



## Strontium isotopic record of signatures of Holocene fluvial sediments in the Loire valley, France

Philippe Négrel, Wolfram Kloppmann, Manuel Garcin, Denis Giot

### ► To cite this version:

Philippe Négrel, Wolfram Kloppmann, Manuel Garcin, Denis Giot. Strontium isotopic record of signatures of Holocene fluvial sediments in the Loire valley, France. *Hydrology and Earth System Sciences Discussions*, 2002, 6 (5), pp.849-858. 10.5194/hess-6-849-2002 . hal-00330842

**HAL Id: hal-00330842**

**<https://hal.science/hal-00330842>**

Submitted on 18 Jun 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Strontium isotopic record of signatures of Holocene fluvial sediments in the Loire valley, France

Philippe Négrel, Wolfram Kloppman, Manuel Garcin and Denis Giot

BRGM, Avenue C. Guillemin, BP 6009, 45060 Orléans Cedex 02, France

Email for corresponding author: p.négrel@brgm.fr

## Abstract

The distribution of Sr contents and isotopes of strontium Sr in the labile fraction of sediments from a channel fillings infill in the Middle Loire alluvial plain is used to highlight aspects of the evolution of the basin over the period from 10 000 yr. BP to the present. The acid extractable matter (AEM) in the sediment samples is variable in amount and in trace element contents. Carbonates and Fe–Mn oxyhydroxides are the principal carrying phases in the labile fraction. The historical record of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio variations in AEM shows two components. In the first, the AEM is consistently low (around 10%) and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios range from around 0.7086 to 0.710. This corresponds to the hydrous Fe–Mn oxides end-member. Fe–Mn oxyhydroxides originate from the Massif Central and their  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios display a larger range than present day Fe–Mn oxides. Furthermore, the mixing proportions between Fe–Mn oxides generated on granitoids and on basalts fluctuated only weakly in the past. The second component has greater AEM (20–50%) and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is almost constant at 0.709–0.7095. This corresponds to a carbonate endmember, clearly different from present day carbonates and may reflect the influence of both authigenic and detrital origins. The low  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio suggests a dominantly authigenic source for the carbonate endmember; this may be linked to groundwater inputs, although a minor influence from a secondary detrital source cannot be discounted. This reflects a different functioning of the river between deposition in the channel and the present day.

**Keywords:** River Loire, Holocene, fluvial dynamics, geochemistry, strontium isotopes

## Introduction

Numerous factors influencing erosion rates and catchment inputs include lithology and relief on the one hand and climate and human history on the other (Meade *et al.*, 1990). Most investigators interpret continental erosion from the composition of the sediment in large rivers as the way to study and promote general laws on continental erosion (Gaillardet *et al.*, 1997, 1999a, b). However, human activities often modify the sediment yield profoundly (Meade *et al.*, 1990; Macaire *et al.*, 1997). Rivers and streams carry the residual products from chemical and mechanical weathering as sediments, some 90% of which seem to be stored in the alluvium for tens or thousands of years (Meade, 1988).

The Loire River in central France is 1010 km long and drains a catchment of 117 800 km<sup>2</sup>, composed of various lithologies including old plutonic rocks (500–300 M yr old), a large volcanic area in the upstream section and carbonate deposits (200–6 M yr) in the central part. Changes with time in the distribution of chemical species in the present day suspended matter and bed load sediments collected over a

hydrological cycle (i.e. one year) at one site in the middle Loire catchment have been described by Négrel and Grosbois, 1999 and Négrel *et al.*, 2000). Once the present day mechanisms of trace metal transfer in a drainage basin, such as biological triggering of calcite and hydroxide precipitation (Grosbois *et al.*, 2000), are elucidated, some aspects of the evolution of the Middle Loire basin can be reconstructed.

In this paper, the distribution of acid-extractable Rb and Sr (cold 0.2N HCl, Négrel *et al.*, 2000; Négrel and Roy, 2002) from the labile fraction of the alluvial sediment in a clayey channel infilling deposited from 11 500 BP to the present is used to differentiate the different sediment sources and to compare present day transport mechanisms with those in the past. This allows the impacts of natural processes like erosion and groundwater inflows on catchment development during the Holocene to be distinguished. This should improve understanding of the functioning of the catchment with regard to anthropogenic impact.

## Materials and methods

### SAMPLING

The sampling site is situated in the middle part of the Loire River (Avaray Valley, Fig.1, Garcin *et al.*, 1999). The drainage basin upstream of the sampling site represents about 40% of the total Loire catchment and includes the entire silicate-dominated basement of the Massif Central and about 25% of the total area of sedimentary rocks (i.e. the Tertiary lacustrine deposits in the Limagne and the Jurassic, Cretaceous and Tertiary lacustrine and marine deposits of the Paris Basin). During the Late-glacial and Holocene, the substratum of the Avaray valley, consisting of Aquitanian lacustrine carbonate, was incised by the Loire River (Garcin *et al.*, 1999 and references therein) and numerous incisions, oxbows and channels related to meander migration have been identified. Five alluvial bodies were investigated (A to E in Fig.1, Garcin *et al.*, 1999). A core for geochemical analysis (M25B) was extracted from 6.3 m of Holocene sediments in an oxbow infilling. The channel infill deposits intersected by the M25B core were trapped over at least 8500 years. The description of the core

and the  $^{14}\text{C}$  ages (Garcin *et al.*, 1999, 2001) allow five main units to be defined. From 6.3 to 4.9 m (i, Fig.2), the sediment consists of coarse to fine sand; from 4.9 to 3.5 m (h to g, Fig.2), it comprises black peat as Middle Boreal (8410  $\pm$  70 BP) at the base and contains much ligneous debris and gastropods (6840  $\pm$  70 BP at 3.58 m); from 3.5 to 2.7 m (f to e, Fig.2), it consists of black clay, with well preserved gastropods and wood fragments (5350  $\pm$  60 BP at 2.77 m, end of Atlantic); from 2.7 to 1.0 m (d to c, Fig.2), the deposit is grey to green clay, with very sparse gastropod debris (3360  $\pm$  50 BP at 2.16 m, Sub-boreal, 2370  $\pm$  50 BP at 1.65 m, Sub-Atlantic); up to the top of the core, the sediment is brown clayey loam and soil (1.0-0.9 m; b to a, Fig.2).

The channel infill, thus, spans part of the Boreal, the Atlantic, the Sub-Boreal and probably a large part of the Sub-Atlantic. A peat bog prevailed for approximately 1500 years from the Boreal to the Middle Atlantic. The channel fill consists mainly of fine clayey sediments deposited during flooding of the river; there is a total absence of coarse clastics and sandy materials in the M25B core except in the lower part. Semi-quantitative XRD analysis of the sediment showed that quartz, K-feldspar, plagioclase and calcite are

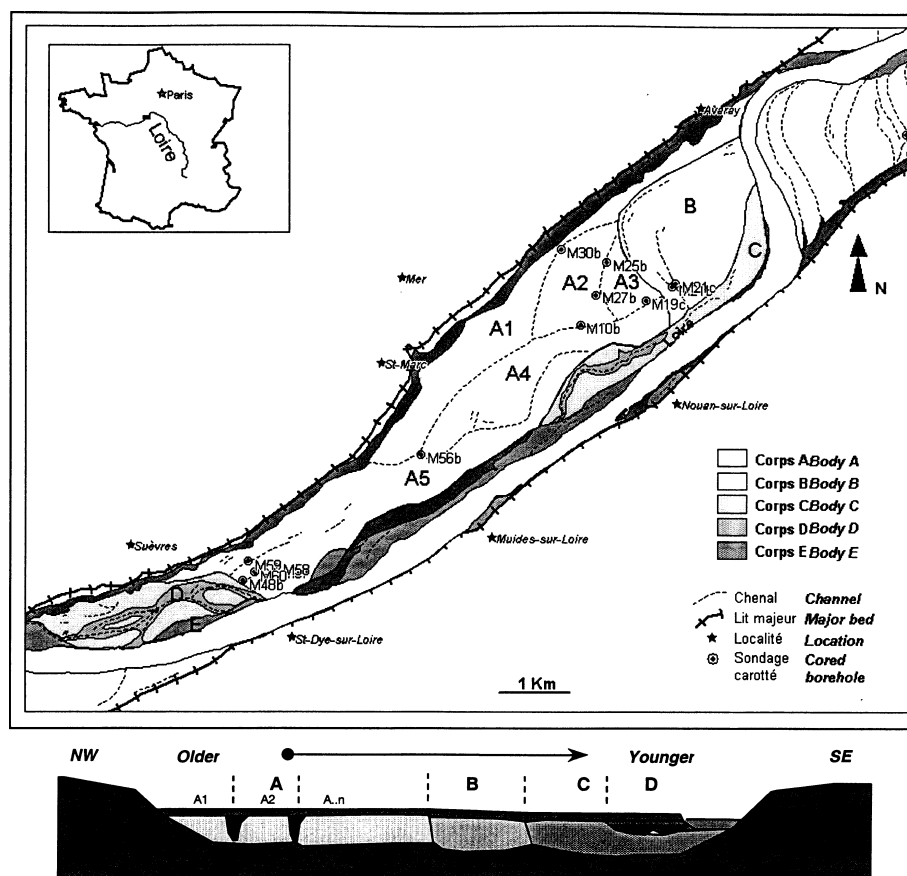


Fig.1. Map of the Val d'Avaray meander. Numbered core sites are indicated and the schematic cross section shows the meander structure and distribution of sediment bodies A-E (from Garcin *et al.*, 1999).

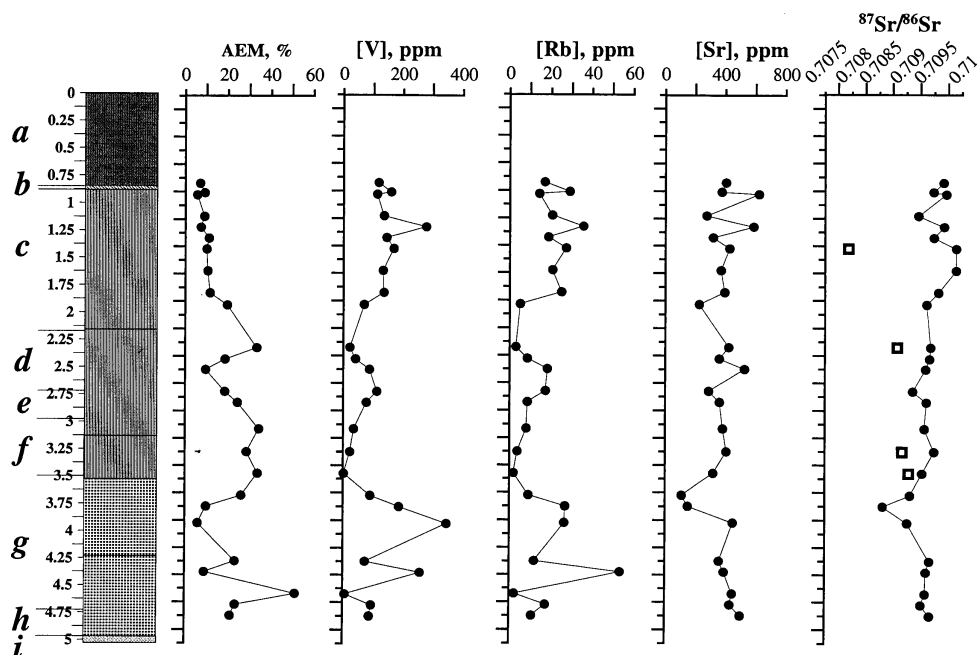


Fig. 2. Lithological log and selected sediment properties in the M25B core. AEM (%), trace elements ( $V$ ,  $Rb$ ,  $Sr$  in  $\mu\text{g g}^{-1}$ ) and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of the M25B are represented by black circles; open squares correspond to the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in gastropods. The sediment comprises: -coarse to fine sand from depths of 6.3 to 4.9 m (i); - black peat from 4.9 to 3.5 m (h to g); - black clay, with well preserved gastropods and wood fragments from 3.5 to 2.7 m (f to e); - grey to green clay from 2.7-1.0 m (d to c); brown clayey loam and soil from 1.0 to 0.9 m (b to a)

the main mineral components and that illite and kaolinite are the dominant clay minerals in the  $< 2\mu\text{m}$  fraction. From the core, 26 samples were collected from 0.8 m depth (lower limit of agricultural reworking) to the bottom of the core (6.3 m) (Table 1). Two further samples were collected from a second core (M30, Fig. 1) at a depth of 2.43 m (medium black sand,  $11,460 \pm 90$  BP, Garcin *et al.*, 1999) and 2.18 m (black clay). A sample of the Aquitanian lacustrine carbonate was collected from a third core (M19) at 5 m depth. Four gastropod tests were collected for analysis at depths of 3.45, 3.25, 2.3 and 1.4 m in the M25B core.

#### EXTRACTION OF THE TRACE ELEMENTS, DETERMINATION OF TRACE-ELEMENTS, AND $^{87}\text{Sr}/^{86}\text{Sr}$ RATIOS ISOTOPE MEASUREMENTS

Around 20 g of sediment, collected with plastic spatulas and stored in polypropylene boxes, were homogenised with double distilled water, sieved through a  $165\mu\text{m}$  nylon mesh and oven-dried at  $70^\circ\text{C}$ . Geochemists use reagents to separate the labile fraction from the residual fraction (Tessier *et al.*, 1979; Chester *et al.*, 1985; Elderfield and Sholkovitz, 1987; Négrel *et al.*, 2000; Négrel and Roy, 2002). In the present study, the labile fraction was extracted from the sediment load using acid leaching (cold 0.2N HCl, 1 h in

ultrasonic bath, Négrel *et al.*, 2000; Négrel and Roy, 2002). Three repetitive ultrasonic baths with double distilled water were used to clean the gastropod tests and the cleaned tests were dissolved in cold 0.2N HCl. This reagent releases the total inventory of non-residual trace elements, i.e. those associated with hydrous Fe-Mn oxides, adsorbed on clays, and occurring in carbonates and sulphides (Chester *et al.*, 1985; Elderfield and Sholkovitz, 1987).

After the extraction procedure, the solid residues of sediments and gastropod tests were separated by centrifuge. The quantity of acid-extractable matter (hereafter referred to as AEM), representing the labile fraction, was determined for each sample by the difference in weight between the initial dried sediment and that after the acid extraction, expressed as a percentage of the total matter content (Négrel *et al.*, 2000; Négrel and Roy, 2002). The error in the determination of AEM is approximately  $\pm 3\%$ . The HCl solution (e.g. the AEM) was evaporated, the residual product weighed and an aliquot analysed for trace elements and Sr isotopes.

The concentrations of Sr, Rb, in the AEM were determined by ICP-MS. The elemental concentrations were expressed in  $\mu\text{g per gram of matter}$  (e.g. the residual product of the acid extraction).

Standard cation exchange chemistry was adopted for

*Table 1.* Acid extractable matter (AEM) content of the sediment (mass %) and trace elements (V, Sr, and Rb in  $\mu\text{g g}^{-1}$ ) and Sr ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) isotope ratios in the AEM of samples from cores M25B, M30 and M19. Samples GAST refers to the gastropod tests collected at different depths in the M25B core.

<i>Ref</i>	<i>ECH</i>	<i>Depth</i> <i>m</i>	<i>AEM</i> <i>%</i>	<i>V</i> $\mu\text{g g}^{-1}$	<i>Mn</i> $\mu\text{g g}^{-1}$	<i>Sr</i> $\mu\text{g g}^{-1}$	<i>Rb</i> $\mu\text{g g}^{-1}$	$^{87}\text{Sr}/^{86}\text{Sr}$
M25B/1/53.5	M25B/A	0.80	7	117	1078	403	17	0.709662
M25B/2/2.5	M25B/Aa	0.89	9	159	880	375	29	0.709483
M25B/2/5/5	M25B/B	0.91	6	112	1913	621	14	0.709713
M25B/3/10	M25B/bA	1.10	9	135	1240	275	20	0.709210
M25B/3/20	M25B/C	1.20	7	277	1225	586	36	0.709675
M25B/3/30	M25B/Ca	1.30	11	144	798	318	19	0.709490
M25B/3/40	M25B/D	1.40	10	168	984	427	27	0.709894
M25B/3/60	M25B/E	1.60	11	132	1581	371	21	0.709893
M25B/3/80	M25B/F	1.80	12	135	2489	395	25	0.709574
M25B/3/91	M25B/Fa	1.91	20	69	1185	226	5	0.709360
M25B/5/30	M25B/G	2.30	33	22	658	422	3	0.709431
M25B/5/40.5	M25B/Ga	2.41	19	40	954	360	9	0.709413
M25B/5/50	M25B/H	2.50	10	87	1368	527	18	0.709342
M25B/5/70	M25B/Ha	2.70	19	112	385	290	17	0.709110
M25B/5/80	M25B/I	2.80	25	77	418	362	9	0.709356
M25B/6/5	M25B/J	3.04	34	35	412	383	8	0.709320
M25B/7/25	M25B/K	3.25	29	23	694	407	4	0.709494
M25B/7/45	M25B/L	3.45	34	2	267	320	2	0.709278
M25B/7/65	M25B/M	3.65	26	90	317	110	9	0.709059
M25B/7/75	M25B/Ma	3.75	10	187	448	151	27	0.708562
M25B/8/5	M25B/N	3.90	6	346	1124	450	26	0.709010
M25B/9/25	M25B/Na	4.25	23	73	762	359	12	0.709413
M25B/9/35	M25B/O	4.35	9	258	877	392	54	0.709350
M25B/9/55	M25B/P	4.55	52	6	370	447	2	0.709335
M25B/9/64	M25B/Pa	4.65	24	94	467	431	17	0.709261
M25B/9/75	M25B/Q	4.75	21	88	662	500	11	0.709416
M30/2.43	M30a	243	21	486	538	257	9	0.708986
M30/2.18	M30b	2.18	21	78	582	328	6	0.709140
M19/5	M19a	5.00	46	3	346	481	0	0.709124
M25B/3/40	GAST/A	1.40	100	nd	nd	299	0.29	0.707936
M25B/5/30	GAST/B	2.30	100	nd	nd	393	0.23	0.708826
M25B/7/25	GAST/C	3.25	100	nd	nd	349	0.15	0.708917
M25B/7/45	GAST/D	3.45	100	nd	nd	200	0.46	0.709036

chemical separation and mass spectrometry for strontium (Négrel and Deschamps, 1996; Négrel and Grosbois, 1999). Mass spectrometry analyses of Sr were performed on a Finnigan MAT 262 multiple collector mass spectrometer on a single W filament with a tantalum activator. The total blank for Sr was less than 0.5 ng for the entire chemical procedure. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were normalised to a  $^{86}\text{Sr}/$

$^{88}\text{Sr}$  ratio of 0.1194. The in-run precision of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is generally better than  $\pm 10 \cdot 10^{-6}$  ( $2\sigma$ ). The reproducibility of the  $^{87}\text{Sr}/^{86}\text{Sr}$  measurements was tested by replicate analysis of the NBS 987 standard and gave a mean value of  $0.710227 \pm 17 \cdot 10^{-6}$  ( $2\sigma$ ,  $n = 70$ ).

## Results and Discussion

### FLOOD SEDIMENTS, PROPORTION OF AEM AND ITS CHEMICAL COMPOSITION

In present day suspended matter in the Loire River, the proportion of AEM relating to the discharge of the river suggests two types of suspended matter corresponding to seasonal changes; one represents high flow conditions in winter and the other low flow conditions in summer (Négre $\acute{e}$ l *et al.*, 2000). During high flow conditions, the AEM is related mainly to erosion products, as indicated by the mineralogy of the suspended matter, which consists mainly of quartz, K feldspar and plagioclase derived from weathering of silicate basement in the Massif Central (Négre $\acute{e}$ l and Grosbois, 1999; Négre $\acute{e}$ l and Roy, 2002). Chemical and isotope data on present day suspended matter carried by the Loire River indicate that, during high flow conditions, suspended matter and its labile fraction AEM are provided mainly by erosion (e.g. Fe-Mn coatings on silicate particles, Négre $\acute{e}$ l *et al.*, 2000). Conversely, during low flow conditions, a rise in calcite contents in the AEM corresponds to a period of the hydrological cycle when CaCO<sub>3</sub> precipitation is dominant (Négre $\acute{e}$ l and Grosbois, 1999; Grosbois *et al.*, 2000).

The proportion of AEM ranged from 6% to 52% in the M25B and M30 cores (Table 1, Fig. 2). From 4.75 m to 3.75 m depth, the AEM percentage decreased irregularly upwards (Table 1). Between 3.75 and 2.5 m it increased and then decreased with a maximum of around 34% at a depth of 3.45–3.04 m. From 2.5 m to the top of the core, AEM decreased regularly, finally reaching a minimum of c. 6–9%. The AEM proportions are similar to those in present day suspended matter of the Loire River (8–47%, Négre $\acute{e}$ l *et al.*, 2000). Semi-quantitative XRD analysis of the sediment showed that quartz, feldspar and calcite are the main mineral components and the clay mineralogy in the < 4 $\mu$ m fraction is dominated by the interstratified smectite-illite (40 to 90%), illite and kaolinite make up the rest of the clay minerals. The positive correlation between calcite and AEM ( $r = 0.86$ ) indicates that the control of AEM content is mainly carbonate and the intercept of the AEM/calcite correlation line shows that the proportion of AEM not derived from carbonate is < 5%. No clear relationship was observed between AEM and clay mineral content. Fe-Mn oxyhydroxides (not detected by the XRD analysis) as well as organic matter could be responsible for some of the largest AEM amounts.

Each sample analysed during this study covers several years (e.g. around 50 years, Garcin *et al.*, 1999) and should contain authigenic, dominant in summer, as well as detrital material, dominant in winter. The detrital material is

provided by mechanical erosion of the river catchment. The source of authigenic material such as calcite, organic matter or Fe-Mn coatings on silicate particles can be local, i.e. *in situ* precipitation within the channel but authigenic material may also be created upstream and then transported as coatings on detrital particles (Robinson, 1993).

The V and Mn contents in the Loire sediments are both negatively correlated with AEM and the relationships between these elements and AEM can be explained by mixing of two endmembers, one of which is a carbonate relatively poor in V and Mn. The V and Mn contents of the Aquitanian lacustrine carbonate correspond to this potential endmember. The second endmember is rich in V and Mn but poor in AEM and could correspond to an oxide and organic matter reservoir. Schiller and Mao (2000) demonstrate that V in river water is correlated with U and Rb, all three elements being derived from silicate weathering. In the present Loire sediment samples, V and Rb contents are strongly correlated ( $r = 0.85$ ,  $n = 29$ , Fig. 3) and the lowest Rb and V contents occur in the lacustrine carbonate endmember. This indicates a silicate source for these elements, such as the basement of the Massif Central. In contrast, Sr does not show any statistically significant relationship with either AEM ( $r = 0.13$ ,  $n = 29$ ) or V ( $r = 0.14$ ,  $n = 29$ , Fig. 3). The removal of dissolved Sr, both by Fe-Mn oxy-hydroxides and by carbonate precipitation, may explain the lack of correlations, as demonstrated by Casanova *et al.* (1999) for hydrous iron oxides and carbonates precipitating at mineral spring outcrops in the Massif Central.

### STRONTIUM CONTENT AND ISOTOPIC VARIATIONS

In core M25B, the Sr content shows large variations from 110 to 621  $\mu\text{g g}^{-1}$  (Fig. 2). From 4.75 m to a depth of 3.90 m, the Sr contents are within the range of the Aquitanian lacustrine carbonate (i.e. 481  $\mu\text{g g}^{-1}$ , Table 1) but then decrease to values of 160  $\mu\text{g g}^{-1}$  near 3.65 m depth. At this depth in the core, the lowest Sr content is reached (around 110 ppm). Between 3.65 and 3.45 m, Sr values increase again, then remain fairly constant with a mean of 350  $\mu\text{g g}^{-1}$ ; however, towards the top of the core, values are more erratic. Samples from the M30 core have a similar range of Sr contents, with 257  $\mu\text{g g}^{-1}$  at 2.43 m depth and 328  $\mu\text{g g}^{-1}$  at 2.18 m depth.

The abundance of the radiogenic isotope  $^{87}\text{Sr}$ , which is produced by the radioactive decay of  $^{87}\text{Rb}$ , is a function of age and of the Rb/Sr ratio. In general, continental sediments rich in carbonates and hydroxides as well as organic matter are in isotopic equilibrium with the water phase from which

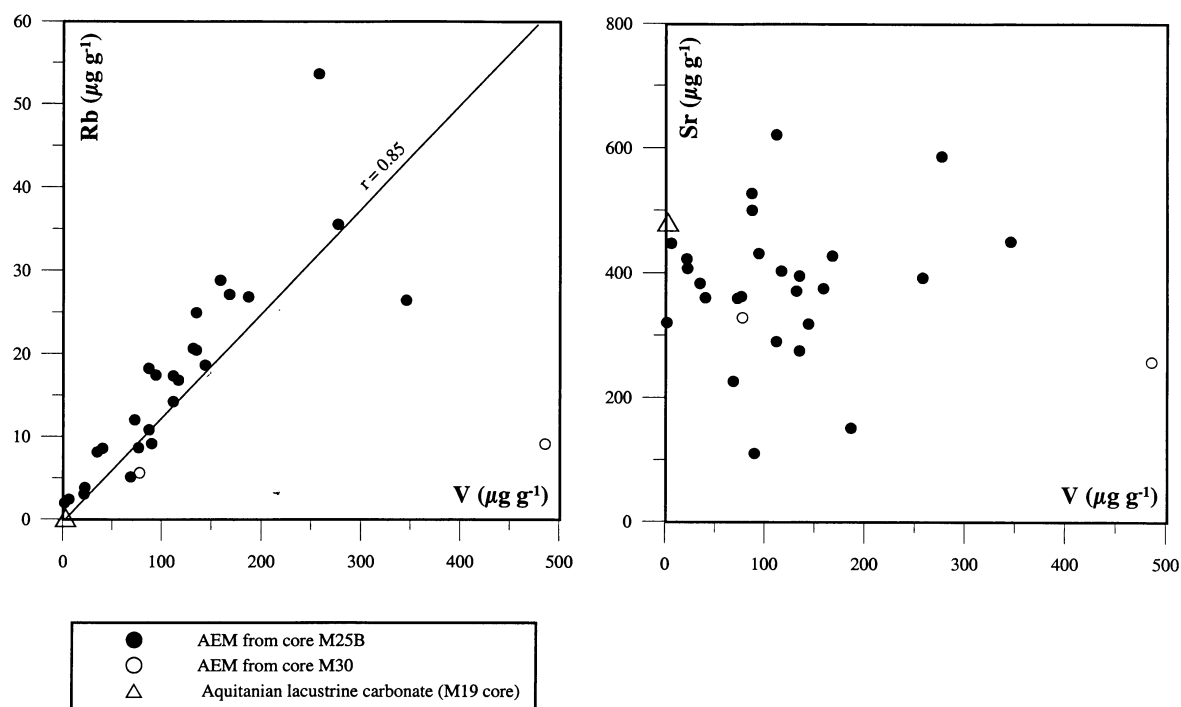


Fig. 3. Relationship between vanadium, rubidium and strontium contents in AEM from core M25B. Two samples from the M19 core (open circles) and one from the Aquitanian lacustrine carbonate from core M30 (open triangle) are shown.

these compounds were precipitated (Casanova *et al.*, 1999). This implies that the strontium Sr isotopic composition of the labile fraction can be used as a proxy for the Sr isotopic composition of these waters at the time these phases were precipitated (Casanova and Négrel, 1995; Négrel *et al.*, 1997a; Holmden *et al.*, 1997; Vonhof *et al.*, 1998). This is valuable for studying long term variations in the catchment. In the M25B core, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio varies from *c.* 0.70856 at 3.75 m depth to 0.70989 at 1.4 and 1.6 m and generally increases from the base to the top of the core (Fig. 3). Most of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from the M25B core are much greater than those in the lacustrine carbonate (0.70912, Table 1). Three of the four points that display  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios less than those in the lacustrine carbonate are around 3.75 m depth in the core.

The Sr contents of the four gastropod tests ranged from 200  $\mu\text{g g}^{-1}$  (3.45 m) to 393  $\mu\text{g g}^{-1}$  (2.3 m), and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from 0.70794 at 1.4 m to 0.70904 at 3.45 m (Fig. 2). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in gastropod tests correspond to those of the water in which they lived and, therefore, record changes in the Sr isotopic composition of water through time. In spite of the small number analysed, most of them have different  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from those of the AEM (Fig. 2). At 3.45 m depth, the ratios in AEM and gastropods are almost the same but, nearer the surface, they diverge and the largest difference occurs at 1.4 m depth. The fluctuation

of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios measured from gastropod samples implies that the Sr isotopic composition of the water varied over the time span in which they lived.

#### EVALUATION OF SEDIMENT SOURCES FROM $^{87}\text{Sr}/^{86}\text{Sr}$ RATIOS

The Sr content does not show any statistically significant relationship with AEM ( $r = 0.13$ ). The removal of dissolved Sr, both by Fe-Mn oxyhydroxides and by carbonate precipitation, may explain the lack of correlations, as demonstrated by Casanova *et al.* (1999) for hydrous iron oxides and carbonates in the Massif Central. Therefore, variations in the Sr isotope ratio of AEM reflects the mixing of Sr with different Sr isotope signatures from two or more sources.

The removal of dissolved Sr by both oxides and carbonates implies that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio cannot be compared directly with the Sr content in classical mixing diagrams (Faure, 1986). Following the methodology of Négrel *et al.* (2000), a hyperbolic relationship between  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios and AEM has been used to identify the theoretical endmembers. (Langmuir *et al.*, 1978). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios plotted against AEM concentrations (Fig. 4) for the present day suspended load analysed by Négrel *et al.* (2000) illustrate a mixing hyperbola, likely to reflect the simple binary mixing which

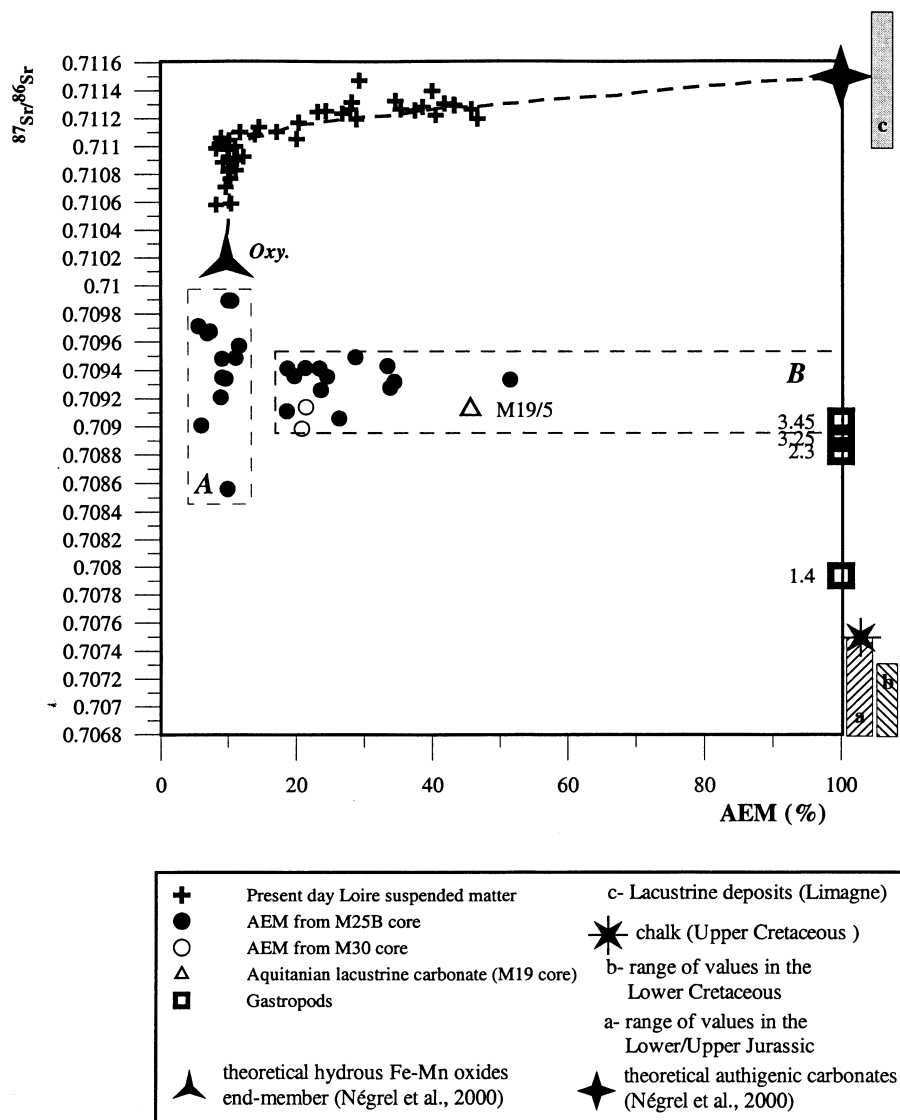


Fig. 4. Relationship between the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the AEM and the total AEM (%) in the M25B core (black circles). Two samples from the M19 core (open circles) and one from the Aquitanian lacustrine carbonate from the core M30 (open triangle) are shown. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the AEM of the present day suspended particulate matter of the Loire River (data from Négrel et al., 2000) are also shown (black crosses). The curve represents the calculated mixing line which relates the theoretical authigenic carbonate endmember to the theoretical hydrous Fe-Mn oxides endmember. Open squares correspond to the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in gastropods (adjacent numbers are depths in the core). The shaded fields represent the various basement rocks from the Loire catchment. Field A (low AEM proportion) is thought to correspond to the dominant influence of the hydrous Fe-Mn oxides endmember. The field B corresponds to carbonate in the sedimentary column

relates the theoretical authigenic carbonate endmember to the theoretical hydrous Fe-Mn oxides endmember. The highest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, close to the authigenic carbonate endmember, are identical to the mean value of dissolved Sr during low flow; the low Sr isotope ratios in AEM measured during high flow ( $\sim 0.7105$ ) differ from those of the dissolved load during low flow ( $0.71143 \pm 0.00020$ ,  $n = 23$ ) (Grosbois et al., 2000; Négrel et al., 1997b, c). The isotopic signature of hydroxides should reflect that of the water from

which they originated. The present day oxides may, therefore, originate in the Massif Central whence they are transported to the sampling point by the upper Loire River and tributaries (Négrel et al., 2000; Négrel and Roy, 2002).

The Holocene record of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in AEM shows data dispersion falling clearly into two fields (A and B) as illustrated by Fig. 4. When AEM is lower than 10% (field A), the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios show a large range from around 0.70860 to 0.70989. This low AEM proportion is thought



to correspond to the dominant influence of the hydrous Fe-Mn oxides endmember. The highest  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio found in the M25B core (1.4 and 1.6 m depth) is similar to that of this the theoretical Fe-Mn oxides endmember defined in present day suspended matter (Négrel *et al.*, 2000). If Fe-Mn oxides originate from the Massif Central, they could have derived their Sr from the weathering of the different bedrock formations in this area. Around 65% of the crystalline basement in the Massif Central consists of granitoids rocks (Pin and Duthou, 1990) emplaced during the Hercynian orogeny. Most of the remaining rocks consist of Tertiary and Quaternary basalts from Tertiary and Quaternary volcanism. Weathering of these silicate rocks yields Sr isotope ratios that range between 0.7030 and 0.7050 for basalt and between 0.7135 and 0.7176 for granite and gneiss (Négrel and Deschamps, 1996; Négrel *et al.*, 1997b, c; Négrel, 1999). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of present day hydroxides for AEM in basalts and granite derived sediments (i.e. 0.7038–0.7049 and 0.714–0.7173, respectively, Négrel and Roy, 2002) is in isotopic equilibrium with the water phase in which they formed. The range in  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the 'oxide' component within field A suggests that the relative proportions of Fe-Mn oxides derived from granitoids and basalts fluctuated only weakly in the past.

The second field (field B in Fig. 4) in the Holocene sedimentary record has greater AEM values (20–50%). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is fairly constant (around 0.709–0.7095) so that there is no covariance of AEM and Sr isotope ratios. An important feature of the Sr isotope signature of field B is its inconsistency with the value of the present day AEM-rich authigenic carbonate (Fig. 4) and with the actual Loire River water at low flow in the main channel ( $0.71143 \pm 0.00020$ ,  $n = 23$  Grosbois *et al.*, 2000; Négrel *et al.*, 2000). Likewise, most of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in field B display values higher than those found in the Aquitanian lacustrine carbonate.

If the carbonate sample occurring in field B is entirely authigenic, the discrepancy between the sedimentary record and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the Loire River water may reflect a change in the Sr isotope signature of the Loire dissolved load in the past. Hence, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the water may have fluctuated in the range observed for the AEM from the sediment cores. However, a detrital origin for the carbonate source cannot be rejected.

#### EVIDENCE OF GROUNDWATER INPUTS

The first step in determining whether the carbonate in field B is authigenic in origin is to investigate the change in the Sr isotope signature of the water. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in

gastropods from the M25B core decreases towards the surface (0.70904–0.70794, Figs. 2 and 4); this suggests a variation in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the water through time. This could have resulted from inputs of local groundwater, or the Sr isotope signature could have changed in the upper catchment. However, changes over time in the Sr isotope composition of the Loire River water in the main channel is unlikely. The Loire flows from silicate basement rocks (basalts, granite and gneiss) to the lacustrine carbonate deposits in the Limagne ( $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the range 0.711–0.712) (Briot and Poidevin, 1998) and marine Jurassic and Cretaceous deposits of the Paris Basin (BRGM, 1996); this suggests that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the dissolved load, even in past times, would be a mixture of low Sr isotope ratios derived from weathering of basalts and Jurassic and Cretaceous rocks and higher Sr isotope ratios derived from granites and lacustrine carbonates in the Limagne. This agrees with the present day  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios from the Allier River (Négrel *et al.*, 1997b) and at the Loire-Allier confluence (Petelet-Giraud *et al.*, 2001) which crosses all bedrocks; these range from 0.70951 (low water) to 0.71266 (high water).

Inputs of local groundwater from the aquifer located in the Aquitanian lacustrine carbonate (Beauce aquifer) should have a  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio similar to that of the bedrock (i.e. the Aquitanian lacustrine carbonate). The bedrock has a Sr isotope ratio similar to that for the gastropod sample from 3.45 m depth, but the progressive decrease in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the other gastropods nearer the surface suggests that another aquifer, with a lower  $^{87}\text{Sr}/^{86}\text{Sr}$  could also have provided groundwater in the area. The most likely candidate is the Upper Cretaceous chalk aquifer, because the chalk has yielded  $^{87}\text{Sr}/^{86}\text{Sr}$  values ranging from 0.7075 to 0.7077 (Fig. 4, Négrel *et al.*, 1989). The Sr isotopic composition of Lower and Upper Jurassic rocks is similar to that of the Upper Cretaceous chalk (Fig. 4) but cannot be the source of the low Sr isotope ratios in the gastropods because there is no hydraulic connection between these rock units and the sample site, but the lack of hydraulic connection does not allow the Jurassic to be the source of the low Sr isotopic composition.

Therefore, the most likely causes of changes in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the oxbow channel of the Loire River are fluctuations in the influence of groundwater from the Beauce and chalk aquifers. However, if the carbonate occurring in the field B were detrital in origin, the highest  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio observed within this field cannot be explained solely by contributions from the Aquitanian lacustrine carbonate so that inputs from another source with higher values of  $^{87}\text{Sr}/^{86}\text{Sr}$  must be presumed. Several areas may have provided detrital particles (lacustrine deposits of the Limagne and/or

marine Jurassic and Cretaceous deposits of the Paris Basin). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of material leached from suspended matter in rivers draining only one sedimentary facies in the Paris Basin are: Lower Jurassic (0.7086), Upper Jurassic (0.7076), Lower Cretaceous (0.7093) and Upper Cretaceous (0.7081) (Négrel *et al.*, 1989). These ranges suggest that the high  $^{87}\text{Sr}/^{86}\text{Sr}$  sources (close to 0.7094) of detrital particles in the carbonate occurring in field B would most likely be lacustrine deposits of the Limagne and the Lower Cretaceous marine deposits of the Paris Basin.

## Conclusion

In the clayey channel infilling in the alluvial plain of the Middle Loire River (France), which covers the period from the Boreal to the Sub-Atlantic, strontium in both the carbonate and the non-carbonate fractions is weakly correlated with AEM. Two important differences between the Sr isotope ratios of AEM in the sediment column and those of modern suspended matter in the Loire River are:

- (i) the small amounts of carbonate show lower and more variable  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the alluvial sediments than in the modern suspended matter. This may be due to different proportions of the potential sources, granites and metamorphic rocks on the one hand and basalts on the other.
- (ii) compared with the modern carbonate endmember in isotopic equilibrium with dissolved Sr in the Loire river, that in the sedimentary column has lower  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, similar to those of both the lacustrine limestone and three of the four gastropods analysed. Since the latter reflect the isotopic composition of dissolved Sr, the AEM from carbonates in the sediments may be authigenic rather than detrital in origin. Groundwater with an isotope signature acquired during percolation through the lacustrine limestone seems to have contributed to the carbonate in the channel sediments. However, a change in Sr isotopic composition of the carbonate may reflect a change over time in the detrital or dissolved contributions from the widespread Jurassic and Cretaceous carbonate rocks in the Loire catchment.

## Acknowledgements

This work was supported financially by the programme 'Morphogénèse Fluviale' in the BRGM Research Division. The Sr isotope analyses were provided by C. Guerrot (TIMS team); A. Cocherie (ICP-MS team), at the joint BRGM-INSU-CEA at Saclay (France), provided the trace elements

results. The authors also thank P. Skipwith for improving the English.

## References

- BRGM., 1996. *Carte géologique de la France au 1/1.000.000, 6ème édition*.
- Briot, D. and Poidevin, J., 1998. Stratigraphie  $^{87}\text{Sr}/^{86}\text{Sr}$  de quelques laminites carbonatées du Rupélien supérieur du fossé de Limagne : incursions marines dans le rift du Massif central français? *C. R. Acad. Sci., Ser. IIA*, **326**, 479–483.
- Casanova, J. and Négrel, Ph., 1995. Signature isotopique et origine des carbonates des sédiments de la longue séquence carottée du Lac d'Annecy (Haute Savoie). In: *Proceedings of the 16th Regional European Meeting IAS*, Aix les Bains 1995, 31pp.
- Casanova, J., Bodéan, F., Négrel, Ph. and Azaroual, M., 1999. Microbial control on the precipitation of ferrihydrite and carbonate modern deposits from the Cézallier hydrothermal springs (Massif Central, France). *Sediment. Geol.*, **126**, 125–145.
- Chester, R., Kudoja, W.M., Thomas, A. and Towner, J., 1985. Pollution reconnaissance in stream sediments using non-residual trace metals. *Environ. Pollut.*, **10**, 213–238.
- Elderfield, H. and Sholkovitz, E.R., 1987. REE in the pore-waters of reducing nearshore sediments. *Earth Planet. Sci. Lett.*, **82**, 280–288.
- Faure, G., 1986. *Principles of Isotope Geology*. Wiley, Chichester, UK. pp 588.
- Gaillardet, J., Dupré, B., Allegre, C.J. and Négrel, Ph., 1997. Chemical and physical denudation in the Amazon River Basin. *Chem. Geol.*, **142**, 141–173.
- Gaillardet, J., Dupré, B. and Allegre, C.J., 1999a. Geochemistry of large river suspended sediments: Silicate weathering or recycling tracer? *Geochim. Cosmochim. Acta*, **63**, 4037–4051.
- Gaillardet, J., Dupré, B., Louvat, P. and Allegre, C.J., 1999b. Global silicate weathering and  $\text{CO}_2$  consumption rates deduced from the chemistry of large rivers. *Chem. Geol.*, **159**, 3–30.
- Garcin, M., Giot, D., Farjanel, G., Gourry, J.-C., Kloppmann, W. and Négrel, Ph., 1999. Tardiglacial and Holocene deposits in the Middle Loire River, the Val d'Avaray case study (Loir et Cher, France). *C. R. Acad. Sci. IIA*, **329**, 405–412.
- Garcin, M., Giot, D. and Farjanel, G., 2001. Radiocarbon dating and palynology of alluvial deposits in the Loire flood plain (Val d'Avaray, Loir et Cher, France). *Quaternaire*, **12**, 1–2, 14 p.
- Grosbois, C., Négrel, P., Fouillac, C. and Grimaud, D., 2000. Chemical and isotopic characterization of the dissolved load of the Loire river. *Chem. Geol.*, **170**, 179–201.
- Holmden, C., Creaser, R. A. and Muehlenbachs, K., 1997. Paleosalinities in ancient brackish water systems determined by  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in carbonate fossils: A case study from the Western Canada Sedimentary Basin. *Geochim. Cosmochim. Acta*, **61**, 2105–2118.
- Langmuir, C.H., Vocke, R.D. and Hanson, G.N., 1978. A general mixing equation with application to Icelandic basalts. *Earth Planet. Sci. Lett.*, **37**, 380–392.
- Macaire, J.J., Bossuet, G., Choquier, A., Cocirta, C., De Luca, P., Dupis, A., Gay, I., Mathey, E. and Guenet, P., 1997. Sediment yield during late glacial and Holocene periods in the Lac Chambon watershed, Massif Central, France. *Earth Surf. Process. Landf.*, **22**, 473–489.
- Meade, R.H., 1988. Movement and storage of sediment in river systems. In: *Physical and chemical weathering in geochemical cycles*, A. Lerman and M. Meybeck (Eds.), Kluwer, Dordrecht, The Netherlands 165–180.

- Meade, R.H., Yuzyk, T.R. and Day, T.J., 1990. Movement and storage of sediment in rivers of the United States and Canada. In: *The geology of North America, Surface water hydrology*. Geol. Soc. of America, 255–280.
- Négrel, Ph., 1999. Geochemical study of a granitic area- the Margeride mountains, France: chemical element behaviour and  $^{87}\text{Sr}/^{86}\text{Sr}$  constraints. *Aquat. Geochem.*, **5**, 125–1650.
- Négrel, Ph. and Deschamps, P., 1996. Natural and anthropogenic budgets of a small watershed in the Massif Central (France): Chemical and strontium isotopic characterization in water and sediments. *Aquat. Geochem.*, **2**, 1–27.
- Négrel, Ph. and Grosbois, C., 1999. Changes in distribution patterns of chemical elements and  $^{87}\text{Sr}/^{86}\text{Sr}$  isotopic signature isotopic signatures in suspended matter and bed sediments transported out by the upper Loire River watershed (France). *Chem. Geol.*, **156**, 231–249.
- Négrel, Ph. and Roy, S., 2002. Investigating the sources of the labile fraction in sediments from silicate-drained rocks using trace elements, and strontium and lead isotopes. *Sci. Total Environ.*, **298**, 163–182.
- Négrel, Ph., Dupré, B., Seimbille, F., Birck, J.L. and Allegre, C.J., 1989. Erosion on the Seine-Yonne basin studied with the strontium isotopes. *Terra Nova*, **1**, 100.
- Négrel, Ph., Casanova, J. and Nicoud, G., 1997a. Caractérisation isotopique (O, C, Sr) des flux sédimentaires Quaternaires du bassin versant du lac d'Annecy. *Bull. Soc. Géol. France*, **168**, 243–253.
- Négrel, Ph., Fouillac, C. and Brach, M., 1997b. Occurrence of mineral water springs in the stream channel of the Allier River (Massif Central, France): chemical and Sr isotope constraints. *J. Hydrol.*, **203**, 143–153.
- Négrel, Ph., Fouillac, C. and Brach, M., 1997c. A strontium isotopic study of mineral and surface waters from the Cézallier (Massif Central, France): implications for the mixing processes in areas of disseminate emergences of mineral waters. *Chem. Geol.*, **135**, 89–101.
- Négrel, Ph., Grosbois, C. and Kloppmann, W., 2000. The labile fraction of suspended matter in the Loire river (France): multi-element chemistry and isotopic (Rb-Sr and C-O) systematics. *Chem. Geol.*, **166**, 271–285.
- Petelet-Giraud, E., Négrel, Ph., Barbier, J. and Gautier, E. 2001. Surficial and ground water relations in the loire catchment (France). An isotopic characterization focuses on a wetland in the upper basin. In: *11th Annual V.M. Goldschmidt Conference, Abstracts 3222- LPI contribution n°1088*, Lunar and Planetary Institute, Houston (CD-ROM).
- Pin, C. and Duthou, J.L. 1990. Sources of Hercynian granitoids from the French Massif Central: Inferences from Nd isotopes and consequences for crustal evolution. *Chem. Geol.*, **83**, 281–296.
- Robinson, G.D., 1993. Major element chemistry and micromorphology of Mn-oxides coatings on stream alluvium. *Appl. Geochem.*, **8**, 633–642.
- Schiller, A.M. and Mao, L., 2000. Dissolved V in rivers: effects of silicate weathering. *Chem. Geol.*, **165**, 13–22.
- Tessier, A., Campbell, P.G.C. and Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.*, **51**, 844–851.
- Vonhof, H.B., Wesselingh, F.P. and Ganssen, G.M., 1998. Reconstruction of the Miocene western Amazonian aquatic system using molluscan isotopic signatures. *Palaeogeog. Palaeoclim. Palaeoeco.*, **141**, 85–93.