

Clay mineral, geochemical and Sr–Nd isotopic fingerprinting of sediments in the Murray–Darling fluvial system, southeast Australia

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Clay minerals, trace elements and isotopic signatures ($^{87}\text{Sr}/^{86}\text{Sr}$; $^{143}\text{Nd}/^{144}\text{Nd}$) were investigated to fingerprint fine-grained sediments ($<2\mu\text{m}$) from the major tributaries of the Murray–Darling fluvial system. Mineralogical, chemical and isotopic signatures in the river clays are clearly inherited from the assemblage of source rocks and soils in the upper catchments of each river. As Murray and Darling tributaries originate in geological formations of different age and composition, significant differences in the respective mineralogical, chemical and isotopic signatures occur between the two river systems. The Darling River system is characterised by abundant smectite, low Ba, K, Rb, Cs, Sn, and high Hf and Zr concentrations, low relatively constant $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.708–0.717) and wide range of $\epsilon\text{Nd}(0)$ values (1.4 to –6.2). In contrast, the Murray River system shows high illite values, high Ba, K, Rb, Cs and Sn concentrations, low Hf and Zr concentrations, a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.726–0.775) and relatively constant $\epsilon\text{Nd}(0)$ values (–8.9 to –10.3). Thus, it is possible to trace provenance of suspended material in individual river systems and, by applying simple mixing equations, budget percentage contributions of tributaries at river junctions can be calculated. Based on Sr and Nd isotopic ratios and concentrations, a contribution of 36% for the Darling and 64% for the Murray to the fine-grained sediment ($<2\mu\text{m}$) downriver was calculated for the main Darling–Murray junction at Wentworth/Mildura.

KEY WORDS: clay minerals, Murray–Darling Basin, rare-earth elements, sediment budgeting Sr–Nd isotopes, trace elements.

INTRODUCTION

The Murray–Darling Basin covers 1 073 000 km² of southeast Australia and drains 14% of the Australian landmass. The Murray–Darling Basin extends over two climatic zones, being influenced by the summer rainfall in the north and the westerlies, and the winter-dominated rainfall in the south, and resulting in highly variable and episodic river discharge and sediment transport. The Murray and Darling Rivers and their tributaries travel through a variety of geological formations, which each has its own peculiarities and specific geochemical and mineralogical compositions. Weathering and erosion of the unique combination of rock formations within each catchment should imprint a characteristic mineralogical, geochemical and isotopic signature onto the sediments transported downriver. The northern tributaries of the Darling River originate in Mesozoic clastic sediments of south-central Queensland, while the eastern tributaries drain the western slopes of the Great Dividing Range. Rock formations in that area consist of widespread Tertiary mafic volcanics, Mesozoic granites and Late Palaeozoic volcanics,

metasediments and granites of the southern part of the New England Fold Belt (Rutland 1976). South of the New England Fold Belt, the Lachlan Fold Belt includes Early Palaeozoic granites, volcanics and metasediments. Similar rock formations continue into the Southern Highlands. Incidentally, all the Murray tributaries originate in the Lachlan Fold Belt or Southern Highlands, while the Darling tributaries, except for the Macquarie River, drain the New England Fold Belt and south-central Queensland. The different compositions and age of these major geological units generate a type of weathering that is characteristic of different soils in both catchments (Butler & Hubble 1978). The suspended loads of the tributaries in the Murray–Darling Basin should therefore contain characteristic signatures or ‘fingerprints’ derived from the parent rocks and soils in the respective catchments. Nevertheless, we had to limit our number of samples and the tributaries in the west and northwest, which can be dry for many years, are under-represented. However, during the course of our study, it became clear that material from these tributaries, e.g. the Paroo, possibly significantly influences the Darling system, but this could not be verified.

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Today, the Murray–Darling fluvial system is largely managed and water flow has diminished to one-third of the natural flow near Murray Bridge (Close 1990). The sediment transported today is mainly suspended clays. The isotopic and geochemical signatures of suspended matter in the Murray–Darling fluvial system also depends on the size fractions (Douglas *et al.* 1995). Considering that a large part of the suspended matter in the Murray–Darling fluvial system consists of the clay fraction, and to keep data from all tributaries comparable, we used the $<2\mu\text{m}$ fraction for all our fingerprinting analyses.

In this study, we show that clay mineral, geochemical and isotopic signatures from all major tributaries in the Murray–Darling Basin can be used to identify the provenance of sediment in the Murray–Darling fluvial system and to quantify the contribution of each tributary to the system. Furthermore, these signatures can be now used to decipher past discharge and flow regimes of the rivers from sediment cores offshore.

MATERIALS AND METHODS

The Murray and Darling Rivers and their tributaries and anabranches were sampled at 30 locations throughout the Murray–Darling Basin. Emphasis was laid on obtaining fine-grained, clayey material. Preferred sampling sites were deposits of suspended matter from the previous flooding events, such as dried-out mudpools in river beds and bank sediments, which contain a sequence of previous flooding events. The samples are not representative of the grain size or bulk mineralogical composition of the material transported in the rivers. However, we believe that they represent the clay mineral suite of the $<2\mu\text{m}$ fraction, which is transported in suspension. Samples were washed through a $63\mu\text{m}$ mesh and the fine fraction was treated with 10% H_2O_2 and weak acetic acid (10%) to remove organic matter and carbonate, respectively. The samples were then split into silt ($2\text{--}63\mu\text{m}$) and clay ($<2\mu\text{m}$) fractions by conventional settling techniques in glass tubes.

The clay fraction was analysed by X-ray diffraction (Phillips PW1700, $\text{CoK}\alpha$ -radiation) for the four main clay mineral groups kaolinite, smectite, illite and chlorite, following standard procedures (Petschick *et al.* 1996). Contents of each clay mineral group in the sample are expressed as relative weight percentages, using the weighting factors introduced by Biscaye (1965). Scans were evaluated with the free-ware program MacDiff (<http://servermac.geologie.uni-frankfurt.de/Rainer.html>). Replicate analysis of the same sample produced results with an error margin of $\pm 2\%$.

Major elements Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn and Fe were assessed by XRF on a Philips (PANalytical) PW2400 X-ray spectrometer. Lithium borate discs were prepared by fusion of 0.27 g of dried sample powder and 1.72 g of '12–22' eutectic lithium metaborate–lithium tetraborate. The major elements were calibrated against 28 international standard rock powders. The lithium borate discs were then dissolved in 2% HNO_3 and after

dilution trace elements Sc, V, Y, Cr, Mn, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Cs, Ba, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb, Lu, Hf, ^{207}Pb , ^{208}Pb , Th and U were assessed by ICP-MS.

Strontium and neodymium isotope measurements were carried out at the Research School of Earth Sciences, Australian National University. The powdered samples were dissolved in HF-HNO_3 in screw-cap Teflon vials. Strontium and the REE were separated from matrix elements by cation-exchange chromatography, following the procedures presented in Crock *et al.* (1984) and Rehkamper *et al.* (1996), in a dedicated positive-pressure laboratory equipped with HEPA-filtered clean-air stations. Neodymium was further purified using chromatography columns loaded with hexyl di-ethyl hydrogen phosphate (HDEHP)-coated Teflon powder (following Richard *et al.* 1976). Distilled reagents and 18 M Ω water were used for all procedures.

Isotope ratios were measured by thermal ionisation mass spectrometry following Wasserburg *et al.* (1981) and Mittlefehldt and Wetherill (1979), using a Thermo-Finnigan Triton TI multicollector mass spectrometer in static mode. Strontium was run on single Ta filaments after loading in H_3PO_4 . Neodymium was run on Ta (evaporation) – Re (ionisation) double filaments after loading in HNO_3 and dilute H_3PO_4 . All filaments were outgassed at 4 A for 30 min prior to loading the sample. Each analysis consisted of 150 cycles using 8.4 s integrations and online corrections for Rb ($^{85}\text{Rb}/^{87}\text{Rb} = 2.5907$), Ce ($^{140}\text{Ce}/^{142}\text{Ce} = 7.9928$) and Sm ($^{147}\text{Sm}/^{144}\text{Sm} = 4.7690$; $^{147}\text{Sm}/^{150}\text{Sm} = 1.5087$) interferences. To correct for mass fractionation, Sr isotope ratios were normalised to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$ and Nd ratios normalised to $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$.

Reference values for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ measured on the Triton mass spectrometer during this study are 0.710224 ± 0.000011 (2σ , $n = 6$) for the NIST SRM-987 Sr standard, and 0.512135 ± 0.000010 (2σ , $n = 4$) for the Ames nNd-1 standard, respectively. This value for nNd-1 corresponds to a value of the La Jolla Nd standard of 0.511838. $\epsilon\text{Nd}(0)$ values (deviation from bulk silicate earth value in parts in 10 000) were calculated relative to $^{143}\text{Nd}/^{144}\text{Nd} = 0.512616$.

RESULTS

Clays

Clay mineral analysis was performed on 30 samples from river clays in the Murray–Darling Basin (Table 1). The clay mineral composition of 26 selected samples are shown on Figure 1. Four datasets were omitted as they are from neighbouring anabranches and are nearly identical to the ones depicted. The spectra clearly show that clay mineral assemblages can be used to distinguish between the Murray and Darling catchments and even to fingerprint individual subcatchments in the Murray–Darling Basin (Figure 2). Smectite, illite and kaolinite are the three main minerals present, while chlorite only occurs in minor percentages, except in the uppermost Murray River (Gingele & De Deckker 2004). In general, smectite is more characteristic for the

Table 1 Coordinates, rivers, sample code, clay mineral percentages of the main clays smectite (S), illite (I) and kaolinite (K), Sr- and Nd-isotope ratios and $\epsilon\text{Nd}(0)$ of the sample set used for this investigation.

| Latitude | Longitude | River | Code | S% | I% | K% | $^{87}\text{Sr}/^{86}\text{Sr}$ | $^{143}\text{Nd}/^{144}\text{Nd}$ | $\epsilon\text{Nd}(0)$ | D/M ^a |
|-------------|--------------|--------------|-------|----|----|----|---------------------------------|-----------------------------------|------------------------|------------------|
| 30°26.047'S | 147°34.163'E | Macquarie | MDB1 | 16 | 46 | 35 | 0.71661 | 0.512325 | -5.7 | M |
| 30°14.777'S | 147°52.917'E | Castlereagh | MDB2 | 31 | 27 | 38 | 0.71040 | 0.512504 | -2.2 | D |
| 30°00.995'S | 148°07.231'E | Namoi | MDB3 | 49 | 16 | 31 | 0.71108 | 0.512550 | -1.3 | D |
| 29°58.552'S | 148°08.847'E | Barwon | MDB4 | 25 | 14 | 52 | nd | nd | nd | D |
| 29°50.056'S | 146°49.593'E | Bokhara | MDB5 | 27 | 25 | 46 | nd | nd | nd | D |
| 29°43.149'S | 146°40.632'E | Birrie | MDB6 | 25 | 22 | 49 | 0.70924 | 0.512454 | -3.2 | D |
| 29°41.486'S | 146°38.744'E | Culgoa | MDB7 | 26 | 23 | 50 | nd | nd | nd | D |
| 29°56.878'S | 146°51.812'E | Barwon | MDB8 | 37 | 26 | 33 | 0.71184 | 0.512663 | 0.9 | D |
| 30°00.494'S | 146°21.268'E | Bogan | MDB9 | 19 | 38 | 39 | 0.71601 | 0.512296 | -6.2 | M |
| 30°03.409'S | 145°57.064'E | Darling | MDB10 | 20 | 27 | 44 | 0.71161 | 0.512541 | -1.5 | D |
| 30°19.092'S | 145°21.571'E | Warrego | MDB11 | 22 | 26 | 51 | 0.70998 | 0.512350 | -5.2 | D |
| 31°33.607'S | 143°22.700'E | Darling | MDB12 | 38 | 23 | 35 | 0.71170 | 0.512553 | -1.2 | D |
| 32°27.778'S | 142°23.554'E | Darling | MDB13 | 36 | 26 | 34 | nd | nd | nd | D |
| 34°10.943'S | 142°10.338'E | Murray | MDB14 | 15 | 52 | 28 | 0.73697 | 0.512087 | -10.3 | M |
| 34°06.485'S | 141°55.248'E | Darling | MDB15 | 39 | 27 | 31 | 0.71315 | 0.512429 | -3.6 | D |
| 34°34.044'S | 139°35.673'E | Murray | MDB18 | 24 | 41 | 32 | 0.72456 | 0.512243 | -7.3 | M |
| 34°38.791'S | 143°33.944'E | Murrumbidgee | MDB19 | 24 | 38 | 35 | 0.73167 | 0.512159 | -8.9 | M |
| 35°44.101'S | 143°54.623'E | Loddon | MDB20 | 6 | 38 | 48 | 0.73858 | 0.512125 | -9.6 | M |
| 36°07.228'S | 144°44.660'E | Campaspe | MDB21 | 16 | 50 | 30 | 0.74618 | 0.512119 | -9.7 | M |
| 36°10.574'S | 145°07.113'E | Goulburn | MDB22 | 12 | 40 | 43 | 0.75470 | 0.512145 | -9.2 | M |
| 35°51.223'S | 144°59.943'E | Murray | MDB23 | 15 | 34 | 45 | 0.75449 | 0.512119 | -9.7 | M |
| 36°03.999'S | 146°12.130'E | Ovens | MDB24 | 7 | 52 | 34 | 0.77512 | 0.512118 | -9.7 | M |
| 25°47.607'S | 146°35.153'E | Warrego | MDB25 | 38 | 5 | 52 | 0.71144 | 0.512627 | 0.2 | D |
| 26°29.121'S | 147°58.840'E | Maranoa | MDB26 | 34 | 10 | 52 | 0.71157 | 0.512544 | -1.4 | D |
| 26°55.596'S | 150°07.907'E | Condamine | MDB27 | 69 | 3 | 23 | 0.70797 | 0.512566 | -1.0 | D |
| 28°33.025'S | 150°18.667'E | Macintyre | MDB28 | 67 | 6 | 21 | 0.71413 | 0.512689 | 1.4 | D |
| 32°32.55'0S | 148°56.535'E | Macquarie | MDB29 | 10 | 57 | 23 | 0.72646 | 0.512215 | -7.8 | M |
| 33°50.045'S | 148°41.014'E | Lachlan | MDB30 | 8 | 51 | 31 | 0.74174 | 0.512155 | -9.0 | M |
| 35°04.158'S | 148°05.466'E | Murrumbidgee | MDB31 | 21 | 29 | 40 | 0.74871 | 0.512133 | -9.4 | M |
| 36°02.772'S | 147°55.835'E | Murray | MDB32 | 2 | 40 | 32 | 0.74848 | 0.512081 | -10.4 | M |

^aD and M indicate if a sample belongs to a tributary of either the Darling or the Murray.
nd, not determined.

Darling tributaries, while illite marks the Murray tributaries (Figure 2). Individual source areas like the young mafic volcanics and associated soils of the New England Fold Belt imprint their smectite-rich signature onto the clay suites of the Condamine, Macintyre and Namoi Rivers. The Lachlan Fold Belt and the plutonic rocks and metasediments of the Southern Highlands are the source of the illite-rich signature of the Murray tributaries. The Murrumbidgee River stands out from this group due to higher smectite contents. The source of these smectites are probably weathering products of Palaeozoic volcanics, which are widespread in the Murrumbidgee catchment. The Macquarie River, which originates in the Lachlan Fold Belt, carries an illite-rich clay signature, similar to the Murray tributaries, but contributes to the Darling catchment and sediment supply. The distribution of clay minerals in the tributaries of the Murray–Darling Basin confirms the general concept (Chamley 1989) that smectite-rich soils form from volcanic parent rocks, while plutonic rocks weather preferentially weather to kaolinite and illite (mica).

Naturally, the clay mineral signature is modified along the course of an individual river by mixing with material of minor tributaries, which drain and erode different source rocks. Examples are the

Warrego and Macquarie Rivers, which we sampled near their headwaters and near their confluence with the Darling River (Figure 1). As, under present flow regimes, no substantial erosion seems to occur once the rivers reach the alluvial plain (e.g. the Darling: Woodyer 1978), we assume that the clay mineral signature is acquired in the upper catchment. The smectite content of the Darling River also increases markedly below Wilcannia, possibly due to a contribution of the Paroo River, which was not sampled in our investigation.

Kaolinite is high in the Warrego and Maranoa Rivers, which originate in the Mesozoic sandstone plateaus of south-central Queensland. In the rest of the Murray–Darling Basin, kaolinite is not suitable to distinguish between the Murray and Darling catchments. However, smectite versus illite contents (Figure 2) clearly separates the tributaries of the Murray and Darling catchment, indicating the different geological provinces these rivers drain. Again, the Bogan River, although draining into the Darling system like the Macquarie River, originates in the Lachlan Fold Belt and carry a clay signature similar to the Murray tributaries.

Input of aeolian dust could contribute to river sediments, in particular in the drier western part of

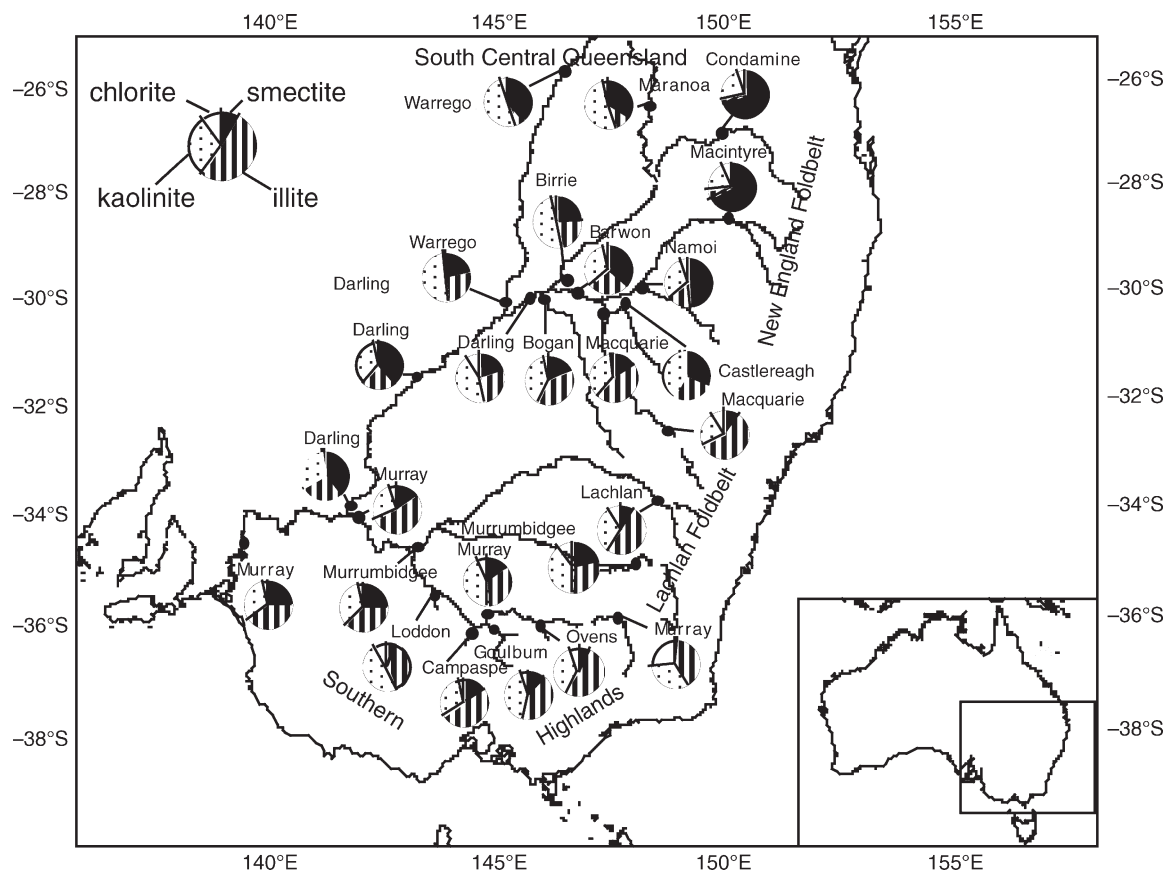


Figure 1 Location of investigation area and clay mineral compositions of sediments in the major tributaries of the Murray–Darling Basin. Clay compositions reflect the combination of source rocks and soils in the respective catchments. Major provinces are south-central Queensland (SCQL), the New England Fold Belt (NEFB), and the Lachlan Fold Belt (LFB) and Southern Highlands (SH). These terms are not used in a strict genetic geological context here, but rather as a geographical description of an assemblage of rocks. Smectite, derived from weathering of young volcanic rocks, clearly dominates the NEFB, while illite originates from the LFB and SH. Incidentally, most Darling tributaries drain the NEFB or SCQL (with the exception of the Macquarie River, LFB) and the Murray tributaries drain the LFB and SH.

the basin where dust storms are frequent. We assume that the direct fallout into the rivers is minor and does not significantly affect the clay mineral signature of the sediments, because the rivers are linear features and comprise only a small area compared to the large catchment areas. However, dust will also settle in the catchments, become entrained in the soil and form a part of their clay signature. Nevertheless, as the dramatic differences in clay composition show, different parent rocks and their soils clearly dominate the clay signature, thus leading to the conclusion that aeolian dust is a minor contributor today.

Trace elements

Major and trace elements were determined on the same 26 samples from the Murray–Darling Basin shown on Figure 1. In total, 11 major elements and 35 trace elements were analysed. The regional distribution of the concentration of each element in the Murray–Darling Basin was studied and assessed for fingerprinting suitability. Potassium and the trace elements Zr, Hf, Sn, Ti, Rb, Sn and Ba show significant differences in

concentration between the Murray and Darling tributaries (Table 2). Figure 3 shows plots of these catchment-sensitive elements: Cs vs Rb, Hf vs Sn, Zr vs Ti, and K vs Ba. Provenance of the river muds from the different geological units—Lachlan Fold Belt and Southern Highlands for the Murray tributaries, and New England Fold Belt and south-central Queensland for the Darling tributaries—are clearly discernible. Overlaps occur, in particular in the case of the Macquarie River (MR, arrow), which is a tributary of the Darling River, but originates in the Lachlan Fold Belt, close to the headwaters of the Lachlan River. The Macquarie River confirms that the geochemical signature is mainly acquired in the upper catchment and not on the long course on the alluvial plain.

In comparison, analyses of material from the October 2002 Canberra dust storm show more similarities to material from the Darling than from the Murray catchment (Figure 3). Some of the dust may have originated in northern New South Wales, in the Darling catchment, possibly also containing an external, central Australian component (F. Gingele & P. De Deckker unpubl. data).

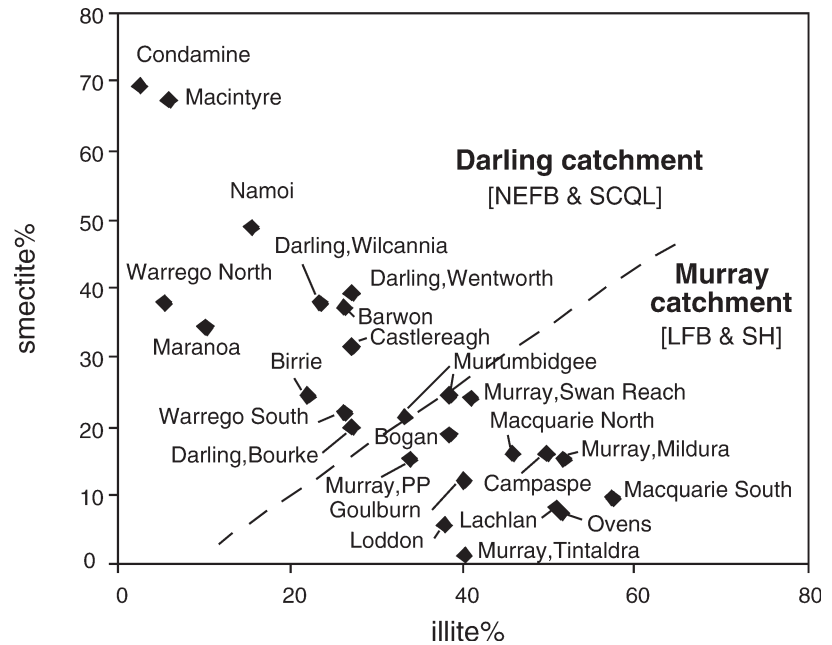


Figure 2 Clay mineral percentages represented by smectite *vs* illite clearly depict major provenances of river clays in the Murray–Darling fluvial system. Murray PP, Murray River at Picnic Point; SCQL, south-central Queensland; NEFB, New England Fold Belt; LFB, Lachlan Fold Belt; SH, Southern Highlands.

Table 2 Concentrations of eight elements which differ significantly between tributaries of the Murray and the Darling fluvial system, due to geologically characteristic catchment areas.

| Sample | Ti (ppm) | Zr (ppm) | Rb (ppm) | Cs (ppm) | Ba (ppm) | K ₂ O % | Hf (ppm) | Sn (ppm) | Rb/Sr | D/M ^a |
|--------|----------|----------|----------|----------|----------|--------------------|----------|----------|-------|------------------|
| MDB1 | 4899 | 115 | 91 | 5.7 | 216 | 2.2 | 3.4 | 3.3 | 1.615 | M |
| MDB2 | 6531 | 194 | 73 | 4.2 | 196 | 1.66 | 5.1 | 3.5 | 1.077 | D |
| MDB3 | 5843 | 130 | 68 | 5.1 | 165 | 1.49 | 3.6 | 3.2 | 1.2 | D |
| MDB6 | 5836 | 134 | 60 | 3.9 | 200 | 1.45 | 3.9 | 2.9 | 0.745 | D |
| MDB8 | 6387 | 146 | 83 | 5.7 | 181 | 1.63 | 4 | 4.3 | 1.28 | D |
| MDB9 | 6445 | 146 | 115 | 7.6 | 245 | 1.99 | 4 | 4.1 | 1.638 | M |
| MDB10 | 6489 | 151 | 83 | 5.7 | 163 | 1.44 | 4.2 | 3.9 | 1.297 | D |
| MDB11 | 5719 | 136 | 69 | 4.7 | 210 | 1.63 | 4.4 | 3.2 | 0.743 | D |
| MDB12 | 5765 | 141 | 75 | 5.4 | 186 | 1.58 | 4 | 3.7 | 1.094 | D |
| MDB14 | 4147 | 81 | 160 | 9.8 | 340 | 2.91 | 2.3 | 5.3 | 3.114 | M |
| MDB15 | 5195 | 129 | 74 | 5.3 | 205 | 1.73 | 3.7 | 3.6 | 1.016 | D |
| MDB18 | 4921 | 115 | 118 | 7.5 | 273 | 2.22 | 3.1 | 4.4 | 2.001 | M |
| MDB19 | 4754 | 103 | 142 | 8.4 | 260 | 2.27 | 3 | 5.9 | 2.991 | M |
| MDB20 | 4997 | 112 | 158 | 10.3 | 394 | 2.68 | 3.3 | 5.1 | 3.299 | M |
| MDB21 | 4151 | 88 | 150 | 9 | 394 | 2.77 | 2.7 | 11.4 | 3.734 | M |
| MDB22 | 4807 | 107 | 195 | 15.2 | 430 | 2.57 | 2.9 | 6.4 | 5.402 | M |
| MDB23 | 4277 | 88 | 205 | 15.6 | 335 | 2.4 | 2.8 | 7.6 | 5.861 | M |
| MDB24 | 4229 | 92 | 251 | 17.5 | 533 | 3.22 | 2.5 | 7 | 7.239 | M |
| MDB25 | 5416 | 157 | 55 | 4.3 | 242 | 1.02 | 4.3 | 2.9 | 0.875 | D |
| MDB26 | 4680 | 130 | 62 | 4.6 | 249 | 1.24 | 3.7 | 2.7 | 1.017 | D |
| MDB27 | 7957 | 180 | 34 | 2.5 | 168 | 0.58 | 4.6 | 2.5 | 0.674 | D |
| MDB28 | 6443 | 138 | 60 | 5.8 | 172 | 0.95 | 3.8 | 3.8 | 1.678 | D |
| MDB29 | 4548 | 117 | 128 | 8.3 | 494 | 2.68 | 3 | 5.9 | 2.111 | M |
| MDB30 | 5770 | 108 | 179 | 9 | 417 | 2.988 | 3.3 | 7.7 | 3.753 | M |
| MDB31 | 7422 | 93 | 159 | 8.2 | 295 | 2.41 | 3.3 | 6.6 | 5.164 | M |
| MDB32 | 6876 | 76 | 195 | 15.9 | 349 | 2.31 | 2.2 | 7.4 | 5.406 | M |

^aD and M indicate if a sample belongs to a tributary of either the Darling or the Murray.

The relatively radiogenic nature of the clays in the Murray tributaries compared to Darling tributaries is evident from high (2–7) Rb/Sr ratios.

Strontium and neodymium isotopes

The clay fraction (<2 μm) from the same 26 samples of river mud from the Murray–Darling Basin were

analysed for ⁸⁷Sr/⁸⁶Sr ratios and ¹⁴³Nd/¹⁴⁴Nd ratios (Table 1). In a diagram of ⁸⁷Sr/⁸⁶Sr ratios *vs* εNd(0), it becomes evident that the rivers of the Darling and

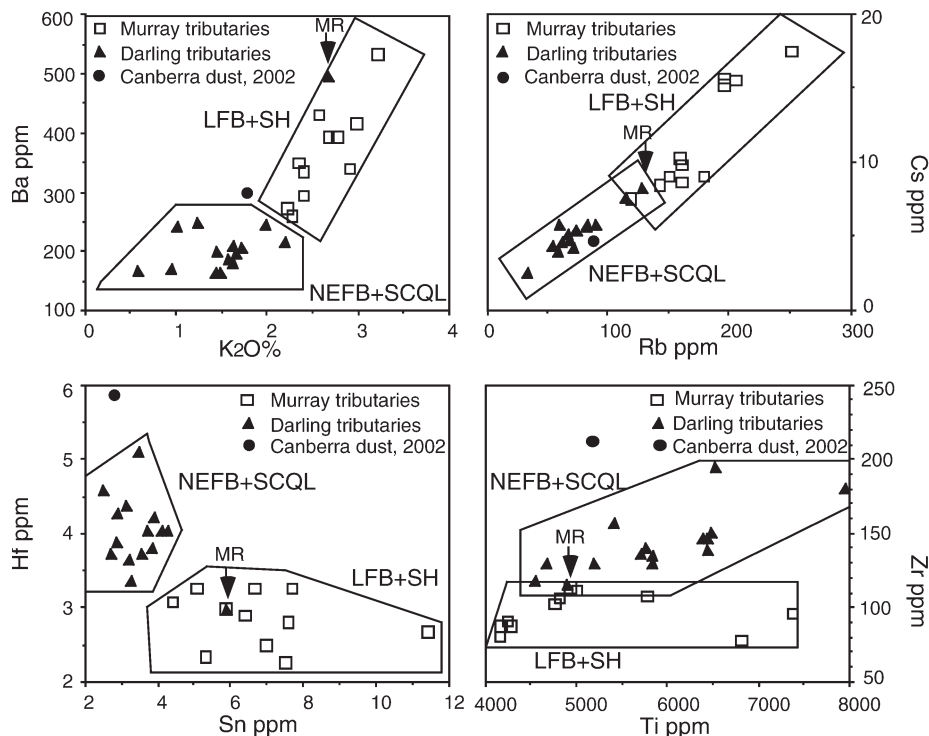


Figure 3 Trace metals K, Cs, Hf, Sn, Rb, Ti and Zr demonstrate that river sediments derived from the New England Fold Belt (NEFB) and south-central Queensland (SCQL) are clearly different from river sediments from the Lachlan Fold Belt (LFB) and Southern Highlands (SH). Again, with the exception of the Macquarie River (MR, arrow), provenances coincide with Murray and Darling tributaries. Also depicted is the composition of aeolian dust from the Canberra dust storm of October 2002, which suggests that some of the dust may have originated in northern New South Wales, in the Darling catchment, mixed with an external component, possibly from central Australia.

Murray catchments plot into two different fields (Figure 4). The Darling tributaries, originating mainly in the New England Fold Belt and south-central Queensland are closely centred around 0.71 for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, but spread over a wide range of $\epsilon\text{Nd}(0)$, from +1.4 to -6.3 (Figure 4). The Murray tributaries show the opposite trend with relatively constant $\epsilon\text{Nd}(0)$ around -9 and a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from 0.725 to 0.775. The sample from the lower Murray at Swan Reach plots exactly between the fields of the Darling and Murray tributaries, thus representing a true mixture of material from both catchment areas. Generally, old Rb-rich silicate rocks, such as Palaeozoic and Precambrian granites, have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than young, Rb-poor silicate rocks, such as Tertiary basalts (Naiman *et al.* 2000). This is because ^{87}Sr is produced by radiogenic decay of ^{87}Rb , which has a half-life of 48.8 billion years (Stewart *et al.* 2001). Thus, it can be expected that the younger rocks of the New England Fold Belt show lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the older rocks of the Lachlan Fold Belt and Southern Highlands. Typical source rocks in the New England Fold Belt are Tertiary basalts with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.703–0.705 and Permian granites with 0.7127 (Hensel *et al.* 1985). Palaeozoic sedimentary rocks have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of around 0.7109 (Graham & Korsch 1985).

The formation of soil from parent rock can shift the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, as shown in a study in the upper Namoi River catchment (Martin & McCulloch 1999). However, the maximum shift was near 0.004 from basalts to

basaltic soils and from the upper catchment to the lower Namoi River. This is one order of magnitude lower than the observed large variation in $^{87}\text{Sr}/^{86}\text{Sr}$ for the River Murray tributaries (0.04). The shift in the upper Namoi River catchment usually is towards higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, which was interpreted as a 10% contribution of aeolian dust from older central Australian sources to soil formation (Martin & McCulloch 1999) rather than a fractionation effect of *in situ* weathering and pedogenesis.

The wider range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios found in the sediments of the Murray tributaries may therefore be explained by a wider range of rock types of different ages in the geological formations these tributaries drain, as in general high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are inherited by clays from their parent minerals (Faure 1986).

Neodymium isotope ratios vary strongly within the New England Fold Belt from positive $\epsilon\text{Nd}(0)$ values in Tertiary basalts to negative values of -5 in New England granitoids and metapelitic rocks (Hensel *et al.* 1985). Incorporation of an exotic aeolian component from central Australia into the soils of the New England Fold Belt can lower $^{143}\text{Nd}/^{144}\text{Nd}$ ratios considerably (Martin & McCulloch 1999), thus explaining the large variation in $\epsilon\text{Nd}(0)$ in sediments of the Darling River tributaries.

Average $\epsilon\text{Nd}(0)$ from typical Palaeozoic components of the Lachlan Fold Belt such as S- and I-type granites and Ordovician metasediments vary narrowly from -9.5 to -11 (McCulloch & Chappell 1982; Chappell & White 1992; Keay *et al.* 1997) and correspond well to

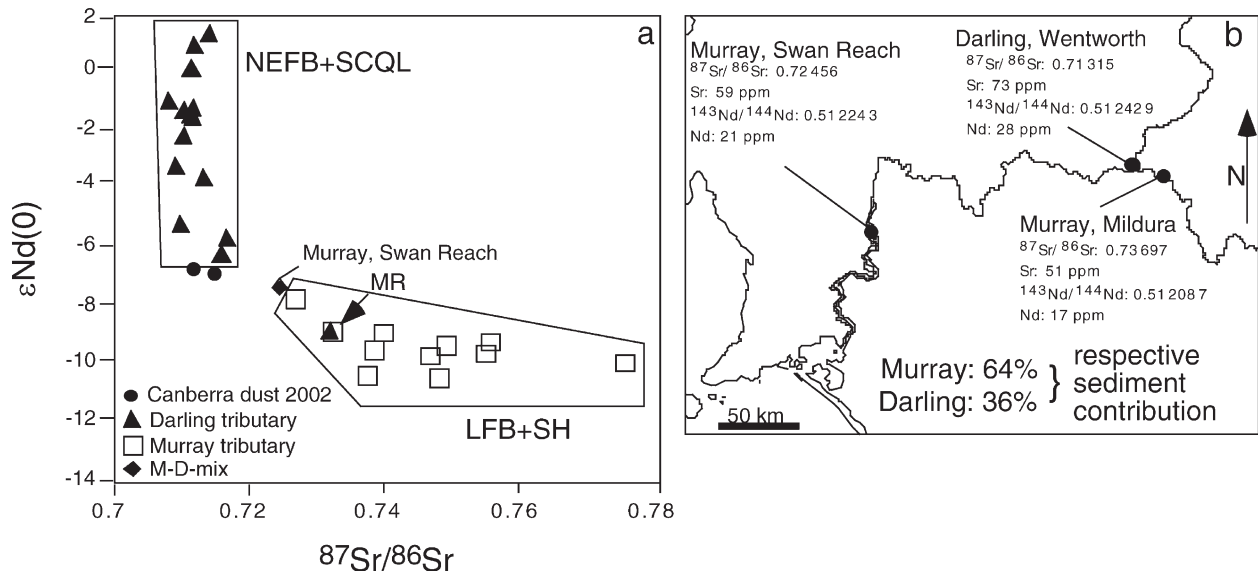


Figure 4 (a) Isotopic ratios $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ [expressed as $\epsilon\text{Nd}(0)$] vary widely in river sediments from the tributaries in the Murray–Darling fluvial system. The provinces already outlined by clay compositions and trace metals clearly show in the isotopic ratios. As expected, the Macquarie River (MR, arrow) plots within the Lachlan Fold Belt (LFB) province. The sample from the Murray at Swan Reach represents a mixture of sediments from the Darling and the Murray catchments. Isotopic composition of two samples from the Canberra 2002 dust storm (Delmonte *et al.* 2004) is very close to the samples from the Darling catchment. SCQL, south-central Queensland; NEFB, New England Fold Belt; SH, Southern Highlands. (b) Samples from the Darling River at Wentworth and from the Murray River at Mildura were used to calculate relative percentage contributions to the mixed sample at Swan Reach. Two independent tracers, Sr-isotope ratios and concentrations and Nd-isotope ratios and concentrations, respectively, were used in a simple binary mixing equation. Although the location of the mixed sample is quite far downstream and not ideal, both approaches produced identical results of 36% for the Darling River and 64% for the Murray River contribution to the mixed sediment at Swan Reach.

$\epsilon\text{Nd}(0)$ values in sediments of Murray tributaries, which drain the Lachlan Fold Belt and Southern Highlands. However, the corresponding $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of these geological formations are only around 0.71, compared to a range of 0.725–0.775 in sediments of the Murray tributaries, implying that there must be a considerable contribution from other, older rock formations. Unfortunately, there are no significant Precambrian source rocks in the Lachlan Fold Belt and Southern Highlands and it seems unlikely that these areas receive more aeolian contribution from older rocks in central Australia than the New England Fold Belt. Dust samples from central and western Australia, analysed by Grousset *et al.* (1992), rarely exceed 0.74 in their $^{87}\text{Sr}/^{86}\text{Sr}$ ratio. However, some Ordovician components of the Lachlan Fold Belt reach $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.755–0.766 (Turner *et al.* 1993). A detailed investigation of subcatchments would be necessary to investigate from which rock formations the Murray tributaries exactly acquire their high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios.

The unradiogenic nature of the river clays in the Darling tributaries originating in south-central Queensland and the New England Fold Belt is also reflected in low Rb/Sr ratios (0.7–1.7), whereas the clays from the Murray tributaries are relatively radiogenic (Rb/Sr ratios 2–7: Table 2).

DISCUSSION

Most tributaries of the Murray–Darling fluvial system originate in the Great Dividing Range and have a

similar profile, with a steep gradient for a short distance in the headwaters and a low gradient for most of the rest of the river course. Consequently, the coarser material, which is eroded in the upper reaches, is quickly dumped as soon as the flat Western Plains are reached (Riley & Taylor 1978). From there on, tributaries of the Murray and the Darling fluvial system flow through Cenozoic alluvial deposits and carry mainly fine silt and clay in suspension. We chose to use the clay fraction ($<2\ \mu\text{m}$) for fingerprinting individual tributaries because we believe that any mineralogical, geochemical and isotopic signature in the clays is inherited from the geologically diverse rock formations in the headwaters and that the clays can then be transported throughout the fluvial system. Douglas *et al.* (1999) have inferred from five samples in the Murray–Darling Basin that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the solid suspended matter reflects mainly precursor mineralogy. As the isotopic signature ($^{87}\text{Sr}/^{86}\text{Sr}$) also varies with particle size (Douglas *et al.* 1995), comparisons between rivers have to be carried out on the same size fraction.

In general, our results show that the mineralogical, geochemical and isotopic signatures of the clay fraction from all analysed tributaries in the Murray–Darling fluvial system significantly reflect the composition and age of the source rocks in the headwaters of the respective tributary.

However, some tributaries like the Macquarie, Murrumbidgee and Warrego Rivers, which were sampled in the headwaters as well as in the lower reaches, show that the mineralogical, geochemical and isotopic signature of the clay fraction can shift

significantly downriver. This could be caused by contribution from smaller tributaries or, in particular in the drier western part of the basin, by influx of aeolian material into the catchment.

The analysis of conservative mineralogical, geochemical and isotopic tracers in river clays allows the assessment of the sediment contribution of two joining tributaries (Parra *et al.* 1999). Ideally, samples should be taken from the tributaries just before their confluence and at a reasonable distance after the confluence, to allow proper mixing. Mixing equations can then be applied using isotope ratio and element concentration. In our sample set only the main Darling–Murray confluence near Mildura/Wentworth is covered adequately, although the sample after the confluence comes from Swan Reach, a considerable distance downstream (Figure 4b). Nevertheless, we calculated contributions of the Darling and the

Murray system based on Sr- and Nd-isotope ratios and concentrations (Table 2) using a binary mixing equation:

$$IR_{\text{mix}} \times C_{\text{mix}} = \alpha[IR_1 \times C_1 + (1 - \alpha) \times IR_2 \times C_2]$$

where IR is the isotope ratio, C the concentration of isotopic element, and α the share of component 1 and 2.

Using $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and Nd concentrations, we calculate the same ratio of 36% to 64% Darling versus Murray sediment contribution for the main junction at Mildura/Wentworth (Table 3). For both isotopic ratios and concentrations, the mixed sample is directly on the mixing line of the components (Figure 5a, b), showing that there can be no significant contribution of a third component downriver of the Darling–Murray junction. Confidence could be further improved by using a mixed

Table 3 The contribution of fine-grained sediment of the Darling and Murray Rivers at Wentworth (WW) and Mildura (Mild.) to a common mix in the Murray at Swan Reach (mix SR).

| River | $^{87}\text{Sr}/^{86}\text{Sr}$ | Sr (ppm) | $^{143}\text{Nd}/^{144}\text{Nd}$ | Nd (ppm) | % Sr-based | % Nd-based |
|-----------------|---------------------------------|----------|-----------------------------------|----------|------------|------------|
| Darling (WW) | 0.71315 | 73 | 0.512429 | 28 | 36 | 36 |
| Murray (Mild.) | 0.73697 | 51 | 0.512087 | 17 | 64 | 64 |
| Murray (mix SR) | 0.72456 | 59 | 0.512243 | 21 | 100 | 100 |

The relative contributions are calculated using a binary mixing equation. The results are nearly identical based on Sr-isotope ratios and concentrations, as well as Nd-isotope ratios and concentrations.

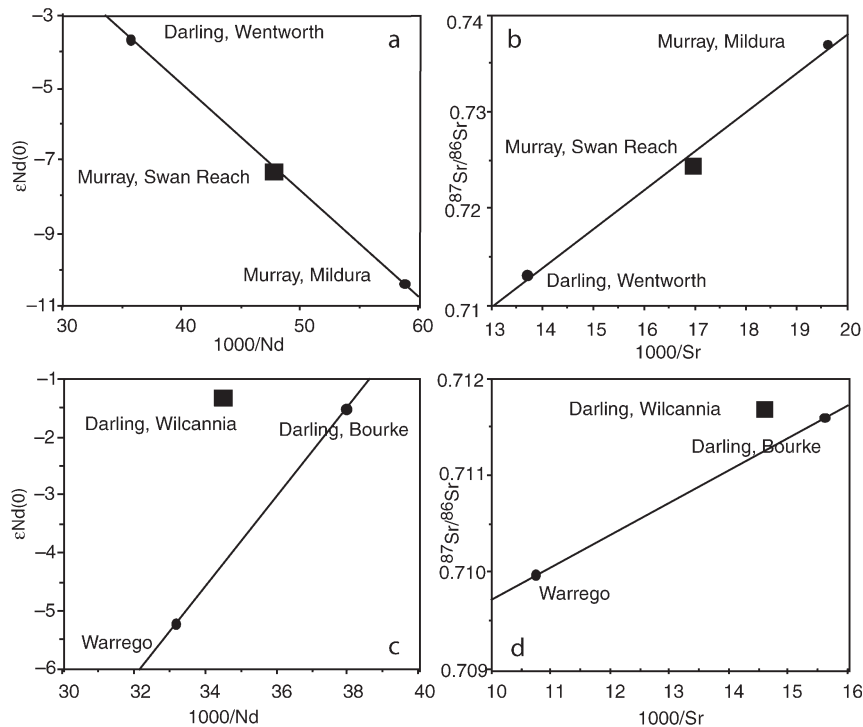


Figure 5 Neodymium and strontium mixing diagrams for two river junctions in the Murray Darling fluvial system. (a, b) The sample from the lower Murray at Swan Reach plots exactly on the mixing line between the samples from the Darling at Wentworth and the Murray at Mildura ($R^2 = 0.999$ and 0.997) showing that there are no significant sediment contributions to the Murray below the major Darling–Murray confluence. (c, d) In contrast, the confluence of the Warrego and Darling Rivers is not well represented by the sample downstream of the confluence at Wilcannia, implying an additional sediment source.

sample closer to the main junction. Also, given a more detailed sample grid, the same approach could be applied to all major junctions in the river system and a comprehensive budget of fine-grained sediment progeny and transport in the Murray–Darling fluvial system could be calculated.

Clay minerals can be used to check for plausibility of mixing calculations. Naturally, the concentration for each mineral after mixing should be between the concentrations of the mixing components. For example, an attempt to budget the contribution of the Warrego River (MDB11: see Table 1 for sample codes) to the Darling, using samples for the Darling at Bourke (MDB10) and Wilcannia (MDB12) (Figure 5c, d) fails as the clay mineral composition at Wilcannia can never be achieved by mixing the concentration MDB11 and MDB10. Smectite concentrations, for example, are much higher in the Darling at Wilcannia than in the contributing rivers, inferring an additional smectite-rich source. That is likely to be the Paroo River, which enters the Darling just before Wilcannia, but only flows episodically. Using Sr and Nd isotopic ratios and concentrations, it is obvious that the mixed sample MDB12 does not plot on the mixing line between samples MDB10 and MDB11 (Figure 5). A contribution from a third component can be inferred.

Although ferric oxides/hydroxides like hematite and goethite are certainly present in the clay fraction in small amounts, we believe that they do not significantly influence isotope compositions, because iron contents are not catchment-sensitive in contrast to Sr and Nd isotopes. Even if the ferric oxides/hydroxides were to influence isotope compositions, this would not affect the main assumptions of our study. We tried to fingerprint catchment areas, with chemical, mineralogical and isotopic compositions of the clay fraction of river-borne material, which is basically eroded regolith. These compositions are the result of weathering of local rocks (probably the main process), soil formation and the addition of exotic components (e.g. dust). These processes combine to form a unique fingerprint for each catchment and it is only of secondary interest how much each of the processes contribute to the signal. Local studies (Martin & McCulloch 1999) have tried to evaluate how isotope ratios change from source rock to river sediment and how much aeolian dust contributes to soil formation and isotope composition. To answer these questions for our regional study area is beyond the scope of the present work and would require many more data from possible source material (parent rock, dust).

CONCLUSIONS

Geological provinces near the watersheds of the Murray–Darling Basin imprint their characteristic clay mineral and isotopic signature onto the clay fraction (<2 µm) of sediments transported in the Murray–Darling fluvial system. Smectite is characteristic for the tributaries originating in the New England Fold Belt and most of the Darling tributaries, while illite dominates most Murray tributaries, which originate in the

Lachlan Fold Belt and Southern Highlands. Associated with the clays are conservative elements like K, Zr, Ti, Hf, Sn, Cs and Rb. Their concentrations can be also used to distinguish between Murray and Darling catchments.

Radiogenic isotope ratios $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ are also catchment-sensitive and can be used to potentially fingerprint individual tributaries in the Murray–Darling fluvial system. The sediment contribution from two joining tributaries can be estimated from isotope ratios and element concentrations. Using the two independent elements strontium and neodymium, a sediment budget has been estimated for the main Darling–Murray confluence at Mildura/Wentworth. An identical figure of 36/64 Darling versus Murray contribution was calculated from both elements.

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REFERENCES

- BISCAYE P. E. 1965. Mineralogy and sedimentation of recent deep-sea clay in the Atlantic Ocean and adjacent seas and oceans. *Geological Society of America Bulletin* **76**, 803–832.
- BUTLER B. E. & HUBBLE G. D. 1978. The general distribution and character of soils in the Murray–Darling River system. *Proceedings of the Royal Society of Victoria* **90**, 149–156.
- CHAMLEY H. 1989. *Clay Sedimentology*. Springer, Berlin.
- CHAPPELL B. W. & WHITE A. J. R. 1992. I- and S-type granites in the Lachlan Fold Belt. *Transactions of the Royal Society of Edinburgh: Earth Sciences* **83**, 1–26.
- CLOSE A. 1990. The impact of man on the natural flow regime. In: Mackay N. & Eastburn D. eds. *The Murray*, pp. 61–74. Murray–Darling Basin Commission, Canberra.
- CROCK J. G., LICHTER F. E. & WILDEMAN T. R. 1984. The group separation of the rare-earth elements and yttrium from geologic materials by cation-exchange chromatography. *Chemical Geology* **45**, 149–163.
- DELMONTE B., BASILE-DOELSCH I., PETIT J.-R., MAGGI V., REVEL-ROLLAND M., MICHARD A., JAGOUTZ E. & GROUSSET F. 2004. Comparing the Epica and Vostok dust records during the last 220,000 years: stratigraphical correlation and provenance in glacial periods. *Earth-Science Reviews* **66**, 63–87.
- DOUGLAS G. B., GRAY C. M., HART B. T. & BECKETT R. 1995. A strontium isotopic investigation of the origin of suspended matter (SPM) in the Murray–Darling River system. *Geochimica et Cosmochimica Acta* **59**, 3799–3815.
- DOUGLAS G. B., HART B. T., BECKETT R. & GRAY C. M. 1999. Geochemistry of suspended particulate matter (SPM) in the Murray–Darling River system: a conceptual isotopic and geochemical model for the fractionation of major, trace and rare earth elements. *Aquatic Geochemistry* **5**, 167–194.
- FAURE G. 1986. *Principles of Isotope Geology*. Wiley, New York.

- GINGELE F. X. & DE DECKKER P. 2004. Fingerprinting Australia's rivers with clay minerals and the application for the marine record of climate change. *Australian Journal of Earth Sciences* **51**, 339–348.
- GRAHAM I. J. & KORSCH R. J. 1985. Rb–Sr geochronology of coarse-grained greywackes and argillites from the Coffs Harbour Block, eastern Australia. *Chemical Geology* **58**, 45–54.
- GROUSSET F. E., BISCAYE P. E., REVEL M., PETIT J.-R., PYE K., JOUSSAUME S. & JOUZEL J. 1992. Antarctic (Dome C) ice-core dust at 18 k.y. B.P.: isotopic constraints on origins. *Earth and Planetary Science Letters* **111**, 175–182.
- HENSEL H.-D., MCCULLOCH M. T. & CHAPPELL B. W. 1985. The New England Batholith: constraints on its derivation from Nd and Sr isotopic studies of granitoids and country rocks. *Geochimica et Cosmochimica Acta* **49**, 369–384.
- KEAY S., COLLINS W. J. & MCCULLOCH M. T. 1997. A three-component Sr–Nd isotopic mixing model for granitoid genesis, Lachlan fold belt, eastern Australia. *Geology* **25**, 307–310.
- MARTIN C. E. & MCCULLOCH M. T. 1999. Nd–Sr isotopic and trace element geochemistry of river sediments and soils in a fertilized catchment, New South Wales, Australia. *Geochimica et Cosmochimica Acta* **63**, 287–305.
- MCCULLOCH M. T. & CHAPPELL B. W. 1982. Nd isotopic characteristics of S- and I-type granites. *Earth and Planetary Science Letters* **58**, 51–64.
- MITTFELDELT D. W. & WETHERILL G. W. 1979. Rb–r studies of CI and CM chondrites. *Geochimica et Cosmochimica Acta* **43**, 201–206.
- NAIMAN Z., QUADE J. & PATCHETT P. J. 2000. Isotopic evidence for aeolian recycling of pedogenic carbonate and variations in carbonate dust sources throughout the southwest United States. *Geochimica et Cosmochimica Acta* **64**, 3099–3109.
- PARRA M., CASTAING P., JOUANNEAU J.-M., GROUSSET F. & LATOUCHE C. 1999. Nd–Sr isotopic composition of present-day sediments from the Gironde estuary, its draining basins and the West Gironde mud patch (SW France). *Continental Shelf Research* **19**, 135–150.
- PETSCHICK R., KUHN G. & GINGELE F. 1996. Clay mineral distribution in surface sediments of the South Atlantic: sources, transport and relation to oceanography. *Marine Geology* **130**, 203–229.
- REHKAMPER M., GARTNER M., GALER S. J. G. & GOLDSTEIN S. L. 1996. Separation of Ce from other rare-earth elements with application to Sm–Nd and La–Ce chronometry. *Chemical Geology* **129**, 201–208.
- RICHARD P., SCHMIZU N. & ALLEGRE C. J. 1976. $^{143}\text{Nd}/^{144}\text{Nd}$, a natural tracer: an application to oceanic basalts. *Earth and Planetary Science Letters* **31**, 269–278.
- RILEY S. J. & TAYLOR G. 1978. Geomorphology of the upper Darling River system. *Proceedings of the Royal Society of Victoria* **90**, 89–102.
- RUTLAND R. W. R. 1976. Orogenic evolution of Australia. *Earth-Science Reviews* **12**, 161–196.
- STEWART B. W., CAPO R. C. & CHADWICK O. A. 2001. Effects of rainfall on weathering rate, base cation provenance, and Sr isotope composition of Hawaiian soils. *Geochimica et Cosmochimica Acta* **65**, 1087–1099.
- TURNER S., FODEN J., SANDIFORD M. & BRUCE D. 1993. Sm–Nd isotopic evidence for the provenance of sediments from the Adelaide Fold Belt and southeastern Australia with implications for episodic crustal addition. *Geochimica et Cosmochimica Acta* **57**, 1837–1856.
- WASSERBURG G. J., JACOBSEN S. B., DEPAOLO D. J., MCCULLOCH M. T. & WEN T. 1981. Precise determination of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions. *Geochimica et Cosmochimica Acta* **45**, 2311–2323.
- WOODYER K. D. 1978. Sediment regime of the Darling River. *Proceedings of the Royal Society of Victoria* **90**, 139–147.

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