Lead isotopic systematics of major river sediments: a new estimate of the Pb isotopic composition of the Upper Continental Crust

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Abstract

The lead isotopic composition of river sediments is reported in the present work for the Earth's major river basins, from old cratonic to young orogenic areas and from subarctic to tropical climates. Sediment samples from these large river basins provide a useful tool to calculate the average upper crustal composition because they are large-scale integrated samples of the weathering products of the present-day Upper Continental Crust (UCC). Two different and complementary calculations were done to estimate the average lead isotopic composition of the UCC. The first, based on the flux weighted average of particulate lead delivered by the rivers, gave values of 19.07, 15.74 and 39.35 for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios, respectively. To avoid over-estimating the contribution of orogenic areas, which produces a bias (because the flux of particulate lead depends strongly on the physical erosion rate), a second calculation was done by averaging with drainage areas of each river basin. This gave values of 18.93, 15.71 and 39.03 for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios, respectively. These direct calculations of the lead isotopic composition of the UCC are similar and are in agreement with previous estimates made using an indirect approach.
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Keywords: Lead isotopes; River sediments; Upper Continental Crust

1. Introduction

By studying the U–Th–Pb isotopic system, we can acquire time-integrated information about fractionations occurring during various geochemical processes such as continental crust formation, igneous differentiation and chemical weathering of the Upper Continental Crust (UCC). One of the best ways to estimate the Pb isotopic composition of the UCC is to investigate the Pb isotopic composition of suspended sediments transported by the Earth's major rivers. Due to their large-scale integrating capacity, river sediments are representative samples of the average composition of the UCC subjected to weathering. Such an approach has been used for Nd isotopes (McCulloch and Wasserburg, 1978; Goldstein et al., 1984; Allègre and Rousseau, 1984; Dia et al., 1990), and Asmerom and Jacobsen (1993) have estimated the average Pb isotope composition of the UCC using river water suspended matter using an indirect calculation based on the negative correlation between Nd and Pb isotopes with

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a mean ε_{Nd} value for the present-day UCC of -16.7 reported by Goldstein and Jacobsen (1988). More recently, Hemming and McLennan (2001) reported the Pb isotope compositions of modern deep-sea turbidites around the globe, which are a good alternative to river sediments for sampling the UCC.

In this study, we determined the Pb isotopic compositions of suspended matter and sands from major river basins of the Earth in a wide variety of settings: from old cratonic to young orogenic areas and from subarctic to tropical climates. After attempting to determine the possible contribution of atmospheric lead pollution, we used the river sediment isotopic data and two different and complementary methods to estimate the average present-day Pb isotopic composition of the UCC. We also characterized the isotopic composition of river sediments flowing into the oceans. Finally, we compared the average values of the UCC and the distribution of the different types of oceanic basalts. Such comparison has important consequences concerning U–Pb fractionations in geodynamic cycles.

2. Sample description

The river sediment samples come from a wide variety of geological settings and climatic conditions (Fig. 1). In terms of discharge, these river basins contribute more than 45% of all of the water flowing into the oceans. Data on river basin sediments sampled at river mouths are listed by geographical area in Table 1, with a distinction being made between our own data and data taken from the literature.

Some of our river sediment samples from North America came from the Mackenzie River Basin in Western Canada, which is one of the largest river basins in North America in terms of water discharge and suspended load. Data for the Red Arctic River, which flows into the Beaufort Sea, is also reported here. Details of sampling locations are given in Millot et al. (2003). Three other large Canadian river basins, the Fraser, Nass and Skeena Rivers, which drain the Western Canadian Cordillera and flow into the Pacific Ocean, were also investigated. For South America, the Pb isotopic composition of the Amazon River Basin
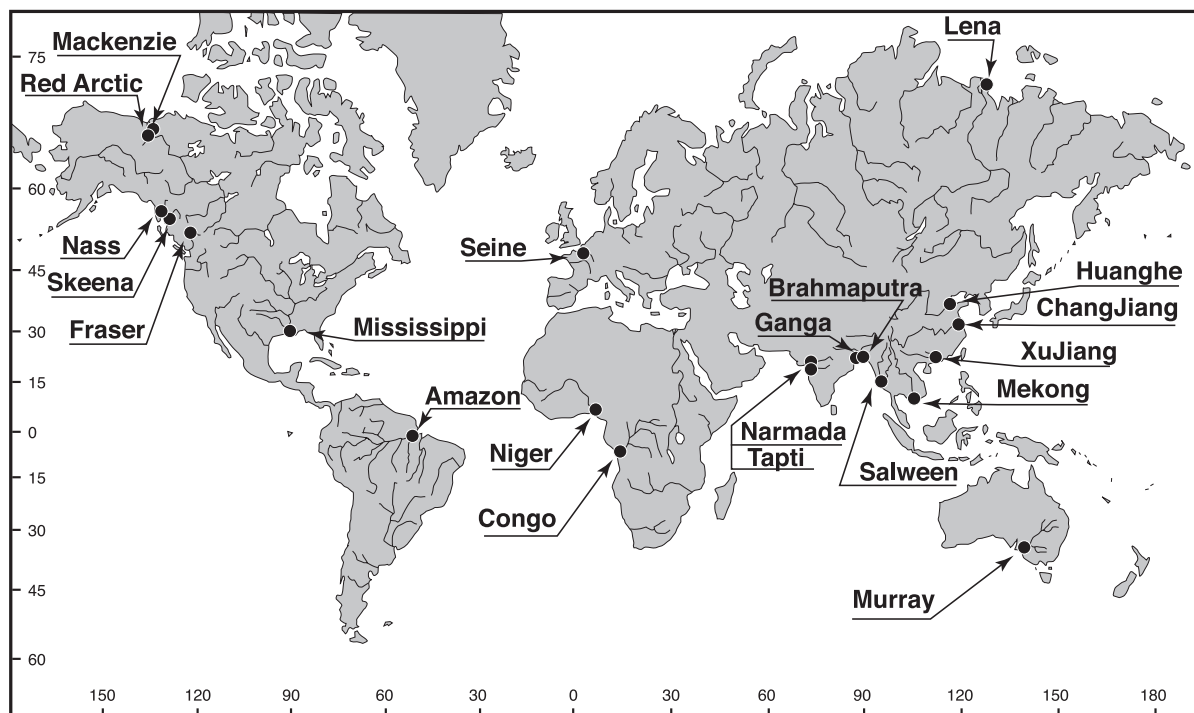

Fig. 1. Map of the river basins investigated in this study, and sampling locations. These are from a very wide variety of settings, from old cratonic to young orogenic areas and from subarctic to tropical climate.

Table 1
Pb isotopic composition of large river sediment samples (river basins sampled at the river mouth)

Continent	River name	Sample #	Sample type	Surface area (10^3 km^2)	River discharge (km^3/year)	Sediment flux (10^6 t/an)	Al (ppm)	Nd (ppm)	Th (ppm)	U (ppm)	Pb (ppm)	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb
Africa	Niger	Niger #1	SM	1200	200	52.0	–	67.5	24.1	5.2	30.0	18.545	15.635	38.964
	Congo[1]	Congo 64	SM	3500	1200	38.4	–	39.0	13.8	2.4	34.7	18.819	15.767	39.080
	Oubangui[1]	Oubangui 34	SM	600	110	–	–	–	17.6	3.0	27.6	19.070	15.853	39.780
Asia	ChangJiang	CH93-1	SM	1900	930	–	88,518	34.0	13.0	3.1	39.8	18.612	15.692	38.895
	ChangJiang	CH94-1	SM	1900	930	–	84,494	36.5	14.0	2.9	43.4	18.645	15.665	38.813
	XuJiang	CH94-4	SM	440	300	–	95,559	34.0	14.8	3.3	39.4	18.865	15.744	39.129
	HuangHe	CH93-6	SM	770	59	–	75,918	30.1	12.4	2.5	32.5	18.155	15.564	38.415
	HuangHe	CH94-6	SM	770	59	–	70,624	31.1	13.7	2.9	28.2	18.401	15.602	38.591
	Mekong	VIET92-1	SM	790	470	150.9	–	39.8	19.9	3.9	44.5	18.767	15.694	39.059
	Tapti	IND98-8	SM	49	18	2.7	–	27.1	4.8	0.9	12.7	18.266	15.650	38.355
	Narmada	IND98-28	SM	88	47	144.3	47,594	13.5	4.9	0.8	10.0	18.897	15.751	39.221
	Ganga	IND99-19	SM	980	630	693.0	233,473	31.8	16.7	3.2	26.0	19.508	15.828	39.766
	Brahmaputra	IND99-20	SM	580	590	625.4	273,000	33.4	17.4	3.4	27.5	18.938	15.746	39.571
	Salween	BIR99-1	S	170	50	–	–	33.1	16.1	3.2	42.6	18.595	15.734	38.979
	Lena	Lena #17	S	2430	533	16.0	76,367	21.1	–	–	14.1	18.191	15.532	38.352
Australia	Murray[2]	–	SM	1100	12	–	–	35.0	–	1.7	28.4	18.472	15.610	38.343
Europe	La Seine	BP42	SM	44	9	–	61,306	28.4	9.5	2.0	57.5	18.260	15.617	38.195
N. America	Mississippi[2]	–	SM	3200	580	–	–	40.8	–	2.4	38.2	19.182	15.614	38.813
	Mackenzie	CAN96-6	SM	1680	284	85.2	70,200	28.0	10.3	3.5	16.6	19.391	15.671	39.171
	Red Arctic	CAN96-7	SM	19	5	1.4	73,535	30.2	10.4	4.4	20.4	19.301	15.659	38.922
	Fraser	CAN99-21	SM	220	112	84.0	92,276	35.9	13.0	2.6	19.7	19.487	15.764	39.691
	Skeena	CAN99-28	SM	42	30	1.6	83,647	19.1	3.8	1.9	10.1	18.985	15.599	38.540
	Nass	CAN99-30	SM	19	25	7.3	73,376	18.7	3.9	1.8	10.1	19.091	15.617	38.620
S. America	Amazon[1]	RAJ 20	SM	4620	5750	1046.5	–	47.4	16.7	3.9	23.5	18.942	15.707	39.028
	Negro[1]	–	SM	700	895	–	–	–	12.5	2.4	62.3	18.960	15.707	38.820
	Solimoes[1]	–	SM	2150	3250	–	–	–	15.4	4.1	39.2	18.930	15.675	38.850

Al, Nd, Th, U and Pb concentrations are given in ppm. Surface area, river water discharges and sediment fluxes are also given. SM = suspended material matter and S = sands. River basins (n = 14) for which sediment fluxes are given are those on which the first estimate of the Upper Continental Crust composition is based. Numbers in superscript correspond to data from Allègre et al. (1996) ([1]) and Asmerom and Jacobsen (1993) ([2]).

has been studied in detail by Allègre et al. (1996) and we used their data for river sediments from the Amazon River mainstream close to the mouth, and for the Negro and Solimoes Rivers. For Europe, we analyzed sediments from the Seine River (France). Sands from the Lena River in Siberia were also analyzed. In Asia, we analyzed samples from two large rivers draining the Himalaya (the Ganga and the Brahmaputra), and large rivers draining the Deccan Traps in Western India (the Narmada and the Tapti). Suspended sediment samples from the ChangJiang, XuJiang and HuangHe Rivers in China were analyzed, as were a sand sample from the little-known Salween River in Burma and suspended matter samples from the Mekong River in Vietnam. In Africa, we analyzed river sediments from the Niger River and report, for comparison, data for the Congo and Oubangui Rivers (Allègre et al., 1996). Two other large river systems were also included, for comparison, in our study: the Murray River in Australia and the Mississippi River in North America (Asmerom and Jacobsen, 1993).

3. Analytical methods

The river sediments were collected after drying and centrifugation of the retentate of river water filtration at 0.2 μm (frontal filtration). The samples were not sieved. About 50 mg of crushed sample was dissolved in 1.5 ml of HF acid (27N) for 24 h at 80 °C. After the HF acid had evaporated, 1.5 ml of HNO_3 acid (16N) was added for 24 h at 80 °C. The residue of the acid dissolution was then dissolved again in two successive volumes of 0.6 ml of HBr (0.5 N), before being placed in a column containing AG1 X8 resin for lead separation.

Chemical extraction of lead was done after two successive extractions on 50 and 10 μl of AG1 X8 resin, then by a purification step through 2 μl of AG1 X8 resin, according to the lead extraction method described by Manhès et al. (1978) and Göpel et al. (1985). Pb isotopic compositions were measured by multicollector ICP-MS (Nu Plasma) at the Department of Earth Sciences, Oxford University, using the Tl doping technique for the mass discrimination correction (Belshaw et al., 1998). Measurement accuracy was checked by running the NBS 981 standard ($n = 11$) which gave values of 16.932 ± 0.003,

15.485 ± 0.003, 36.675 ± 0.007, 0.91452 ± 0.00006, 2.16602 ± 0.00008 (2σ) for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$, respectively. Chinese river sediments were analyzed in Paris by TIMS with an internal precision of 0.011, 0.014 and 0.046 (2σ) for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$, respectively. Measurements by TIMS were calibrated against SRM981 NBS standard measurements, with a statistical mass discrimination factor of $1 \pm 0.3\text{\textperthousand}$ per amu. The total precision is better than 0.05% (2σ) per mass unit difference in the isotopic ratio. Blanks for the total chemical extraction were less than 200 pg of lead, which represents a 10^{-4} blank/sample ratio. Lead, thorium, uranium, aluminium and neodymium concentrations were determined by ICP-MS with a precision better than $\pm 5\%$ at the University of Toulouse.

4. Results

Lead isotopic ratios for the river sediments range from 18.16 to 19.51, 15.53 to 15.85 and 38.20 to 39.78 for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$, respectively (Table 1). Ganga River suspended matter has the highest $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios. The HuangHe River has the lowest $^{206}Pb/^{204}Pb$ ratio, the Lena River has the lowest $^{207}Pb/^{204}Pb$ ratio and the Seine River has the lowest $^{208}Pb/^{204}Pb$ ratio.

Lead concentrations in the suspended matter are between 10.0 ppm (Narmada River, India) and 62.3 ppm (Rio Negro, Brazil), with a mean value of around 30 ppm. This is higher than the mean value of 20 ppm given for the Upper Continental Crust by Taylor and McLennan (1985). Thorium concentrations are more variable, ranging from 3.8 ppm for the Skeena River in Western Canada to 24.1 ppm for the Niger River in central Africa. Uranium contents are between 0.8 ppm for the Narmada River in India and 5.2 ppm for the Niger River.

5. Discussion

5.1. Is there a contribution of anthropogenic lead?

Since lead is omnipresent in the environment, we investigated the possible contamination of our sam-

ples by anthropogenic lead. Fluxes of anthropogenic lead have increased sharply since the late 1970s and the onset of rapid development of industrial activities, due to the emission of fine particles derived essentially from the combustion of leaded gasoline and coal (Chow and Patterson, 1966; Nriagu, 1979; Settle and Patterson, 1982; Patterson and Settle, 1987).

The addition of anthropogenic lead will raise Pb concentrations in river sediments above their natural levels (Spencer and Mahoney, 1995). In the sediments analyzed in this study, lead concentrations span a wide range (from 10.0 to 62.3 ppm). However, we have found no correlation between lead content and lead isotopes. In most of the sediments, both Al/Pb and Nd/Pb elemental ratios are close to or slightly higher than Taylor and McLennan's values for the Upper Continental Crust (1985). Al and Nd are considered to be natural insoluble elements. Mean ratios for Al/Pb and Nd/Pb are 4600 and 1.3, respectively, in our suspended sediments, whereas they are 4000 and 1.3 in the UCC (Fig. 2). However, river sediments from China (ChangJiang, XuJiang and HuangHe Rivers) and from the Seine River have an excess of lead and consequently have lower Al/Pb and Nd/Pb ratios than the UCC. This excess is very significant and these samples were, therefore, not included in our initial

calculations. For the same reason, the Mississippi River sample (Nd/Pb ratio around 1.07, lower than that of the UCC) was also excluded. In addition, Spencer and Mahoney (1995) reported that one-third of the Pb in riverine sediments at the mouth of the Mississippi in the mid-1980s was anthropogenic.

On the global scale, the Pb isotopic signature of the atmospheric contribution is now well constrained. Bollhöfer and Rosman (2000, 2001) have given the lead isotopic signatures for atmospheric aerosols collected between 1994 and 1999. In order to determine the atmospheric contribution to the lead isotopic composition of river sediments, we plotted river sediment ratios for $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ and, on the same graph, indicated mean signatures for atmospheric lead in the USA, Canada, France, China and Russia (Fig. 3). On the global scale, atmospheric lead has lower $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$ ratios than river sediments. However, because of the wide scatter observed for the signature of atmospheric lead for each region, it is difficult to determine the possible contribution of atmospheric lead. Atmospheric deposits might, however, affect some river basins, in particular those in China and Europe because the Chinese and Seine river sediments are close to the field defined by atmospheric aerosols of these areas and also present an excess of
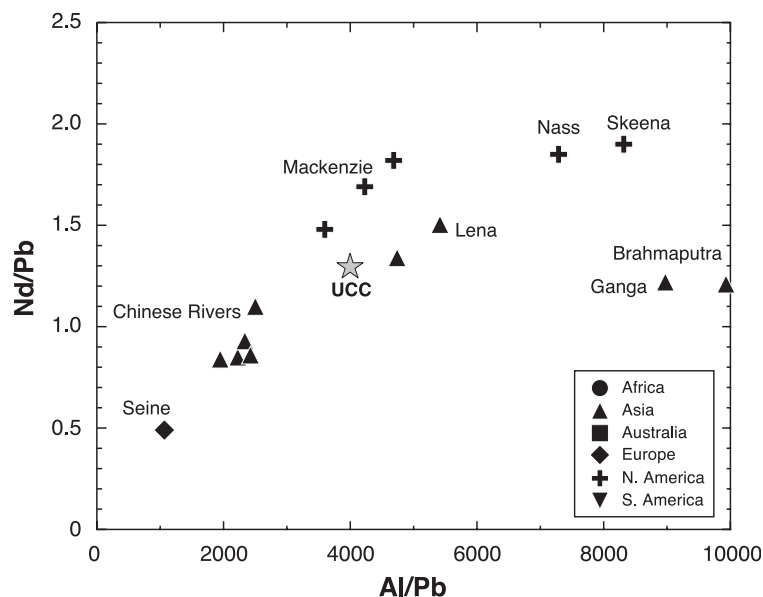

Fig. 2. Nd/Pb vs. Al/Pb elemental ratios in river sediments sampled at river mouths. The mean value for the Upper Continental Crust (UCC) is taken from Taylor and McLennan (1985).
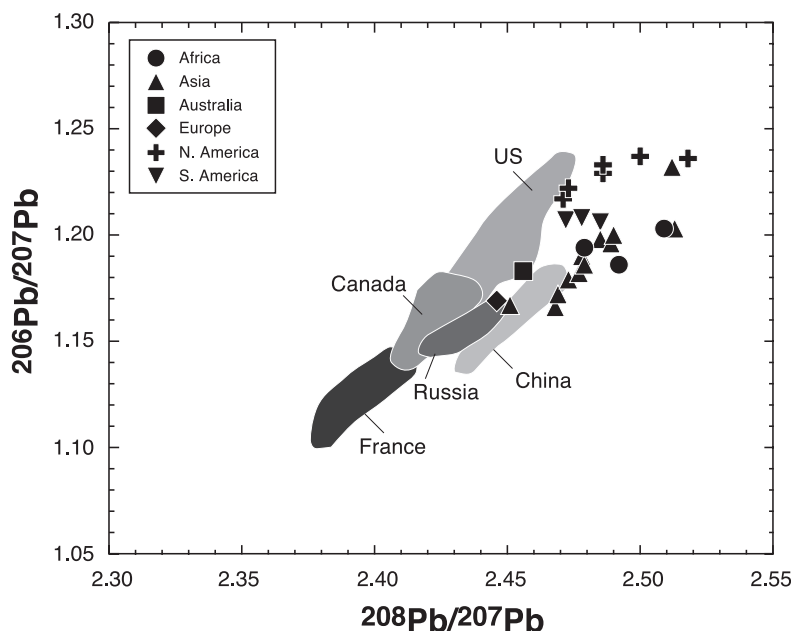
Fig. 3. $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$ diagram for river sediments. The field for atmospheric aerosols is reported. Data are from a recent compilation by Bollhöfer and Rosman (2000, 2001).

lead (low Al/Pb and Nd/Pb ratios). The contribution of anthropogenic lead by atmospheric input in river sediments of the Seine River has, moreover, been documented elsewhere (Roy, 1996). Nevertheless, it is important to keep in mind that the lead isotopic signature of this input is already the result of mixing between natural and anthropogenic lead. Even if the lead isotopic composition of river sediments is close to the field defined by the atmospheric signature of each region, we cannot precisely determine the anthropogenic lead contribution.

Anthropogenic lead derived from atmospheric deposits is not constitutive of river sediments because it is not derived from the erosion of the bedrock itself, but adsorbed on the surface of the suspended sediments transported by the river. Several researchers have leached river sediments to extract the adsorbed lead fraction (Tessier et al., 1979; Erel et al., 1994). Unfortunately, no clear conclusions can be drawn from these experiments. Lead released by dilute acid leaching has an isotopic composition more radiogenic than the bulk sediment itself. However, this radiogenic signature could not be clearly interpreted as an anthropogenic contribution. Dilute acid leaching has

shown that accessory minerals (being less resistant) are able to release Pb more easily than the whole sediment (Harlavan and Erel, 2002). In addition, these minor phases may contain considerable concentrations of incompatible elements (including U and Th) and therefore high concentrations of radiogenic Pb. Moreover, leaching experiments done on river sediments in the Seine Basin (Roy, 1996) have shown that most of the lead transported by the river is adsorbed on the surface of the suspended sediment and can be easily leached with HBr acid.

Our river sediment data are in a very good agreement with turbidite data reported by Hemming and McLennan (2001). Turbidites are common components of sedimentary accumulations at the edges of continents and therefore constitute large-scale and long-time integrated samples of the weathering products of the UCC. The entire range of variation for lead isotopes is the same for our modern river sediment data and for the turbidite data (Fig. 4). This is true even at the regional scale. Samples from the Congo River lie on the curve of turbidite samples from the Angola Sea (Fig. 5). This seems to prove that the modern river sediments investigated in this study are little affected
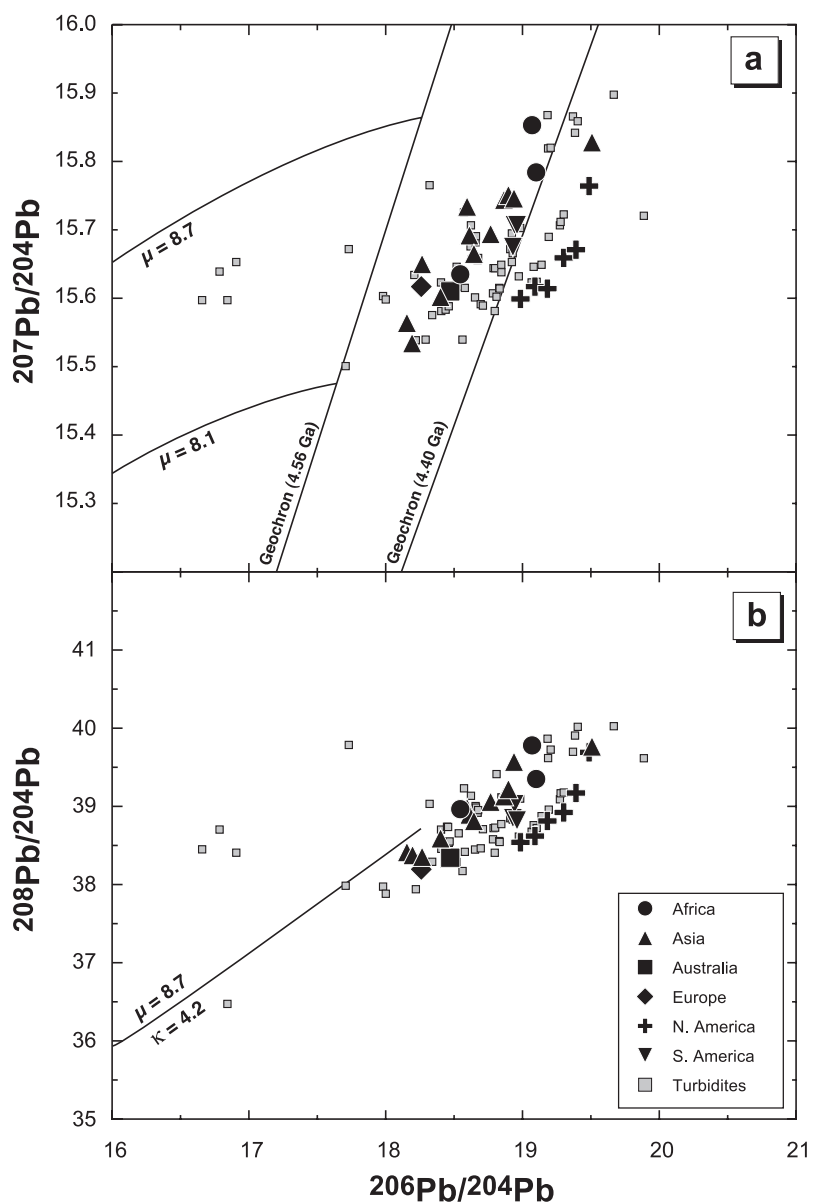
Fig. 4. ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb and ^{208}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb diagrams for river sediment samples. Lead isotopic compositions of river sediments (sampled at the river mouth) and turbidites from Hemming and McLennan (2001) are also plotted, for comparison. The Geochron (at 4.56 and 4.40 Ga) is also plotted in the ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb plot, as are growth curves for $\mu = 8.7$ and $\kappa = 4.2$.

by anthropogenic contribution because most of the turbidites samples reported by Hemming and McLennan (2001) are pre-industrial. The few turbidite samples lying outside the river data range correspond to continental margins not covered by rivers analyzed in the present study.

Based solely on Pb contents (more precisely on Al/Pb and Nd/Pb ratios), it is evident that many river sediments clearly contain an excess of lead. It is, however, difficult to precisely quantify the anthropogenic contribution based on isotopic constraints and we, therefore, did not use the river sediment data for the
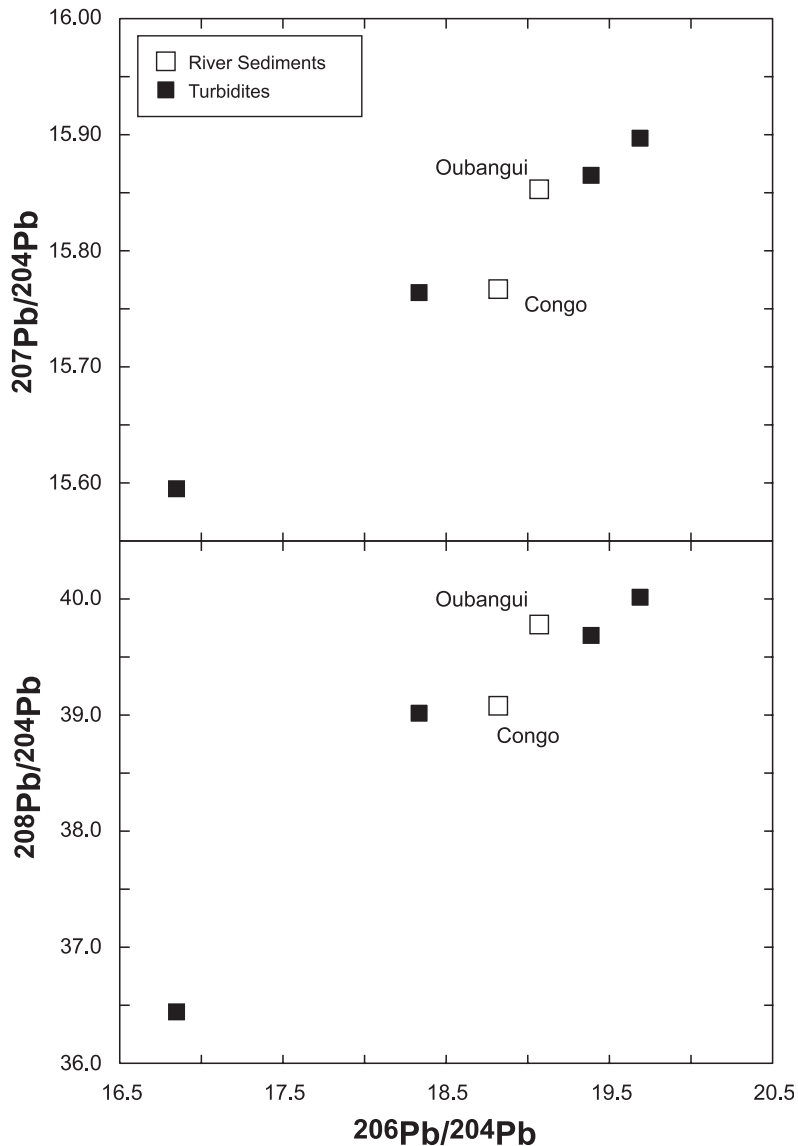
Fig. 5. Comparison of lead isotope data for river sediments in the Congo basin (Congo and Oubangui Rivers) and turbidites of the sedimentary region (Angola Sea, samples RC13-220 and RC13-222) reported by Hemming and McLennan (2001).

Seine River Basin, the Chinese Basins (ChangJiang, XuJiang and HuangHe) or the Mississippi River Basin in the following calculations. However, even anthropogenic lead comes ultimately from the crust. The lead in both leaded gasoline and coal is extracted from the Upper Continental Crust. Any contribution of atmospheric lead to the mass budget of lead carried by river sediments does not have any significant effect on the estimated average Pb isotopic of the UCC.

5.2. Pb isotopic composition of the upper continental crust

Taylor and McLennan (1985) have started the exercise of estimating the chemical composition of the continental crust by the use of fine sediments. Following Patterson and Tatsumoto with the analyze of detrital feldspars to estimate the bulk continental crust composition (Tatsumoto and Pat-

terson, 1964; Patterson and Tatsumoto, 1964), McCulloch and Wasserburg (1978) have estimated the mean Nd isotopic composition of continents by the use of sediments and shales. We have endeav-

ored, using river sediments, to test whether this kind of technique could be applied to lead isotopes and lead concentrations. Two different approaches were used.

Table 2
Lead isotopic composition and surface area of river basins on which the second estimate of the upper continental composition is based ($n = 44$)

Continent	River name	Sample #	Surface area (10^3 km^2)	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Africa	Oubangui[1]	C89-1-1 Pk0	475	19.100	15.784	39.350
	Lobaye[1]	C89-22	31	18.470	15.703	38.750
	Oubangui[1]	C89-34	600	19.070	15.853	39.780
	Zaire[1]	C89-35	1660	19.780	15.872	39.500
	Sangha[1]	C89-45	250	18.731	15.732	39.230
	Alima[1]	C89-49	50	18.121	15.638	38.440
	Kasai[1]	C89-62	900	18.536	15.722	39.060
	Congo[1]	Congo 64	3500	18.919	15.767	39.080
	Niger	Niger #1	1200	18.545	15.635	38.964
Asia	Mekong	VIET92-1	790	18.767	15.694	39.059
	Salween	BIR99-1	170	18.595	15.734	38.979
	Narmada	IND98-28	88	18.897	15.751	39.221
	Tapti	IND98-8	49	18.266	15.650	38.355
	Ganges	IND99-19	980	19.508	15.828	39.766
	Brahmaputra	IND99-20	580	18.938	15.746	39.571
	Lena	Lena #17	2430	18.191	15.532	38.352
Australia	Murray [2]	–	1100	18.472	15.610	38.343
N. America	Mackenzie	CAN96-6	1680	19.391	15.671	39.171
	Red Arctic	CAN96-7	18.6	19.301	15.659	38.922
	Liard	CAN96-26	275	19.299	15.660	39.072
	Little Smoky	CAN96-14	3.01	19.270	15.655	39.042
	Smoky	CAN96-16	51.3	19.397	15.663	39.148
	Fort Nelson	CAN96-23	43.5	19.453	15.674	39.196
	Slave	CAN96-38	616.4	19.382	15.667	39.154
	Athabasca	CAN96-42	131	19.312	15.666	39.091
	Athabasca	CAN99-5	9.78	19.329	15.685	39.321
	Fraser	CAN99-21	220	19.487	15.764	39.691
	Bulkley	CAN99-24	12.3	18.960	15.601	38.517
	Skeena	CAN99-28	42.2	18.985	15.599	38.540
	Nass	CAN99-30	19.2	19.091	15.617	38.620
	Bell Irving	CAN99-31	5.16	19.045	15.617	38.595
	Blue	CAN99-45	1.7	19.568	15.706	39.253
	Liard	CAN99-46	33.4	19.661	15.727	39.731
	Hyland	CAN99-51	9.45	19.635	15.741	39.586
	Trout	CAN99-57	1.19	19.947	15.739	39.829
	Toad	CAN99-60	2.57	19.519	15.725	39.445
	Racing	CAN99-64	1.9	20.143	15.746	39.734
	Muskwa	CAN99-67	20.3	19.478	15.672	39.230
S. America	Negro[1]	RAJ1	700	18.960	15.707	38.820
	Solimoes[1]	RAJ4	2150	18.930	15.675	38.854
	Madeira[1]	RAJ7	1343	18.672	15.659	38.840
	Trombetas[1]	RAJ16	247	19.945	15.924	39.930
	Tapajos[1]	RAJ19	500	18.960	15.678	38.925
	Amazon 20[1]	RAJ20	4620	18.942	15.707	39.028

Numbers in superscript correspond, respectively, to data from Allègre et al. (1996) ([1]) and Asmerom and Jacobsen (1993) ([2]).

Table 3
Average estimates of the lead isotopic composition of the Continental Crust

Continental Crust	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
UCC avg. 1 balanced by sediment flux	19.07	15.74	39.35
UCC avg. 2 balanced by surface area	18.93	15.71	39.03
Bulk cont. crust (Allègre and Lewin, 1989)	18.59	15.59	39.56
Bulk cont. crust (Rudnick and Goldstein, 1990)	18.04–18.35	15.51–15.62	–
UCC (Asmerom and Jacobsen, 1993)	19.32	15.76	39.33
UCC (Hemming and McLennan, 2001)	19.22	15.78	39.58

5.2.1. The average values carried to the oceans by rivers

Data from 14 river basins (Table 1, not including those in China, the Seine or the Mississippi for the reason given above) were used to calculate the average values carried to the oceans by rivers. Each of these river basins has a lead signature characterized by

lead isotopic composition (I_i) and lead concentration (C_i), with a river flux of particulate matter (Γ_i). The mean lead concentration of a given river basin is:

$$\bar{C} = \frac{\Sigma\ C_i\Gamma_i}{\Sigma\Gamma_i} \tag{1}$$

For each river, we can deduce the mass fraction for the flux of lead (X_i). We can then calculate the mean values for each of the three isotopic ratios using the following equation:

$$\bar{I} = \Sigma\ I_i X_i \tag{2}$$

Samples should be collected at the river mouths. This was the case for all of the river basins considered here except the Fraser River Basin in which the sediments were collected upstream, in the Canadian Rocky Mountains.

5.2.2. The continental crust averaged sampled by rivers

In this case, instead of using only data for river sediments at the river mouth, we included all of the
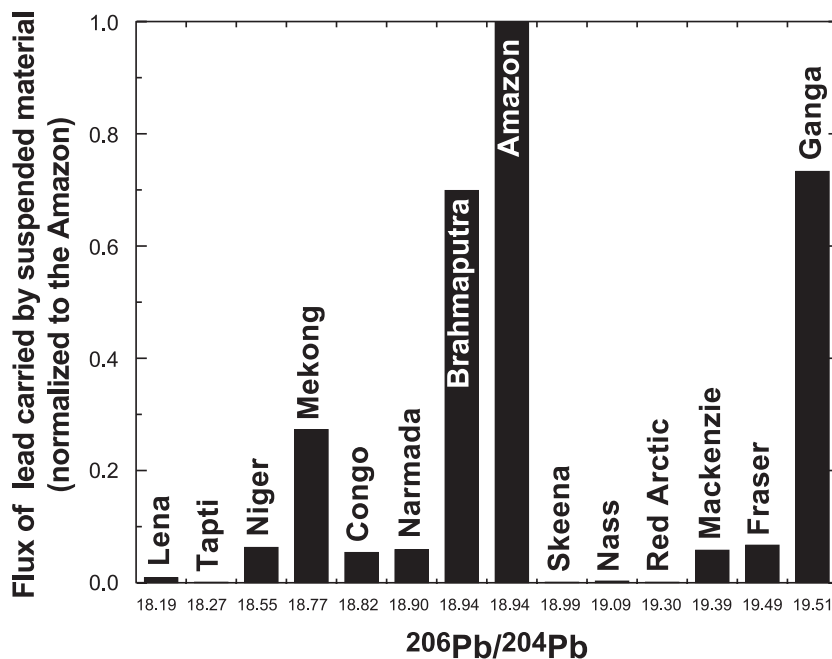

Fig. 6. Flux of particulate lead flowing to the ocean plotted as a function of $^{206}Pb/^{204}Pb$ ratio. The Y-axis correspond to the relative contribution of each river basin to the suspended material matter flux of lead normalized to the input of the Amazon.

tributaries for which we have lead isotopic data (Table 2). These 44 river basins represent more than 31% of the total surface area of the globe drained by rivers (Milliman and Meade, 1983). In this case, the lead isotopic composition was weighted using the drainage areas of the river basins. For each of the three isotopic ratios, we then calculated the mean values for each basin using the following equation, S_i being the surface area of the river basin:

$$\bar{I} = \frac{\Sigma\ I_i\ S_i}{\Sigma\ S_i} \tag{3}$$

The main difference between the two approaches is that in the first one, averaging is done using the flux of lead carried by the river, which is very dependent on both the river discharge and the rate of mechanical erosion of each continental area, whereas in the

second case, the averaging is done using the surface area of the drainage basin.

5.2.3. Results and comparison

For the first calculation, we obtained values of 19.07, 15.74 and 39.35 for the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios, respectively. For the second calculation, we obtained mean lead isotopic composition values of 18.93, 15.71 and 39.03 for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$, respectively. These results and those of four other authors are given in Table 3.

Concerning the representativity of our samples in the first calculation, the Pb isotopic compositions of river sediments were weighted by the flux of particulate lead, which is a direct function of lead concentration and the physical erosion rate. Such an approach produces a bias by over-representing orogenic areas
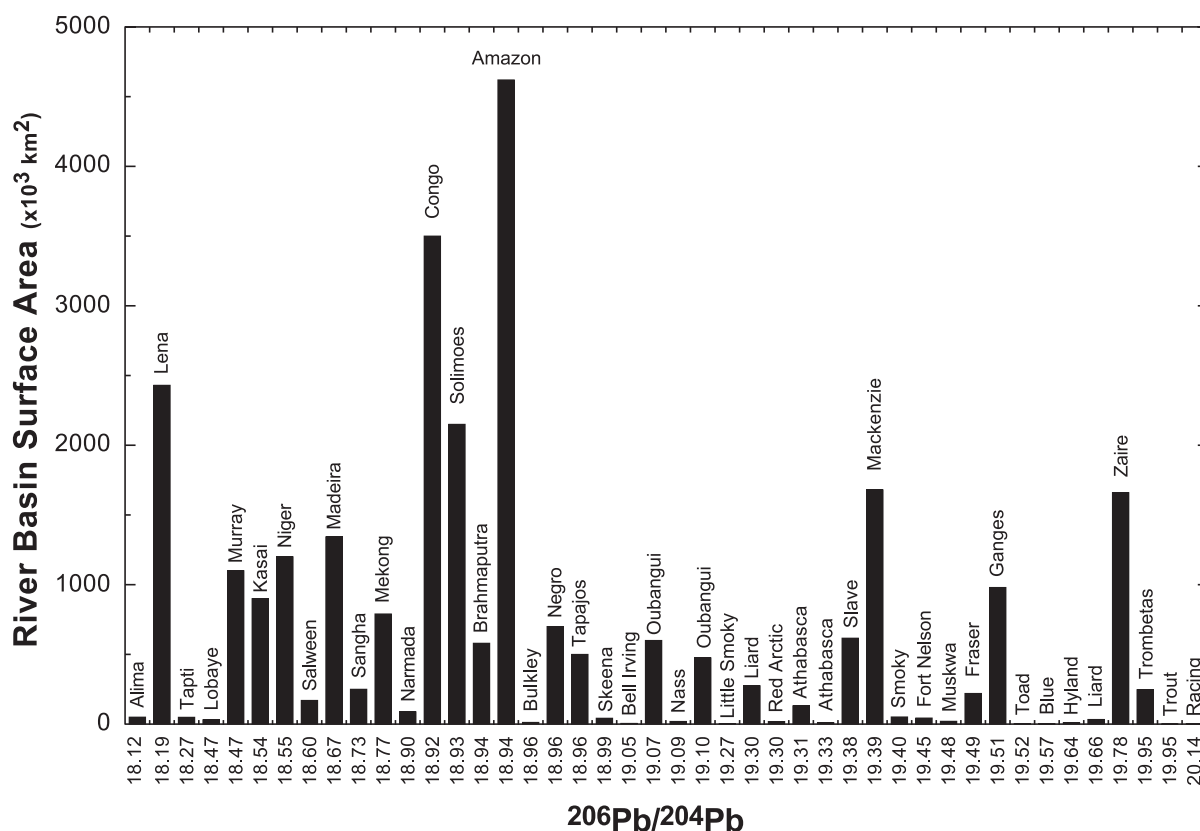

Fig. 7. River basin surface area plotted as a function of $^{206}Pb/^{204}Pb$ ratio. The lead isotopic composition of the Upper Continental Crust calculated by weighting with the surface area is dominated by the lead isotope signatures of river basins, such as the Amazon, Congo, Lena, Solimoes, Mackenzie and Zaire, having the greatest surface area.
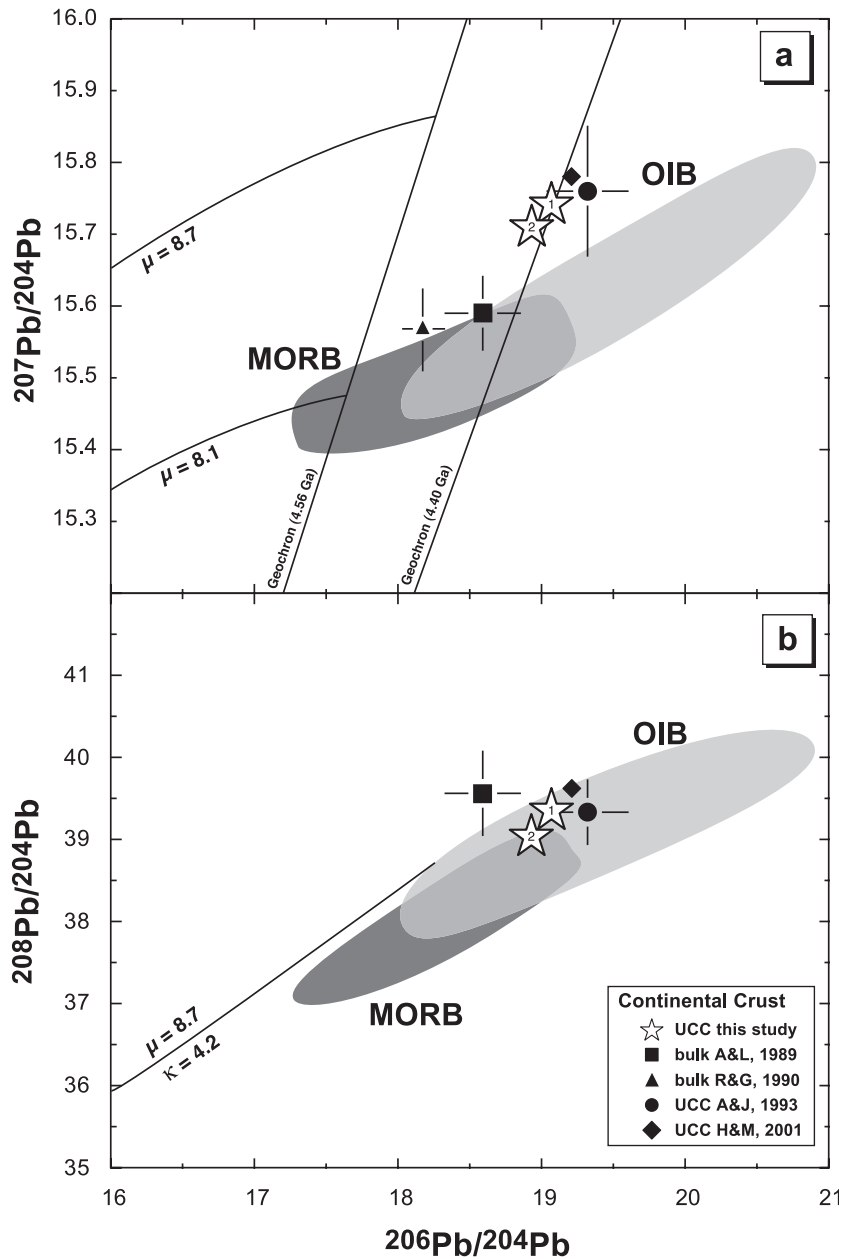
Fig. 8. Lead isotopic diagrams showing the two estimated average compositions of the present-day Upper Continental Crust. The first estimate (1) corresponds to the value weighted by particulate flux of lead delivered by the rivers to the Oceans. The second (2) corresponds to the isotopic composition weighted by individual drainage basin surface areas. Other values of mean isotopic composition are from Allègre and Lewin (1989) [A&L] as well as from Rudnick and Goldstein (1990) [R&G] for the bulk continental crust, from Asmerom and Jacobsen (1993) [A&J] and from Hemming and McLennan (2001) [H&M] for the UCC. Pb isotope compositions for Mid-Oceanic Ridge Basalts (MORB) and Oceanic Island Basalts (OIB) are also plotted as field area (data compiled from published data).

having high physical denudation rates because of higher altitude (Allègre and Rousseau, 1984; Goldstein et al., 1984; Asmerom and Jacobsen, 1993). On the other hand, since lead is transported by rivers mainly in the solid load (suspended and sandy phase), rivers carrying large sediment loads have to be included in our calculation. River basins producing a large flux of sediments (Milliman and Meade, 1983) were taken into account by including Andean tributaries of the Amazon River and the rivers flowing from the Western Cordillera in Canada, both in active margins, and river basins draining large flood basalt provinces such as the Deccan Traps in India. The sediment input of river basins in volcanic islands such as Indonesia was not, however, included in our calculation despite the fact that these rivers carry high sediment loads.

In the second estimate, on the other hand, river sediment data were weighted only by the surface area of the basin and not by the lead concentration. Here, we assume that the lead concentrations are relatively constant compared to the range of variation of the surface areas of the basins considered (varying by more than three orders of magnitude, from 1.2×10^3 km^2 for the Trout River in the Canadian Rocky Mountains to 4620×10^3 km^2 for the Amazon Basin).

The two average isotopic composition values that we obtained are very similar (Table 3). When the flux of particulate lead is plotted as a function of the ^{206}Pb/^{204}Pb ratio (Fig. 6), we see clearly that the global flux of lead delivered to the oceans is dominated by the lead coming from the Amazon, Ganga, Brahmaputra and Mekong Basins. In the second estimate, because of the method of calculation, the lead isotopic composition of the UCC is dominated by large river basins such as the Amazon, the Congo, the Lena, the Solimoes, the Mackenzie and the Zaire (Fig. 7).

In order to test the sensitivity of the method, the calculations were done again, this time including the river basins that had been previously excluded (the Chinese rivers, the Seine and the Mississippi). For particle-weighted lead isotopic composition, we obtained significantly lower isotopic ratios, due primarily to the contribution of the Chinese river sediments. The mean estimates were 18.79, 15.59 and 39.05 for ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios, respectively. With the surface area-weighted estimate, we obtained values much closer to the previous estimate with 18.86, 15.69 and 38.95 for

^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb, respectively. In this case, the inclusion of the additional river basins had little affect on the results and the mean is clearly dominated by large river basins such as the Amazon, the Lena, the Congo and the Mackenzie (Fig. 7).

The two estimates of the lead isotopic composition of the Upper Continental Crust are similar and when they are plotted along with the mean estimates reported by Allègre and Lewin (1989), Rudnick and Goldstein (1990), Asmerom and Jacobsen (1993), and Hemming and McLennan (2001) (Fig. 8). We see clearly that our two direct estimates are in a good agreement with the Pb isotopic composition for the bulk continental crust (Allègre and Lewin, 1989; Rudnick and Goldstein, 1990) and the UCC composition reported by Asmerom and Jacobsen (1993) using an indirect approach, as well as with Hemming and McLennan's (2001) estimate of the UCC from turbidite samples. All of these different approaches are, therefore, able to produce the same estimate of lead isotopic composition of the UCC.

6. Consequences for geodynamic cycles

In addition to being able to estimate the composition of UCC from the lead isotopic composition of river sediments, our study enabled us to characterize the Pb isotopic composition of the global input of river sediments into the oceans.

Suspended sediments carried by major rivers are powerful samples because they are large-scale integrated samples of the present-day Upper Continental Crust. Fig. 4 shows that our data for major river sediments are in a good agreement with those of Hemming and McLennan (2001) for turbidites.

In Fig. 8 (lead isotopic composition of the UCC and oceanic volcanics), we see that the domains of the UCC and Mid Oceanic Ridge Basalts (MORB) for ^{206}Pb/^{204}Pb isotopic ratios are very similar. However, the ^{208}Pb/^{204}Pb isotopic ratios of the UCC lie slightly above the MORB domain. The greatest difference is seen for the ^{207}Pb/^{204}Pb isotopic ratios, the UCC being clearly above the MORB trend. In addition, both UCC and MORB domains are to the right of the 4.56 Ga Geochron. Since the MORB isotopic signature is considered to be the result of depletion created by the extraction of the continental crust, the values of

the UCC and MORB system (primitive mantle) should be to the left of the 4.56 Ga Geochron. However, bulk UCC lie on the 4.40 Ga Geochron, considered to be the true terrestrial Geochron determined by the end of the Earth accretion-differentiation phase (Allègre et al., 1995; Galer and Goldstein, 1996). The dispersion of the $^{206}Pb/^{204}Pb$ isotopic ratios is clearly in agreement with the idea that μ values ($\mu = ^{238}U/^{204}Pb$) for UCC and MORB domains are not strongly different in most of the geological time. Today, μ values are probably around 8 for the UCC and 5 for the MORB source (Allègre et al., 1988). The fact that UCC $^{208}Pb/^{204}Pb$ isotopic ratios are slightly above the MORB domain is in good agreement with the idea that the bulk continental crust should have a κ value ($^{232}Th/^{238}U$) which began at 4.2 and converges today at 2.5 (Allègre et al., 1995). However, the small difference observed for the UCC suggests that high κ ratios should be found in the lower continental crust, which is consistent with the observations of heat flow (Roy et al., 1972) and the compilation of Rudnick and Fountain (1995), which

gave $^{232}Th/^{238}U \sim 6$ for the lower continental crust. The UCC sampled in river sediments should then be lower, around $^{232}Th/^{238}U = 3.6$.

The large difference between the UCC and MORB $^{207}Pb/^{204}Pb$ isotopic ratios reflects the old differentiation of the continental crust and the preservation of such material by reworking. To estimate a model age for such early differentiation, we split the data on river sediments into two domains: North America and the rest of the world. In the $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram (Fig. 9), the intersection of the best line for the UCC with the curve for the growth of the mantle, with $\mu = 8.7$, is around 3.2 Ga, which corresponds to the model age of the differentiation of the continental crust. This figure is in good agreement with the start of the continental growth curve as determined by Allègre and Lewin (1989).

The comparison with Oceanic Island Basalts (OIB) data clearly shows that the OIB domain of so-called HIMU islands is much wider than the UCC domain. Consequently, in agreement with several other authors (Hofmann and White, 1982; Allègre and Turcotte,
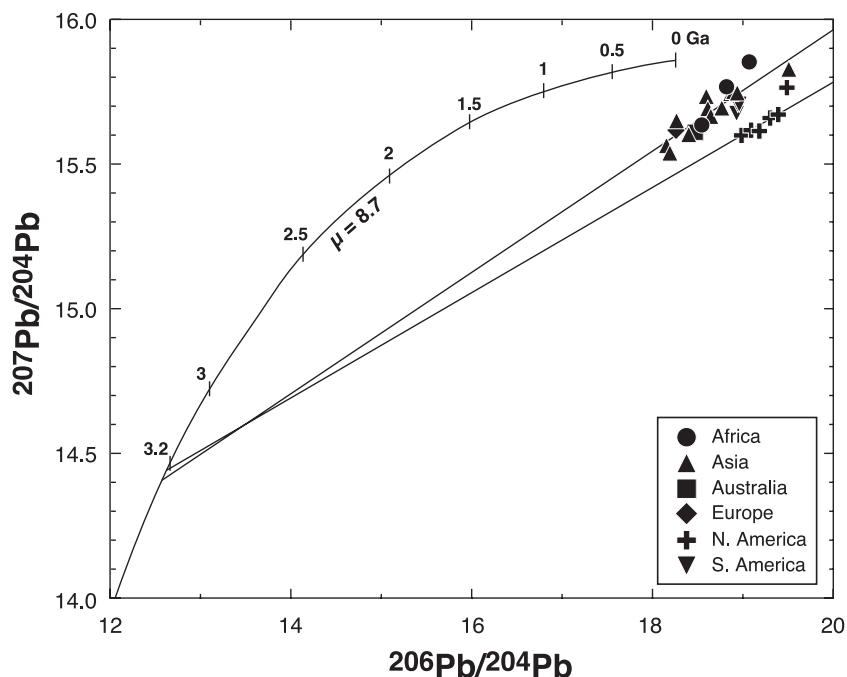

Fig. 9. $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ diagram on which the growth curve for the mantle evolution has been plotted ($\mu = 8.7$). The intersection of the two lines (for North American river sediments and the rest of the world) with the growth curve of the mantle give a mean model age of around 3.2 Ga for the differentiation of the Upper Continental Crust.

1985; Allègre et al., 1986/87; Hofmann, 1988; Hart, 1988; Chauvel et al., 1992), it is probably impossible to generate these isotopic signatures by the reinjection of UCC into the mantle. These isotopic signatures might, however, have been generated by the reinjection of oceanic crust stayed into the mantle something like 1 Ga (Hart, 1988; Allègre and Lewin, 1989).

7. Conclusions

We investigated the lead isotopic composition of river sediments from a very wide range of geological and climatic settings. Sediment samples from the mouths of these large river basins provide a useful tool to calculate average upper crustal composition because they represent large-scale integrated samples of the weathering products of the present day Upper Continental Crust.

Using these data, after disregarding some river basins due to possible anthropogenic contribution (based on excess lead in sediments), we have estimated a weighted average of the lead isotopic composition of the UCC.

Two different approaches were used to calculate these estimates. In the first, lead isotopic compositions of river sediments were weighted by the mass fraction of the particulate lead flux carried by the rivers to the oceans. We obtained values of 19.07, 15.74 and 39.35 for the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios, respectively. A second estimate, taking into account many more river basins, was calculated by weighting with drainage basin surface areas. We obtained the following mean lead isotopic compositions: 18.93, 15.71 and 39.03 for the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios, respectively.

These direct calculations of the lead isotopic composition of the UCC are similar and are in good agreement with previous estimates reported by Allègre and Lewin (1989), Asmerom and Jacobsen (1993) and Hemming and McLennan (2001) using an indirect approach.

Acknowledgements

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