The use of Pb isotope ratios determined by magnetic sector ICP-MS for tracing Pb pollution in marine sediments near Casey Station, East Antarctica

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Magnetic sector inductively coupled plasma mass spectrometry (ICP-SMS) was used to measure lead concentrations and isotope ratios in marine sediments and other samples collected from near the Australian Antarctic Station Casey. Precisions obtained from the repetitive analysis of a standard Broken Hill Pb sample at a concentration of ~ 40 ng g^{-1} in solution were $< \pm 0.2\%$ for ratios involving ^{204}Pb, and $< \pm 0.1\%$ for those referenced to ^{206}Pb or ^{207}Pb ($n = 12$ replicates over 2 days, values as 1s). Ratios were accurate to within $\sim \pm 0.1\%$ for the analysis of this standard sample. Comparative measurements between ICP-SMS and TIMS had typical differences in values of $< 0.4\%$ for contaminated samples, irrespective of ratio. For marine sediment samples with Pb concentrations in the sample digest of > 10 ng g^{-1}, instrumental capability was characterised by isotopic precisions ranging from 0.1-0.5% (1s) for ratios involving ^{204}Pb, and $< 0.25\%$ (1s) for ratios with ^{206}Pb or ^{207}Pb as the basis (typically found from triplicate analyses). For sediments of low Pb concentration (< 10 ng g^{-1} in the sample digest), isotope ratios to ^{204}Pb were found to be limited by instrument counting statistics when using standard ICP-SMS. To help overcome this problem, Pb isotope ratios for these samples were measured with a capacitive decoupling Pt guard electrode employed, offering considerable signal enhancement (5–10 $\times$). These natural background sediments were found to display typical Pb isotope ratios of 40.5, 15.5, 18.6 and 1.19 for ^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{206}Pb/^{204}Pb and ^{206}Pb/^{207}Pb. For comparison, the most contaminated samples had Pb isotope ratios of approximately 36.2, 15.4, 16.4 and 1.06 for ^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{206}Pb/^{204}Pb and ^{206}Pb/^{207}Pb, respectively. Evidence of simple two component mixing between anthropogenic and natural geogenic Pb was found near Casey Station. Runoff from the Thala Valley tip site, adjacent to the bay, was identified as a clear source of Pb pollution, with impacted sediments displaying an isotopic signature approaching that of abandoned lead batteries collected from the tip. These batteries possessed Pb isotope ratios identical to Australian Broken Hill lead. In this study, the use of Pb isotope data has proved to be a sensitive method of assessing contamination levels in the Antarctic marine environment adjacent to a waste disposal site. Lead isotope ratios have proved superior to simple elemental concentration determinations when distinguishing between impacted and non-impacted samples. ICP-SMS has been shown to offer relatively fast, accurate and cost effective Pb isotope ratios, with precisions suitable for many environmental applications.

Introduction

Australia has an extensive and proud record of exploration and discovery in Antarctica, dating back to Mawson in 1911. Currently, Australia has governance of 42% of the southern-most continent, the largest by any nation, and maintains three permanently manned stations, Mawson, Davis and Casey (along with a sub-Antarctic base on Macquarie Island).

Casey Station is located in the Windmill Islands, East Antarctica, and was established on its present site in 1989 (Fig. 1). This is the third major station located in the area, with two predecessors being Wilkes (built by the United States and operated by them from 1957–58 before transfer to Australia) and "Old" Casey (operational from 1969–89). The current Casey Station is located 500 m southwest of the old station, and approximately 3 km south of the original Wilkes Station (across Newcomb Bay).

The Madrid Protocol of 1998, to which Australia was a signatory, was a collective agreement by participating nations to protect and preserve the Antarctic environment and subsequent eco-systems.[1] A component of this agreement calls for participants to clean up all past and present research and station sites, unless greater environmental damage would result in doing so. Australia has responded by undertaking an extensive process of identifying and treating possible contaminated sites.

With regard to Casey Station, work by Deprez et al.[2] identified approximately 20 sites at the Old and New Casey Stations as potentially contaminated. These included the locations of old mechanical workshops, power generation buildings, nearby waste disposal tips (Thala Valley tip), and areas known to have been contaminated following fuel spills.[3] Snape et al.[3] found elevated concentrations (over unpolluted control samples) of elements such as Fe, Mn, Ni, Cu, Cr, As, Pb, Cd and Zn in sediments from near the Thala Valley tip, extracted using various water and acid media. Metals contamination from Thala Valley tip runoff was detected in sediments collected from the adjacent Brown Bay (an inlet of Newcomb Bay). The element found to be most enriched above background was Pb. Because Pb is an isotopically diverse
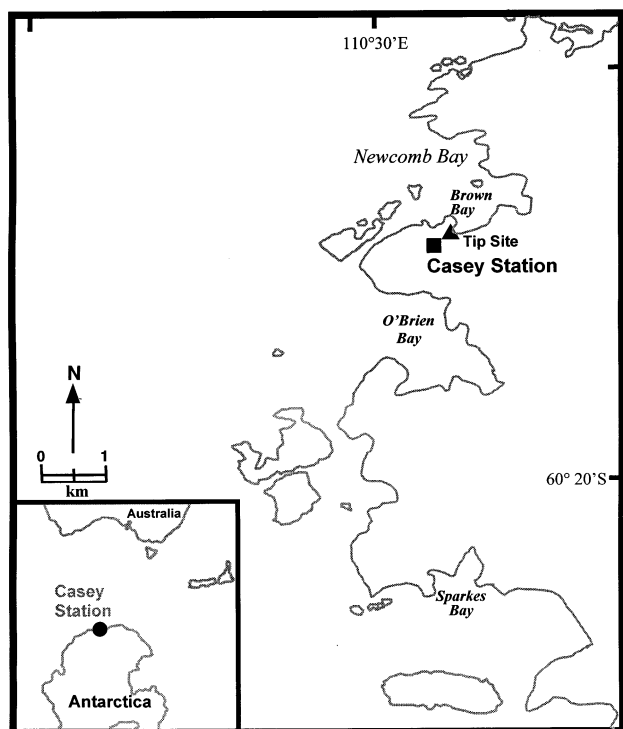
Fig. 1 Map of Antarctica (as inset) and the location of impacted and background sites discussed in this study (Casey Station; Brown, O'Brien and Sparkes Bays).

element, the various stable Pb isotope ratios offer the potential to trace the source, fate and effects of such pollution. As any contamination in this supposedly pristine environment is of concern, techniques that can discern relatively small anthropogenic enrichments are useful if they can be measured in a timely and cost effective way.

The key analytical features offered by magnetic sector ICP mass spectrometers (ICP-SMS), namely excellent sensitivity, low detection limits, and ability to separate analytes of interest from spectral interferences, have been attractive and well utilised by polar researchers.[4–7] Work by Barbante, Boutron and co-workers has principally focussed on the analysis of pristine ice and snow samples from the Greenland and Alpine regions by ICP-SMS.[4–7] These researchers have also recently looked at ice samples from Antarctica in some detail.[8] Earlier work from our laboratory in Tasmania also looked at snow and ice samples from Antarctica using ICP-SMS.[9] To date few reports have appeared using magnetic sector ICP-MS instrumentation for the analysis of samples from contaminated sites from the Polar Regions.

It has now also been well established that for many isotopic pairs, ICP-SMS instruments offer isotopic ratio precisions superior to those obtainable using quadrupole units.[10,11] Ratio precisions less than 0.1% are often available (depending on the isotopic pair, elemental concentration, *etc.*), which is more than adequate for many environmental applications. Although not as precise as the established TIMS or the rapidly emerging multi-collector ICP-MS methods, the shorter analysis time and the relative cost of the instrumentation makes ICP-SMS an attractive method for this type of work. To date TIMS has been the method of choice for the measurement of Pb isotope ratios in polar snow and ice samples,[12] although recently Doring *et al.*[13] applied ICP-SMS to the measurement of Pb isotope ratios in snow samples collected from two high alpine sites in Switzerland. ICP-SMS units also offer the opportunity to analyse the same sample for a range of elements, as well as providing quality isotopic data, using the same instrumentation.

It was the aim of this present study to use ICP-SMS to measure Pb isotope ratios of anthropogenically impacted sediments and other samples collected from near Casey Station, East Antarctica. Measured Pb isotope ratios would reflect the source location and age of the Pb ore from which the contamination originated. Data obtained may help determine the level and extent of Pb pollution in the area, while possibly providing information as to the historical source of the Pb pollution. To our knowledge this is one of the first studies to measure Pb isotopic signatures of contaminated sediments from Antarctica using ICP-SMS instrumentation.

Experimental

Sample collection and preparation

Sediment cores were collected from the Casey Station area by divers during the southern summers of 1997-98 and 98-99, using an acid-washed plastic corer. In particular 4 cores were collected from Brown Bay, adjacent to the Thala Valley tip. Sample locations were selected at various distances from the tip site to ascertain the level of contamination from waste runoff. A number of cores were also taken from O'Brien and Sparkes Bays, 3 and 10 km respectively south from Casey Station. These samples from two isolated inlets had had minimal anthropogenic exposure, and were used as background control markers for this study. Pb concentrations in these samples were typically $< \sim 10$ µg g^{-1} (in the sediment), 20-150 times lower than some of the most contaminated sediments considered from Brown Bay. A further 40 sediment samples from these locations were also collected and were analysed independently for Pb concentration only.[14]

Sample cores were typically divided into 3 mm length fractions. Once separated, a number of these fractions were dried in a mild oven at 60 °C, sieved to a particle size <2 mm or <63 µm, and finally homogenised. Other work in our laboratories[14] has shown little difference in Pb concentration with particle size, and no variation or fractionation of isotope ratio with particle size was expected. 0.1 g sub-samples were subsequently taken and digested with HNO$_3$ (0.5 mL, BDH, AnalaR grade)–HF (2 mL, AnalaR grade) in Teflon beakers for 48 h at 130–150 °C.[15] After evaporation to incipient dryness (twice), all digests were finally taken up in nitric acid (final concentration 2%) and were diluted to final volume (100 mL) using ultra-pure water (Modulab Pure One system, >16.7 MΩ^{-1}) before being stored in sealed polycarbonate containers.[15] As samples were diluted by 1000 ×, all subsequent concentrations can represent Pb in the sediment (as µg g^{-1}), or Pb in the digest (as ng g^{-1}).

Two intact abandoned solid batteries were also sampled, and their Pb component was simply digested in 25% nitric acid prior to ICP-SMS analysis.

ICP-MS measurements

All isotope ratio determinations were made using a double focussing magnetic sector ICP-MS (ELEMENT, Finnigan MAT, Bremen, Germany). This instrument was equipped with a standard Fassel torch and a concentric nebuliser coupled to a Scott double-pass spray chamber (cooled to 1–2 °C). For samples of relatively low Pb concentration (typically uncontaminated sediments of $\sim$1–10 ng g^{-1} Pb in the sample digest), a capacitive decoupling Pt guard electrode offering increased signal sensitivity (5–10 ×) was utilised. The construction and operation of this electrode has been discussed previously.[16] Although the ELEMENT has three fixed resolution modes available, the lowest resolution setting of $m/\Delta m \sim 300$ (offering maximum ion throughput and hence maximum instrumental sensitivity) was used for this work. Isotopes of interest were

Table 1 Some typical instrument configuration and method parameters used for Pb isotope ratio measurements. Further details are provided elsewhere[17,18]

Instrument	Finnigan MAT ELEMENT
Resolution ($m/\Delta m$)	300 (low)
Rf power	1250 W (normal operation); 1100 W (with guard electrode)
Nebuliser	Meinhard concentric
Coolant argon flow rate	~12.5 L min^{-1} ^{a}
Auxiliary argon flow rate	~1.05 L min^{-1} ^{a}
Nebuliser argon flow rate	~1.15 L min^{-1} ^{a}
Spray chamber	Scott (double pass) type cooled to 1–2 °C
Sampler cone	Nickel, 1.1 mm aperture i.d.
Skimmer cone	Nickel, 0.8 mm aperture i.d.
Instrument tuning	Performed using a 1, 5 or 10 ng g^{-1} multi-element solution
Typical ion transmission	~2.5–4 × 10^5 counts s^{-1} for 1 ng g^{-1} ^{208}Pb (normal operation)
Scan type	Fixed magnet with electric scan over small mass range
Number of sweeps	1200 scans
Isotopes analysed	^{201}Hg, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb
Sample uptake and equilibration time	2 min
Rinse time between each sample	3 or 4 min with 5% HNO$_3$

^{a}Adjusted in order to maximise signal intensity and stability for operation with or without guard electrode inserted.

scanned 1200 times (for a total analysis time of approximately 2 min) using electric scanning with the magnet held at fixed mass. Mathematical correction was performed to account for any small contribution from Hg on the signal at ^{204}Pb (typically <300 counts, or below 0.4% of the total ^{204}Pb signal). Instrumental conditions and some method parameters employed are outlined further in Table 1 and were similar to and based on earlier more detailed work by Vanhaecke *et al.*[17] and Townsend *et al.*[18]

To ensure that all Pb isotopes could be analysed with the detector in the same operational mode (namely "counting"), each sample digest was diluted to a Pb concentration appropriate to whether the instrument was operated in standard or guard electrode configuration. Where possible each sample digest was typically analysed 2–4 times (consecutive repetitions), with subsequent data shown being average values from these multiple assays. All isotope ratios were calculated after blank subtraction and were corrected for mass discrimination and detector dead-time effects. The detector dead time was typically 21–22 ns, and was determined by the method proposed by Russ[19] involving the measurement of Pb isotope ratios at different Pb concentrations.[18–20] In this work mass discrimination effects were measured by analysing a suitably concentrated NIST SRM 981 natural Pb isotope standard (Gaithersburg, MD, USA), before and after each unknown digest. Considering 15 random analyses of NIST SRM 981, the mass discrimination or difference between found and reference ratios, calculated as % u, was ~0.6% u.

The ICP-SMS introduction system was rinsed with 5% nitric acid for 3–4 min between each sample analysis.

Results and discussion

Pb isotope ratios with ^{204}Pb as the ratio basis (*e.g.*, ^{208}Pb/^{204}Pb, ^{206}Pb/^{204}Pb) are often presented for studies with a geological bias or focus,[18,21–25] while for many environmental applications, ratios based on the ^{206}Pb and ^{207}Pb pair are more often reported.[13,26–29] This difference can be attributed to:

(i) The need for geologists to determine very accurate ratios of radiogenic to non-radiogenic lead which, in turn, can be related to geological process and age. Until recently the highly accurate, precise and labour intensive TIMS technique has been the analytical method of choice, as ratios measured using some other techniques and involving the low abundance ^{204}Pb isotope (1.4%) may be prone to instrumental counting limitations. Also, in many geological situations, Pb isotope ratios may only cover a very narrow range of values, outside the scope of other less precise instrumentation.

(ii) The observation that in some cases, ratios of lower precision are adequate for many environmental studies, which has often allowed cheaper and faster (but less precise) quadrupole and magnetic sector ICP-MS instrumentation to be applied. To maximise analytical precision using this type of equipment, ratios using the adjacent or most abundant Pb isotopes [^{206}Pb (24.1% abundant), ^{207}Pb (22.1%), and ^{208}Pb (52.3%)] have usually been presented.

(iii) A choice by the researchers involved to only present data using the Pb isotope ratio(s) that provides the greatest or clearest differentiation between samples.

For ease of comparison with other studies, and to highlight the analytical capabilities of ICP-SMS as applied to a real life environmental situation, we have measured Pb isotope ratios with ^{204}Pb as the basis, as well as ratios using the more abundant ^{206}Pb and ^{207}Pb isotopes.

Accuracy and precision of data

The repetitive analysis of a Broken Hill galena digest was one method by which analytical accuracy was assessed in this work. As an example, data presented in Table 2 shows Pb isotope ratio values obtained from 12 analyses of this in-house reference sample at a concentration of ~40 ng g^{-1} (in solution). Five replicate measurements were initially made, followed by a further 7 values determined randomly over the course of 2 consecutive days. Excellent agreement with previously presented TIMS data[18] was found, with the difference between the two being less than ±0.14% for all ratios considered. The external precision associated with the 12 analyses of this Broken Hill sample were approximately ±0.2% (1s) for ratios with ^{204}Pb as the basis and approximately ±0.1% (1s) for those referenced to ^{206}Pb or ^{207}Pb. These values are approximately twice those previously reported;[17,18] however, earlier data was obtained on newly commissioned instruments from 10 consecutive repetitions (not a random selection of measurements over a number of days as presented in this work).

Although the measured external precisions obtained for the Broken Hill reference sample are excellent for this type of instrument, they are somewhat unrealistic as this many analyses ($n = 12$) of the one sample cannot be labelled as routine. Each sample digest from near Casey Station was

Table 2 Average Pb isotope ratios measured by ICP-SMS compared against TIMS reference values for the Broken Hill lead in-house standard. ICP-SMS measurements were made using a solution of approximate [Pb] 40 ng g^{-1}

	^{208}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{206}Pb/^{204}Pb	^{206}Pb/^{207}Pb
Measured ratio ($n = 12$)	35.548	15.358	15.990	1.041
Reference TIMS values[18]	35.599	15.370	15.994	1.041
Difference between ICP-SMS and TIMS values (%)	0.14	0.08	0.03	0
s of ICP-SMS measurements (as %, $n = 12$)	0.23	0.21	0.17	0.08

typically only analysed 2–4 times, and poorer precisions were obtained, depending on the concentration of Pb in solution. For concentrations between 10 and 50 ng g^{-1} (in the prepared digest solution), standard deviations typically ranging from ±0.1 to 0.5% (1s) for ratios involving ^{204}Pb, and values to $\pm0.25\%$ (1s) for ratios with ^{206}Pb and ^{207}Pb as the basis, were found. These values can be considered more realistic from routine operation on environmental samples, and agree closely with values reported by De Wannemacker et al.[30] also using an ELEMENT ICP-SMS of similar age. At lower Pb concentrations between 1 and 10 ng g^{-1} (in solution), experimental precisions worsened (by an approximate factor of 2).

A selection of sediment digests from Brown, O'Brien and Sparkes Bays near Casey Station were also analysed by TIMS at the Victorian Inst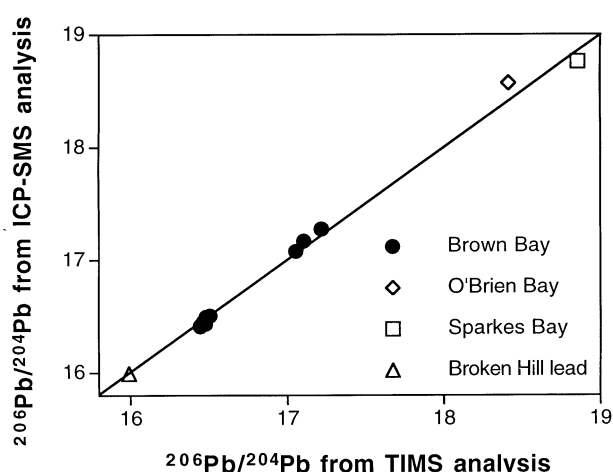itute for Earth and Planetary Studies (VIEPS), Latrobe University (Melbourne, Australia), and at the Geology and Geophysics Department, University of Adelaide (Adelaide, Australia). Fig. 2 clearly highlights the correlation between the two methods, considering the ratio ^{206}Pb/^{204}Pb as an example, with a theoretical 1 : 1 relationship line shown as a guide. Assuming that the uncertainty of the TIMS data with respect to the "true values" is negligible over the concentration range 1–250 ng g^{-1} considered here, there was no statistically defined bias using ICP-SMS. A simple linear regression estimate is ^{206}Pb/^{204}Pb$_{ICP\text{-}SMS}$ = 0.98 × ^{206}Pb/^{204}Pb$_{TIMS}$ + 0.3 (r^2 = 0.995, for n = 11), with the 95% confidence range estimated for the slope as 0.93–1.04, and for the intercept as −0.62–1.18. The correlation between the ICP-SMS and TIMS techniques is limited by the precision of the ICP-SMS instrument. Similar agreement between the two analytical methods was also found for the ^{208}Pb/^{204}Pb and ^{206}Pb/^{207}Pb ratios (slopes = 0.95 and 1.01), while a poorer correlation was found for ^{207}Pb/^{204}Pb, possibly due to the small difference in ratio values considered. Overall, the difference in ratios found between the two methods was generally $< \pm0.4\%$ for contaminated samples from Brown Bay. Based on the conformity of the 2 analytical methods, and coupled with reliable Broken Hill reference sample results, considerable confidence was placed in the measured ratio data obtained for Antarctic sediments from near Casey Station.

Uncontaminated background samples

A number of uncontaminated sediment samples were collected independently from O'Brien and Sparkes Bays. Sediments taken from these areas were found to possess relatively low Pb concentrations of 1–10 µg g^{-1} (in the solid, 1–10 ng g^{-1} in the digest). At these low Pb levels, blank effects can become more pronounced, making analytical precautions against Pb contamination important (e.g., the use of ultraclean reagents during digestion, use of a certified clean room for sample preparation, etc.). Blank subtraction of the isotopic signal associated with the reagent blank was also crucial. Ratios are shown in Table 3, and were typically 40.5, 15.5, 18.6, and 1.19 for ^{208}Pb/^{204}Pb, ^{207}Pb/^{204}Pb, ^{206}Pb/^{204}Pb and ^{206}Pb/^{207}Pb, respectively.

Fig. 2 Comparison between ^{206}Pb/^{204}Pb ratios measured in sediment samples collected from Brown, O'Brien and Sparkes Bays obtained using ICP-SMS and TIMS. Broken Hill lead reference data are also shown, along with a 1 : 1 correlation line as a guide. The average ICP-SMS standard deviation for all values was calculated but is smaller than the symbols shown.

Table 3 Pb concentrations and average isotope ratios measured by ICP-SMS in: uncontaminated sediments from O'Brien and Sparkes Bays; contaminated sediment samples collected from Brown Bay; and two battery samples. Comparartive TIMS data for selectedsamples are also shown.

| Sample code	Depth/mm	[Pb]/µg g^{-1}	n^a	^{208}Pb/^{204}Pb ICP-SMS	TIMS	^{207}Pb/^{204}Pb ICP-SMS	TIMS	^{206}Pb/^{204}Pb ICP-SMS	TIMS	^{206}Pb/^{207}Pb ICP-SMS	TIMS
O'Brien Bay—											
OBB1	0–150	8.4	3	41.127	41.442	15.539	15.682	18.412	18.572	1.185	1.184
Sparkes Bay—											
S1P2	0–150	1.8	6	40.160		15.540		18.613		1.197	
S2P2	0–150	1.5	4	40.574	40.638	15.734	15.694	18.858	18.760	1.198	1.196
Outer Brown Bay—											
A068	3–6	24.2	3	37.478	37.522	15.551	15.541	17.054	17.080	1.096	1.099
A072	51–54	17.7	3	38.154		15.558		17.263		1.109	
A050	69–72	19.9	3	37.900	38.142	15.533	15.547	17.218	17.278	1.108	1.111
Middle Brown Bay—											
A034	9–12	81.3	3	36.295	36.349	15.428	15.448	16.480	16.495	1.068	1.068
A036	30–33	103	2	36.270	36.350	15.429	15.422	16.503	16.505	1.069	1.069
A038	57–60	52.3	3	36.808		15.486		16.672		1.076	
A057	66–69	37.0	3	38.441	38.589	15.499	15.545	17.105	17.171	1.103	1.105
Inner Brown Bay—Station 2—											
A096	9–12	147	3	36.365	36.320	15.436	15.414	16.461	16.447	1.066	1.067
A093	45–48	90.5	2	36.279		15.376		16.449		1.070	
A074	57–60	46.5	2	36.257	36.161	15.468	15.420	16.442	16.412	1.063	1.064
Inner Brown Bay—Station 4—											
A100	31–34	215	3	36.066		15.442		16.388		1.061	
A084	58–61	191	3	36.323	36.173	15.477	15.418	16.473	16.432	1.064	1.066
Battery samples—											
1	—	—	3	35.796		15.427		16.047		1.040	
2	—	—	3	35.653		15.379		16.017		1.041	

$^a n$ = number of isotope ratio measurements.
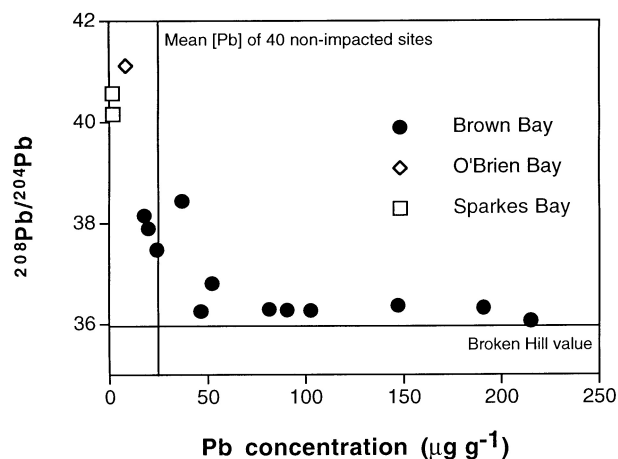
Fig. 3 $^{208}Pb/^{204}Pb$ ratios measured by ICP-SMS *versus* Pb concentration for contaminated sediments collected from Brown Bay, and natural background samples sourced from O'Brien and Sparkes Bays. Broken Hill lead reference value and the mean Pb concentration of 40 non-impacted sites[14] are shown as lines. The average ICP-SMS standard deviation for all values was calculated but is smaller than the symbols shown.

A more comprehensive suite of 40 samples from non-impacted areas were also analysed for Pb concentration only,[14] and were found to have a mean Pb concentration of 24.6 ± 5.4 μg g^{-1} (1*s*). The control samples chosen for isotopic measurement were at the lower end of this suite. It is worthy of note that several potentially contaminated samples from Brown Bay (see discussion below) lie within the natural background range as determined from the analysis of these 40 samples (Fig. 3 and Table 3).

Isotopic signature of impacted sediments from Brown Bay

Lead concentrations and isotope ratios of 12 sections collected from 4 sediment cores sampled from Brown Bay are also shown in Table 3. In terms of proximity to the Thala Valley tip site: samples A068, 72 and 50 were from the outer part of the bay ($\sim$150 m from the tip site); samples A034, 36, 38 and 57 were from the "middle" section of the bay ($\sim$100 m); while A096, 93, 74, 100 and 83 were collected from 2 cores closer to the tip location ($\sim$40 m). The sediment core from the outer reaches of Brown Bay displayed Pb concentrations of approximately 20 μg g^{-1}, irrespective of section depth, while the 3 other cores nearer to the Thala Valley tip possessed higher Pb concentrations. Considering the sediment core from the middle of the bay, Pb concentrations ranged from $\sim$80–100 μg g^{-1} in sections near the surface, falling to 37 μg g^{-1} at a depth of 66–69 mm. As expected the 2 cores closest to the waste disposal area had the highest Pb concentrations (Station 2: 147 μg g^{-1} in the section from a depth of 9–12 mm to 46 μg g^{-1} at 57–60 mm; Station 4: 215 μg g^{-1} at 31-34 mm to 191 μg g^{-1} at 58–61 mm). These measured concentrations would suggest that Pb contamination from run off is severest with proximity to the tip (as expected), reducing with distance and also with depth for outer sample sites. It should be noted, however, that samples were only analysed from cores to a maximum depth of 70 mm, and all samples considered here displayed Pb concentration far in excess of those measured from the uncontaminated O'Brien and Sparkes Bay sites.

In terms of Pb isotopic signature, the $^{208}Pb/^{204}Pb$ ratio is perhaps the most useful for discriminating between these samples in this instance. Sections from the outer core possessed a $^{208}Pb/^{204}Pb$ ratio of near 38 (at all depths considered). Samples closer to the surface of the middle core displayed a $^{208}Pb/^{204}Pb$ ratio of ~36.3 consistent with some contamination by Pb of Australian origin (Broken Hill Pb has a $^{208}Pb/^{204}Pb$

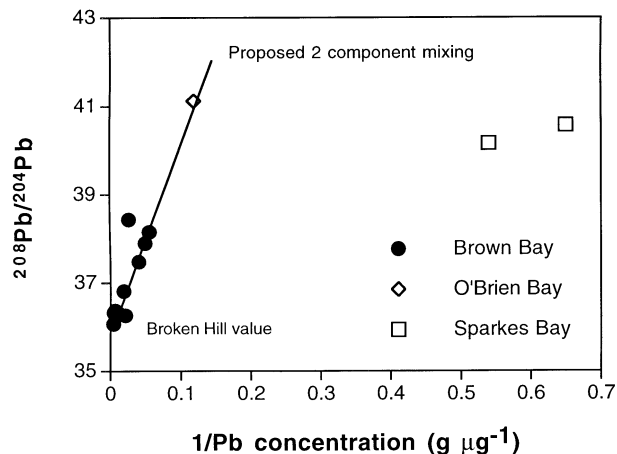**Fig. 4** Plot of $^{208}Pb/^{204}Pb$ ratios measured by ICP-SMS *versus* 1/Pb concentration for contaminated sediments collected from Brown Bay, and natural background samples sourced from O'Brien and Sparkes Bays. The average ICP-SMS standard deviation for all values was calculated but is smaller than the symbols shown.

ratio of $\sim$35.6), rising to $\sim$36.8 at a depth of 57–60 mm. A ratio similar to that recorded from outer Brown Bay of $\sim$38 was measured in the section from the lowest depth of 66–69 mm for this middle core. For the 2 most contaminated inner cores, $^{208}Pb/^{204}Pb$ ratios of $\sim$36.3 were found, irrespective of depth (to a maximum of $\sim$60 mm), indicating more extensive pollution. All $^{208}Pb/^{204}Pb$ ratios were significantly different to that typically measured from the uncontaminated sites considered ($\sim$40.5). Similar trends can be seen in the values for the other 2 ratios with ^{204}Pb as the basis, and to a lesser extent when using ratios based on ^{206}Pb and ^{207}Pb.

Fig. 3 shows $^{208}Pb/^{204}Pb$ ratios (as an example) plotted against measured Pb concentration for sediments collected from Brown Bay. A clear mixing curve is evident for most samples analysed, irrespective of location (proximity to Thala Valley tip) or depth, with natural background or geogenic lead, and Broken Hill anthropogenic lead, as end members. Faure[31] has suggested that when an isotope ratio is plotted against the inverse of the concentration of the element concerned, a straight line will result if two component mixing is taking place (each component with a different isotope signature). When the data shown from Brown and O'Brien Bays in Fig. 3 was treated in this manner, a linear correlation ($r^2 = 0.90$) tending towards the ratios displayed by the uncontaminated sample from O'Brien Bay was found (Fig. 4). A theoretical mixing line is also shown in Fig. 4. The 2 samples from Sparkes Bay did not fall neatly onto this theoretical mixing line because of their comparatively low Pb concentration ($\sim$1 μg g^{-1} in sample, 1 ng g^{-1} in digest) and the dramatic effect that this can have on the 1/Pb value. Despite this limitation, the data shown suggests that sediments sampled from the Brown Bay area display Pb isotope ratios with 2 distinct end members, namely Broken Hill anthropogenic and natural background lead. Clearly we have identified the isotope ratio of the background end member, and the concentration of Pb in the background is probably similar to the concentrations found in sediments from the nearby O'Brien Bay rather than Sparkes Bay. The proposed 2 component mixing model would suggest that run off from the nearby Thala Valley tip site has mixed with and has contaminated the natural sediments of Brown Bay with Australian sourced Pb.

As expected, ratios tended towards the characteristic Broken Hill $^{208}Pb/^{204}Pb$ signature value of $\sim$35.6 with increasing Pb concentration (Figs. 3 and 4). However, what was surprising was the rapid decrease in isotope ratio observed in samples with Pb concentrations below 50 μg g^{-1}. These figures further highlight that even a small increase in Pb concentration
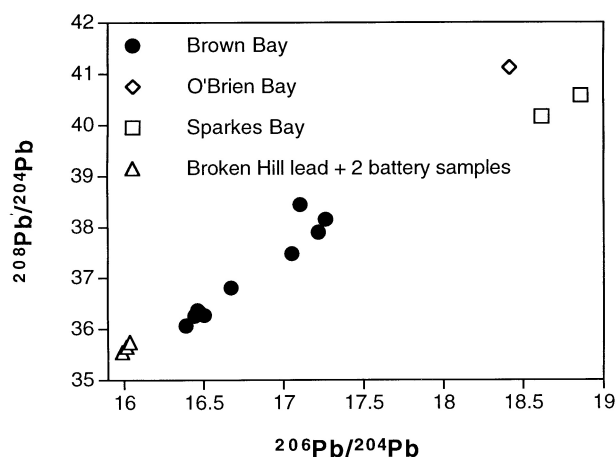
Fig. 5 Relationship between $^{208}Pb/^{204}Pb$ against $^{206}Pb/^{204}Pb$ for both contaminated and uncontaminated samples (all values shown were measured by ICP-SMS). The average ICP-SMS standard deviation for all values was calculated but is smaller than the symbols shown.

resulting from anthropogenic input may have a noticeable effect on sediment isotope composition. The inclusion of Pb isotope data in this and related studies may offer a more sensitive method of assessing contamination levels at impacted sites than simple concentration data alone. This is perhaps one of the key findings in this study and should be emphasised further. It has been clearly shown that by using a single detector ICP-SMS instrument (not TIMS or multi-collector ICP-MS), and measuring isotope ratios (not simply total concentration alone), the extent of contamination in a relatively pristine environment has been successfully evaluated. With the large number of ICP-MS units worldwide, this approach should be taken up by many more laboratories.

When Pb isotope data for samples sourced from Brown Bay as well as the uncontaminated control sites are presented in an isotopic correlation diagram, the mixing between unpolluted sediments and anthropogenically impacted samples is again clear. This is shown by way of example in Fig. 5, where $^{208}Pb/^{204}Pb$ ratios are plotted against $^{206}Pb/^{204}Pb$. Similar trends were also found when $^{207}Pb/^{204}Pb$ ratios were plotted against $^{206}Pb/^{204}Pb$, and when $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios were both plotted against $^{206}Pb/^{207}Pb$ (data not shown). Again it is evident that sediment samples from Brown Bay display isotopic signatures intermediate between Broken Hill lead and that naturally occurring in the area. The isotopic signatures of 2 battery samples are also shown in Fig. 5 (ratio data presented in Table 3). As these two samples displayed isotope ratios virtually identical to Broken Hill lead, it can be deduced that both batteries most likely originated from Australia, and are typical of the type of pollution impacting on the sediments of Brown Bay.

The end-member isotopic compositions identified in the two-component mixing model were apparent because of their distinctive isotopic signatures. The potential contribution of both sea-water and atmospheric sources of anthropogenic lead were considered, but were discounted because: (1) they have different isotopic composition(s);[32,33] (2) they have very low Pb concentrations when compared to the relatively large lead concentrations found in the contaminated sediments (up to 250 $\mu g\ g^{-1}$);[32,33] and (3) there is no reason to suspect Brown Bay as an area of Pb deposition from global processes. The observation that the Pb concentration in the sediments dramatically increases with proximity to the Thala Valley tip site, which is known to contain damaged Pb batteries with isotopic signatures virtually identical to Broken Hill lead (Table 3), strongly suggests that this is the major source of Pb to the nearby environment. Broken Hill Pb also has a

distinctive isotopic signature (in comparison to other major anthropogenic sources of Pb[34]), and significant natural Pb enrichment has not been reported from the Casey region. This study is the first to measure Pb isotope ratios from near Casey Station, so there is little baseline Pb isotope data available for meaningful comparison.[35] It is planned to collect and analyse further samples to help elucidate regional background Pb signatures in sediments and waters to establish this baseline prior to further human disturbance and possible Pb contamination. Sediments collected adjacent to the former American Wilkes station have also displayed isotopic signatures from sources other than Australian Broken Hill lead, and this will be the topic of a future report.

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