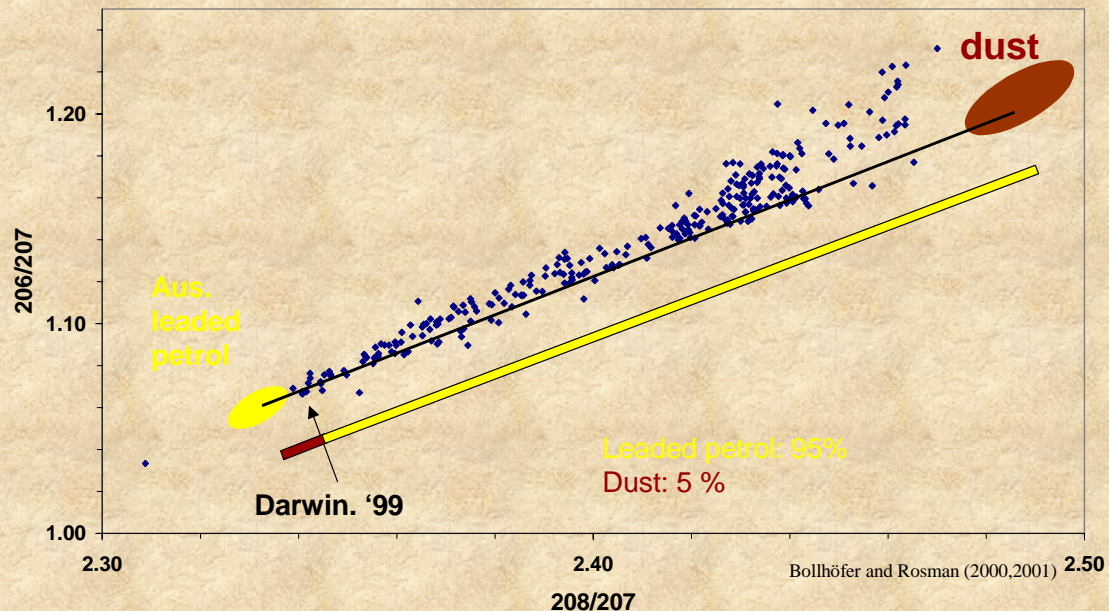
Lead isotope data are usually plotted in a three isotope plot. In environmental applications, Pb-206/Pb-207 is plotted versus Pb-208/Pb-207 ratios (sometimes it is the Pb-207/Pb-206 plotted versus the Pb-208/Pb-206) as those are the isotopes that can be measured at the highest precision.

If a mixing of two sources with different lead isotope ratios occurs, the lead isotopic composition of the mix will lie somewhere on the line AB. If three sources mix, the mixture will have an isotopic composition somewhere within the triangle, ABC.

Th-rich materials tend to have higher Pb-208/Pb-207 ratios as Pb-208 is produced from the decay of Th-232. U-rich materials will head towards the top left corner of a three isotope plot, as Pb-208/Pb-207 ratios are relatively low (as the decay of U-235 produces Pb-207) and Pb-206/Pb-207 ratios increase as there is relatively more Pb-206 produced than Pb-207.



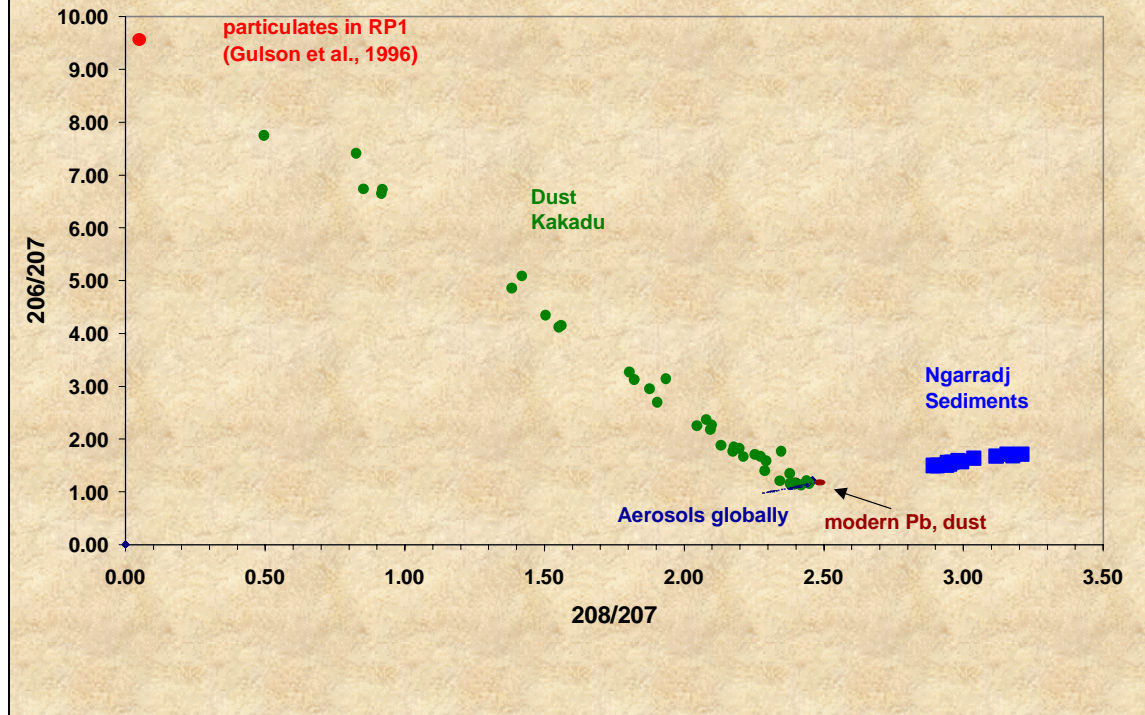
# Global airborne lead isotope ratios



This slide shows an example of how lead isotope ratios can be used to calculate contributions to airborne lead levels from different sources.

In Darwin, Pb-206/Pb-207 isotope ratios were  $\sim 1.07$  in 1999. Assuming a mixing of Australian leaded petrol (Pb-206/Pb-207  $\sim 1.06$ ) and dust (Pb-206/Pb-207  $\sim 1.20$ ) one can calculate (using simple trigonometry) that the contribution of leaded petrol to airborne lead levels was approximately 95% whereas dust only contributed approximately 5% of the lead.

## Lead isotope ratios in KNP



Notice the different scale in this slide compared to the previous slide! Global aerosol lead isotope ratios only take up a tiny area in this three isotope plot.

These are data acquired in the last two years. Lead isotope ratios in dust deposited on acacia leaves have been measured via Thermal Ionisation Mass Spectrometry at Curtin University of Technology, Perth, as part of a collaborative project between *eriss* and the Centre of Excellence in Mass Spectrometry. Lead isotope ratios in Ngarradj sediments were determined via ICP-MS at Northern Territory University, Darwin.

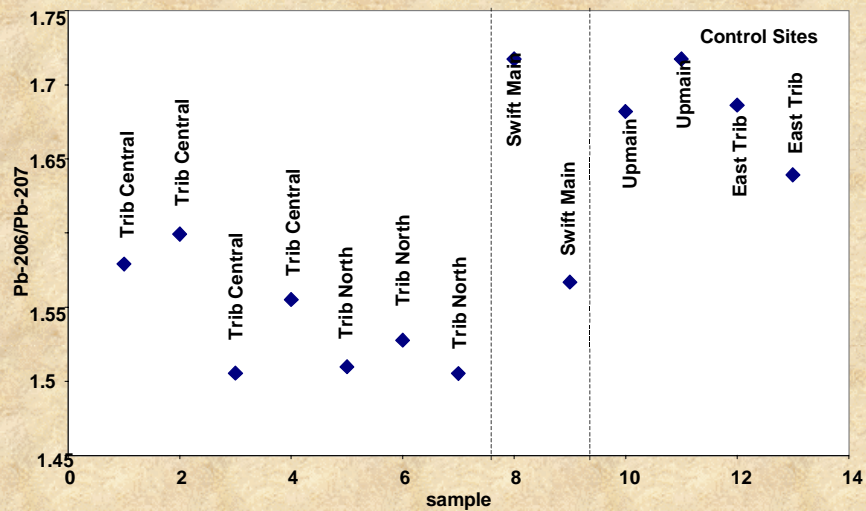
Lead isotope ratios in dust deposited in KNP exhibit a mixing of natural dust with particulates originating from Ranger uranium mine with high  $\text{Pb-206}/\text{Pb-207}$  and low  $\text{Pb-208}/\text{Pb-207}$  ratios, typical for U-rich sources. Lead isotope ratios measured in particulates in RP1 by Gulson et al. in 1996 exhibit lead isotope ratios of  $\text{Pb-206}/\text{Pb-207} = 9.68$  and  $\text{Pb-208}/\text{Pb-207} = 0.049$ . This is an example of a simple two source mixing.

Ngarradj sediments show elevated  $\text{Pb-206}/\text{Pb-207}$  and  $\text{Pb-208}/\text{Pb-207}$  ratios. This indicates that U and Th rich material may be the source of radiogenic Pb in the samples.

In the following slides the results of the two projects are discussed in more detail:



## Radiogenic (Pb) and radioactive (Ra) isotopes in Ngarradj sediments

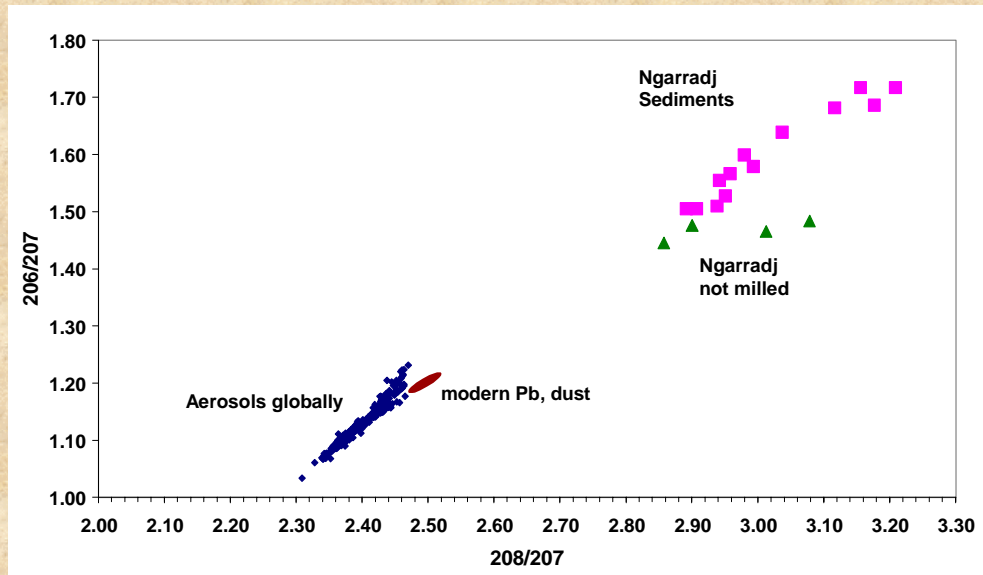


Pb-206/Pb-207 ratios are more radiogenic in sediments from the control sites than in Trib North and Trib Central.

Trib North and Trib Central are next to Jabiluka site and if erosion of U-rich material occurred this should be the other way around.

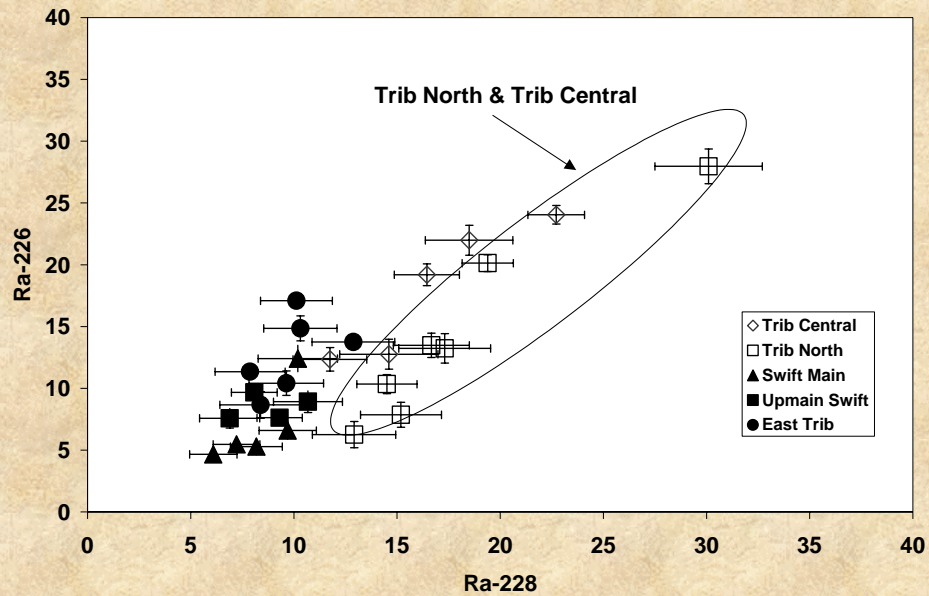
Contamination of the samples during sample preparation?

# Three isotope plot



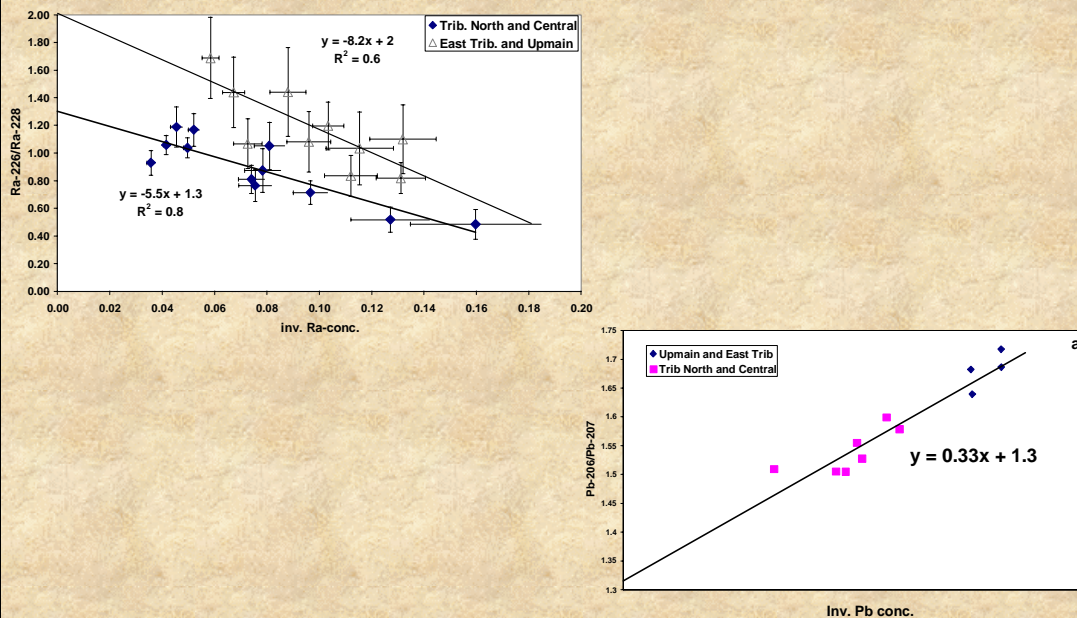
Three isotope plot rules out contamination, as unprocessed Ngarradj samples show similar ratios as processed samples.

# Radium isotopes



Radium isotopes show that there is relatively more Ra-228 than Ra-226 in sediments from Trib Central and Trib North as compared to the control creeks. Therefore, Ra-226/Ra-228 ratios higher in control creeks. Again, if erosion of U-rich material occurred we would expect the opposite.

# Inverse concentration plots



Inverse concentration plots clearly identify the isotopic compositions (radioactive and radiogenic isotopes) of the “contaminating” endmember.

Ra-226/Ra-228 activity ratio of “contaminating” endmember, Trib North and Central:

$$Ra-226/Ra-228 = 1.3$$

Pb-206//Pb-207 isotope ratio of “contaminating” lead endmember:

$$Pb-206/Pb-207 = 1.3$$

## Results

- Relatively less  $^{226}\text{Ra}$  in North and Central Trib.  
Activity ratio of 'contaminating' endmember:  
$$^{226}\text{Ra}/^{228}\text{Ra} = 1.3$$
assuming sec. Equil.  $\rightarrow U_{\text{ppm}}/\text{Th}_{\text{ppm}} = 0.4$   
 $\rightarrow$  crustal
- Lead isotope ratios of 'contaminating' endmember:  
$$^{206}\text{Pb}/^{207}\text{Pb} = 1.3 \pm 0.07$$
$$^{208}\text{Pb}/^{207}\text{Pb} = 2.65 \pm 0.12$$
 $\rightarrow$  dust, clays
- U and Th rich minerals (e.g. Monazites) in sand  
'contaminated' with clays but not with U-mineralized material

Complete discussion of results in:

Bollhöfer A & Martin P 2003. Radioactive and radiogenic isotopes in Ngarradj (Swift Creek) sediments: a baseline study. Internal Report 404, February, Supervising Scientist, Darwin. Unpublished paper.

# Dust deposition around Ranger

Collaborative project with Centre of Excellence in Mass Spectrometry, Curtin University, Perth

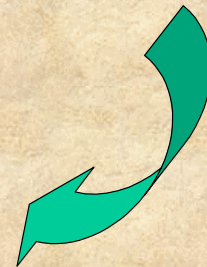
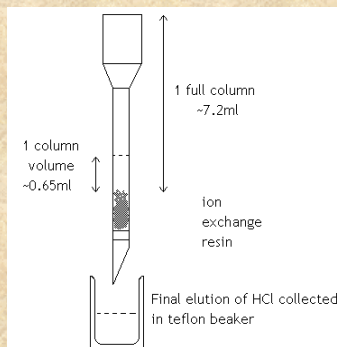
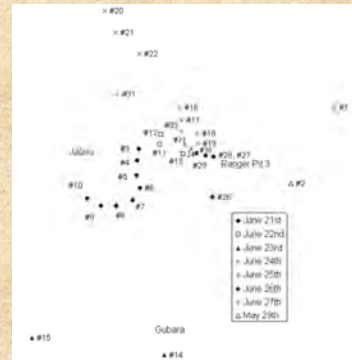
-> highly precise data

Leaves as dust collectors -> spatial data

Annual cycle of lead isotope ratios at Jabiru East



# TIMS measurements



Collection of leaves: upwind of car, at least 500 m from main road. Gloves and lab coat to avoid contamination of acacia leaf samples

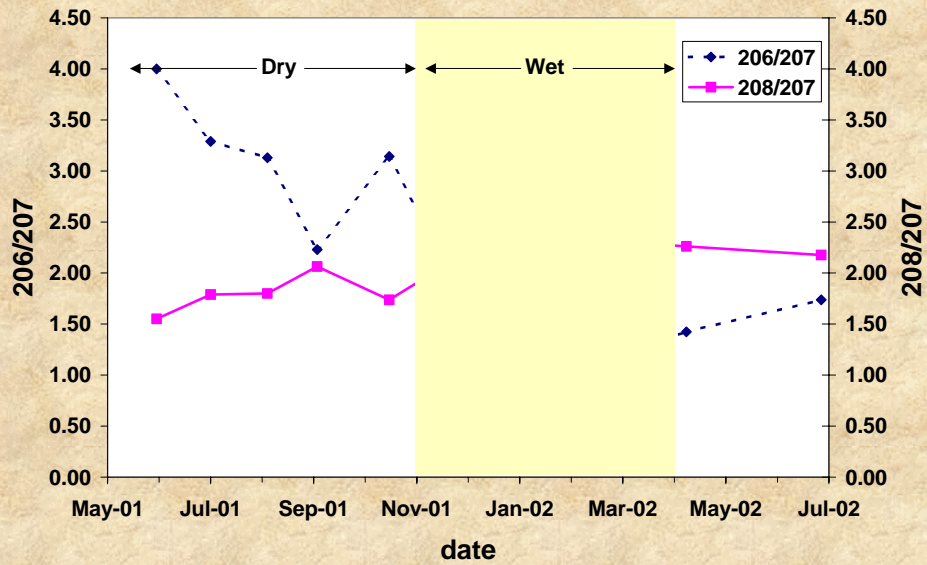
Reasonable coverage in main wind direction.

Chemistry procedures involve ion exchange chemistry. All the 'hard work' done at Curtin University of Technology, Perth, by Russel Honeybun, in 2002.

Finally, TIMS measurements on VG345 Thermal Ionisation Mass Spectrometer.

Low volume air filters were prepared following the chemical procedure of Bollhöfer et al. 1999 and were measured at Curtin University's Thermal Ionisation Mass Spectrometer in 2003 by A. Bollhöfer.

## Annual cycle

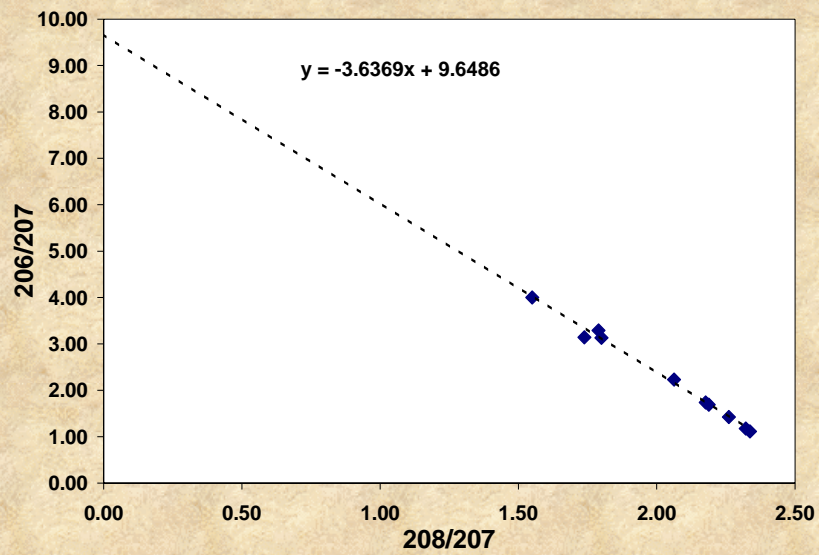


Results are discussed in detail in:

Bollhöfer A, Honeybun R & Rosman K 2003. Atmospheric transport of radiogenic lead in the vicinity of Ranger uranium mine determined using lead isotope ratios in dust deposited on acacia leaves. Internal Report 451, August, Supervising Scientist, Darwin. Unpublished paper.

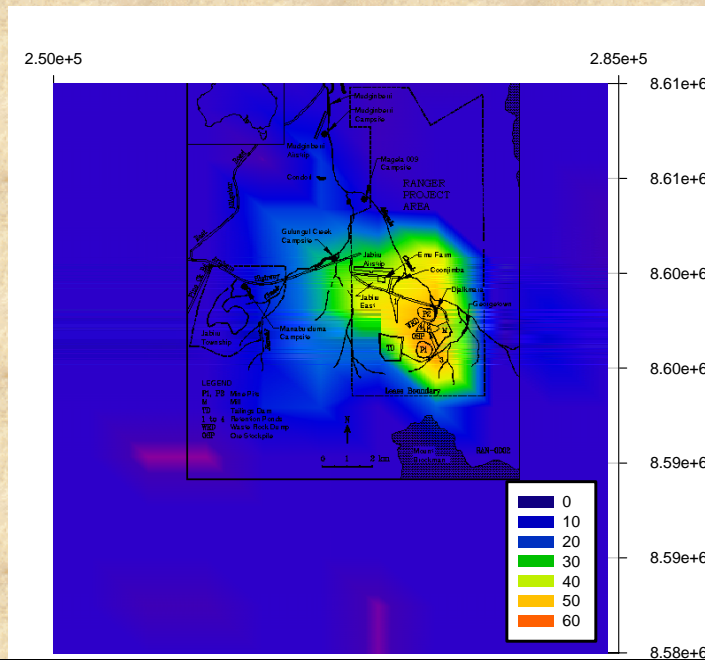


## Three isotope plot

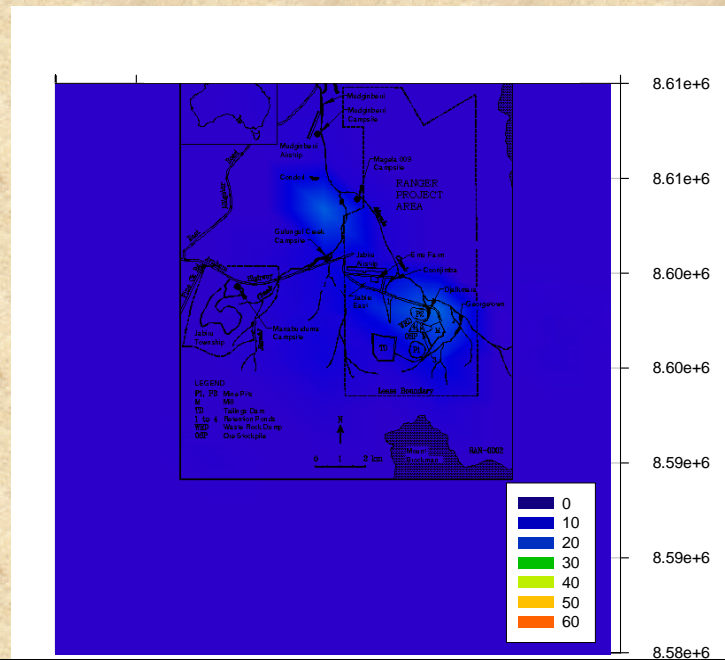


Source clearly identified as Ranger U ore in the filters.

## Percentage contribution of dust from Ranger – dry season



## Percentage contribution of dust from Ranger – wet season



## Results

- In theory contribution from mine to Pb deposition throughout Kakadu detectable ~40 km from mine
- Average annual contribution in Jabiru East: 13 %
- This represents an upper limit for Ranger's contribution to airborne lead levels as fine particles are preferentially collected on leaves.
- Health physics point of view: 1.4 micro Sv from Ranger LLAA at Jabiru East -> negligible

From the average annual contribution the LLAA concentration can be calculated:

13 % of lead on average from Ranger. This is 13 % of approximately  $2 \text{ ng/m}^3$ ,  $\sim 0.25 \text{ ng/m}^3$  Pb from Ranger.

U/Pb in Ranger ore: appr. 4 (Noller 1991)

Therefore:  $1 \text{ ng per m}^3$  U from Ranger.

Which equals a uranium activity of:  $12.35 \times 10^{-6} \text{ Bq per m}^3$

Assuming radioactive equilibrium of all uranium progeny: -> 8 alpha decays

Therefore: total alpha activity in air (annual average) from Ranger:

$10^{-4}$  alpha decays per second per  $\text{m}^3$ .

Average annual long lived alpha activity in Jabiru East: appr.  $2 \times 10^{-4}$  alpha decays per second per  $\text{m}^3$ .

-> 50 % from Ranger

## Outlook

Student projects through NTU to obtain radionuclide and Pb isotope ratios for:

- Ranger source terms (waste rock, RP1 etc)
  - Gulungul, Georgetown, Magela, control creeks
- Aim to have baseline datasets for use after rehabilitation
- Magela/Gulungul to assess erosional stability of Ranger after and during rehab
- Cooper Creek, erosion at Nabarlek and deposition in sediment pockets along the Creek

-> ARC Linkage Grant Application with NTU

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