TEMPORAL VARIATIONS OF SR ISOTOPIC RATIOS, MAJOR AND TRACE ELEMENTS COMPOSITION OF THE OUBANGUI RIVER BASIN : IMPLICATIONS FOR THE SOURCE OF MATERIAL.

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ABSTRACT

Strontium isotopic ratios have been measured for dissolved and suspended loads firstly on samples taken monthly from the Oubangui River in Central African Republic. Secondly, on samples taken on time of high discharge from all of the rivers of this drainage basin.

For the dissolved load of the Oubangui river, the 87Sr/86Sr ratios range from 0.7185 to 0.7205 between times of low and high discharge. We observe also a general decrease of major and trace element concentrations (Cl, Ca, Na, Mg, Sr) associated with the increasing discharge. These variations cannot be explained simply by dilution of the basic flow by an input of rain water, because the mean strontium isotopic composition of rain water in CentralAfrica (0.7104) is not consistent with the increase of the 87Sr/86Sr ratio on the Oubangui River.

For all the samples, the 87Sr/86Sr ratios measurement is associated with major and trace cation ratios (Na/Sr, Ca/Na) determination. The coupled variation of isotopic ratios and major element contents clearly implies that on the small watershed, a part of the variation in cation ratios results from the mixing of at least two different water pools. The 87Sr/86Sr ratios of springs and on the soluble fraction of soil samples implies that the first pool is located in calcareous rocks (which are not exposed) and the second in the soil zone. A two component mixing model shows a predominance of the soil reservoir during the rainy season. On the Oubangui River, the existence of a third pole is clearly shown on low water period. This third component is linked with the hydrological functioning of this basin. On low water period, the Uele River is the principal tributary of the Oubangui River. The Uele River drains an 2000 M. a. granite-gneiss basement and exhibits isotopic and cation characteristics different from those of the other reservoirs.

For the suspended load, the isotopic data range from 0.741 to 0.723 between times of high and low discharge. Associated with these variations, the strontium concentrations exhibit great variations (45 to 160 ppm). These results show that the suspended load carried by the Oubangui River during the year have not a single origin. We proposed that the clay minerals came either from different levels of the weathering profile or from different areas (as dissolved load), and contribution differently as a time function. The isotopic heterogeneity originates in the existence of waters in the soils zone of different isotopic composition.
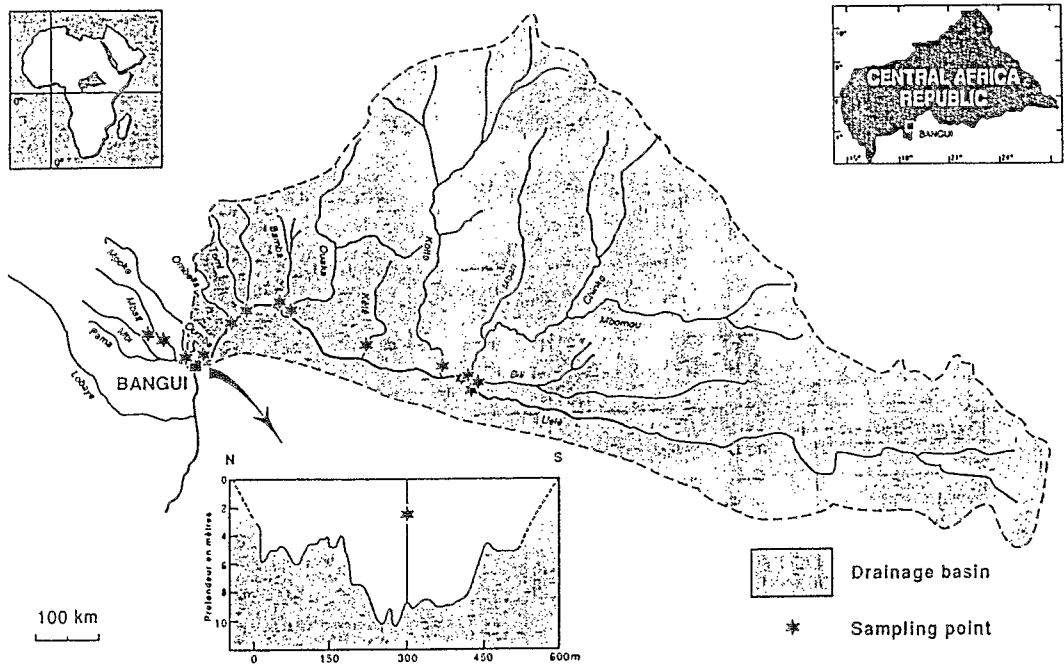
1 - INTRODUCTION

The chemical and isotopic surface water characteristics result from chemical weathering of different rock types. Investigation of the variations in major and trace elements chemistry of a river reveal informations about hydrological functioning and weathering processes (Gibbs, 1972; Miller and Drever, 1977; Stallard and Edmond, 1981; Sarin et al., 1989). Investigation of variations in isotopic compositions of a river help us understand the cycle of elements (Wadleigh and Veizer, 1985; Stettler and Allegre, 1977; Goldstein and Jacobsen, 1987, 1988; Sarin et al., 1990). The large basin (like Amazon, Congo...) study require the knowledge of the different element sources (Carbonnel and Meybeck, 1975; Stallard, 1980; Sarin et al., 1989).

The purpose of this study is to examine the strontium isotopic variations of dissolved and suspended loads of a tropical drainage basin in complement of major and trace elements investigation in order to improve the knowledge of these sources. Rocks of different characteristics release strontium into surface waters by chemical weathering. The strontium isotope ratio is quite different as a rock type function provides different 87Sr/86Sr ratios. Waters which drains old rubidium rich silicates rocks exhibit high 87Sr/86Sr and low Sr content (Steele and Pushkar, 1973; Wadleigh and Veizer, 1985). On the contrary, water draining rubidium poor rocks such as carbonates have low 87Sr/86Sr ratios (Albarède and Michard, 1987) because these
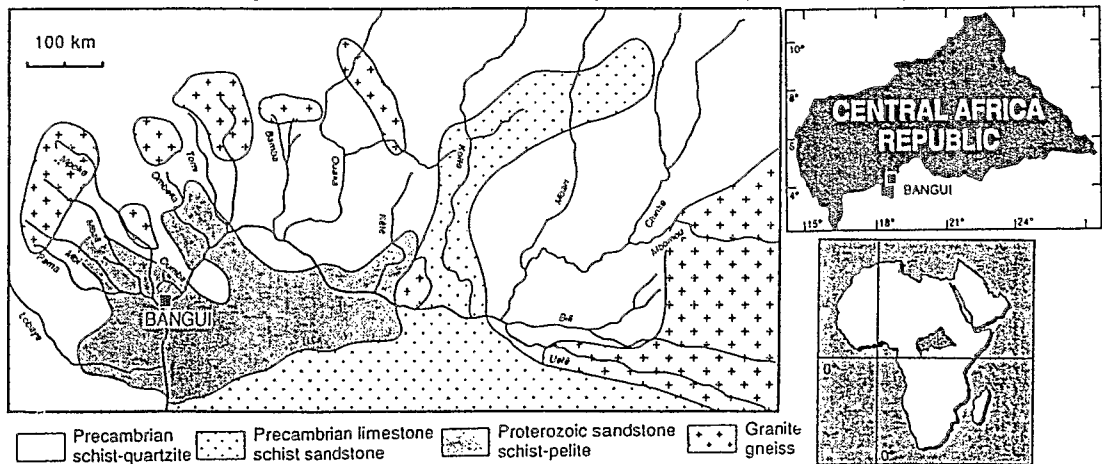
ratios are related with the strontium isotopic composition of sea-water at time of deposition (Veizer and Compston, 1974).

2 - THE OUBANGUI BASIN

The Oubangui drainage basin is located in the centre of the African continent (Fig. 1). This basin extends on the Central African Republic from 25°E (Sudan - Uganda) to 15°E (Congo) and from 10°N to 4°N (Congo - Zaire).

Figure 1
Oubangui river and its tributaries drainage basin. Sample location map.

Precambrian schist-quartzite   Precambrian limestone schist sandstone   Proterozoic sandstone schist-pelite   Granite gneiss

Figure 2
Geologic and lithologic map of the Oubangui river drainage basin.

The Oubangui river drainage basin occupies an area of about 619,000 Km2 at the Oubangui - Congo - Zaire confluence (Olivry et al., 1988). At the Bangui station, this drainage basin is about 480,000 Km2 (Boulvert, 1987). The Oubangui tributaries came as a whole from the right bank and implies a dissymmetrical form for the drainage basin (Fig. 1).

The main stream of the Oubangui is formed after the confluence of the Uele and Mbomou rivers. The Uele river comes from the Zaïre equatorial forest, the Mbomou river is more tropical. From its origin to Bangui, the Oubangui river shows great variations in its flow trend: E-W up to the confluence Oubangui-Tomi and then N-S. The river gauge range from 100 m to 1500 m. The mean grade is weak, around 0.09m. km-1 (Boulvert, 1987). This implies a weak erosion power and a younger origin from the actual course of the river (Boulvert, 1987).

The geological structure of the Oubangui basin is mainly represented by a vast peneplanation surface. This surface is strongly eroded and is only perceptible as residual hill (Cornacchia and Giorgi, 1976). Several types of geological features have been recognised in this basin. The simplified geological map (Fig. 2) shows that the Oubangui basin is occupied mainly by 2 geological units (Cornacchia and Giorgi, 1976; Poidevin, 1985).

(1) The basal complex with crystalline (granite-gneiss) and metamorphic rocks (schists, quartzite, micaschists)

(2) The sedimentary cover with sandstones, limestones, pelites.

These differents rock types are Proterozoïc (Cornacchia and Giorgi, 1976; Poidevin, 1985). The results of U-Pb Zircon, Rb-Sr and Sm-Nd whole rocks analyses from the Central African basement in Cameroon and Central African Republic (Pin and Poidevin, 1987; Lasserre et al., 1976) clearly show two mains generations of rocks. U-Pb, Rb-Sr and Sm-Nd give an Paleoproterozoic age (800 M.a. - 2200 M.a.). Rb-Sr on granitic whole rocks give a Neoproterozoic age (500-700 M.a.)

The soils present in this area are greatly developed, largely ferralitic and ferruginous (Kinga-Mouezo, 1986, Boulvert and Salomon, 1988), more or less coloured. Previous studies (Kinga-Mouezo, 1986, Boulvert and Salomon, 1988) indicate that kaolinite is the principal clay mineral. For the most part, the soils are indurated by a lateritic or ferruginous cuirass. This induration is more important on acid than on basic rocks (Boulvert and Salomon, 1988).

The geographic situation of this basin in the Northern hemisphere ($\sim$ 4°N) awards a contrasted climate (tropical-boreal climate). Rainy and dry seasons characterise this climatic rhythms. The mean annual rainfall for the drainage basin vary between 1540 mm. y-1 at the Bangui station and more than 1600 mm. y-1 in area which are not preserved by hills (Callede and Arquisou, 1972). Estimates of potential evaporation (ETP) for tropical Central Africa (Riou, 1972) show good agreement with the real evaporation (ETR). The mean monthly rainfall can be used in conjunction with the mean potential evaporation, to evaluate the term Δ involving the water shortage ($\Delta < o$) or the water excess ($\Delta > o$). The calculation shows that between May and November, this parameter is positive and negative between December and April.

The annual discharge fluctuations of the basin rivers regime are mainly determined by the climatic conditions (rainfall, evaporation) and the proper characteristics of the drainage basin (hydrogeology, topography). These fluctuations are typical for the tropical zone (Rodier, 1983; Nkounkou, 1989). The mean water discharge data for the Oubangui river (Fig. 3) shows that the moderate peak discharge occurs between January and March while the peak load occurs in October-November (Olivry et al., 1987; 1989).

3 - SAMPLING METHODOLOGY; SAMPLING COLLECTION ANALYTICAL METHODS

The river samples were collected from several locations (Fig. 1) along the Oubangui main stream and its tributaries. 3 types of sampling have been made with the O.R.S.T.O.M hydrologists co-operation. Firstly, on the Oubangui river, samples were taken monthly during one year. Surface water was sampled at the Bangui St Paul station (Olivry et al., 1987). This station is the outlet of the basin before the important shift of outflow direction (E-W to N-S). The sampling site location depth situation is detailed in figure 1, the sampling was made by an automatic PVC collector (Sigha and Bricquet, 1987). The river gauge is around 600 m, the depth is around 10 m (Dugas and Thiebaux, 1989). Associated with the water sampling, the monthly

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discharge has been determined (Olivry et al., 1987). Secondly, 3 rivers near Bangui: Mbali, Mpoko, Mondjo have been sampled during different seasons (February and November) representing peak and moderate flow conditions. Finally, the Oubangui tributaries were collected during November 1989 on high water period.

Two samples of shallow groundwaters were collected on the Mbali-Mpoko basin. These two springs represented the overland flow and were collected during the wet (November) and dry (February) season. Samples of deep groundwater were also collected during different seasons (February, June, and November). These samples originated in the O.R.S.T.O.M drill. This drill is located in the granite gneiss basement at more than 60 m depth.
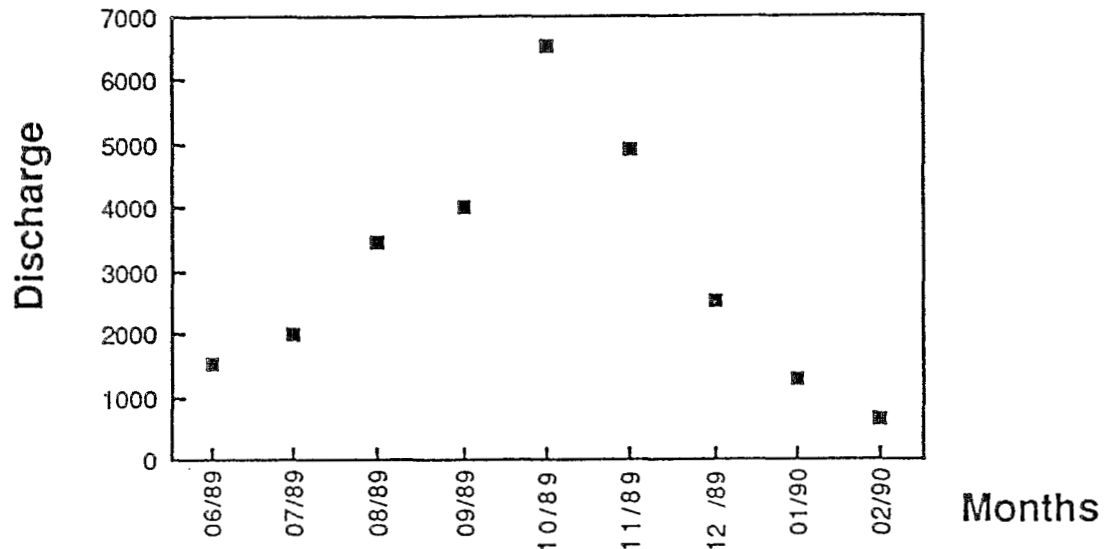
Figure 3
Monthly mean discharge for the Oubangui river (in m3/s). Data from Olivry et al. 1987.

Because the drill water is used as soft water, the samples were collected before the chloration to prevent eventual contamination. Four soil samples were collected throughout the Mpoko basin and also near the O.R.S.T.O.M centre.

Water samples were collected in acid washed polypropylene bottles on small rivers and springs and with a PVC water sample on the Oubangui river. After collection, samples were filtered through 0.2 µm acetate cellulose filters with a pressurised 47 mm diameter Sartorius® polycarbonate filtration unit. After, samples were stored in 125, 250 or 500 cc polypropylene acid washed containers for cations and isotopes determination. The filtrates were acidified with 2 drops of ultra pure HNO3 15N. An aliquot (60 cc) was collected before acidification for anions determination. Suspended samples were isolated from water by filtration of 1l through 0.2 µm acetate cellulose filters.

Analytical procedure for water studies in laboratory including : acid titration for HCO3, ionic chromatography for Cl and SO4. Molybdenum blue colorimetry for Si. Conventional flame atomic absorption spectrophotometry procedures for Ca, Na, Mg, K, Rb and Sr concentrations were determined by mass spectrometry using the isotopic dilution technique with a mixed 41K; 87Rb; 84Sr spike solution after chemical separation. The analytical precision for the measurement of major ions (Ca, Na, Mg, Cl, SO4) by atomic absorption and ionic

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chromatography is less than 15%. Using the mass spectrometry techniques, the analytical precision is around 3%.

The strontium isotopic compositions were determined on a solid source mass spectrometer. The separation of dissolved Ca, Rb, Sr from the water samples was carried out by cation-exchange chromatography (Birck, 1986; Négrel, 1988). The strontium contamination during sampling and chemical processing was estimated through a blank determination. The result is around 100 pg of Sr and is negligible in terms of the total quantity of strontium processed in water analysis. Mass fractionation corrections were applied by normalising the average $^{87}Sr/^{86}Sr$ ratios to a $^{86}Sr/^{88}Sr$ ratio of 0.1194. The accuracy of the $^{87}Sr/^{86}Sr$ analyses was evaluated by analysing the NBS 987 standard. Our mean value is 0.710254 ± 6 (2σ; 40 measurements).

Suspended load was separated from the filter by ultrasonning procedure. The particles were transferred into a Teflon container and subjected to standard dissolution procedures in hot HCl, HNO_3, HF and $HClO_4$. An aliquot of these samples were then spiked with a ^{41}K, ^{87}Rb, ^{84}Sr tracers. After chemical separation, concentrations and strontium isotopic ratios were determined by mass spectrometer. Total blanks were less than 1ng for Sr.

Exchangeable fraction is determined by cold extraction with bidistilled water. After 1 hour of interaction, the water is separated from the particles by filtration.

4 - RESULTS

4.1. Results on Dissolved load

The data on dissolved load are given in table 1. Element contents are given in 10^{-6} moles. l^{-1}. The major cations and trace elements in surface waters show large content variations. These variations are higher than analytical errors. The $^{87}Sr/^{86}Sr$ ratios also show variations clearly higher than analytical errors (mean: 3.10^{-5}). The HCO_3 content was determined on the samples collected monthly on the Oubangui, and on the Mpoko and Mbali Rivers in November 1989. On these samples, the observed charge balance (Table 1) between cations ($\Sigma+$) and anions ($\Sigma-$) shows a shortage of the negative charge (excepted for the 09/89, 12/89 and 01/90 Oubangui samples). This shortage range between 2 and 16% and can be explain by the existence of high organic acids content in the rivers water. This weak shortage is an added proof of the validity of our data.

On the Oubangui samples, a general decrease of the major and trace element concentrations (Cl, Ca, Na, Mg, Sr) associated with the increasing discharge is observed (Fig. 4); on the contrary, K, Si and Rb do not vary with the increasing discharge. It is important to point out that the major element concentrations decrease is also observed on the other rivers of this drainage basin (Mbali, Mpoko, Mondjo) between time of low and high discharges. Correlations are observed between the elements taken two by two. Taking in account the analytical errors, only the correlations between Na-Cl; Ca-Sr; Na-Sr have an intersect close to the origin. On the Oubangui samples, the strontium isotopic data show variations around 2.10^{-3} between the lower value (0.7185) observed in February and the higher value (0.7208) observed in October. On the other rivers (Mbali, Mpoko, Mondjo), the isotopic data fluctuate with a $2-4.10^{-3}$ variation between low and high water discharges. Good correlations are observed between $^{87}Sr/^{86}Sr$ ratios and the Oubangui river discharge (Fig. 5). On the Mbali, Mpoko Mondjo and Oubangui monthly samples, good correlations exist between $^{87}Sr/^{86}Sr$ Ca/Na and Na/Sr ratios (Fig. 6).

The different tributaries of the Oubangui Basin collected during peak discharge exhibit variable cation and isotopic ratios. These variations are related to the lithology of the catchment basin. The strontium isotopic ratios are correlated with the Ca/Na (Fig. 7) and Na/Sr ratios. Two river samples (Oumba, Ombella) are remote from the correlation, these two rivers drain shales.

Deep groundwater samples originate from the O.R.S.T.O.M drill, and the element concentrations in groundwater samples are consistently higher than those of rivers (table 1). These concentrations are constant as a time function. The range of variations for Ca and Na is less than 5%, less than 2% for Mg and Sr. The isotopic ratio is 0.740, also constant as a time function.
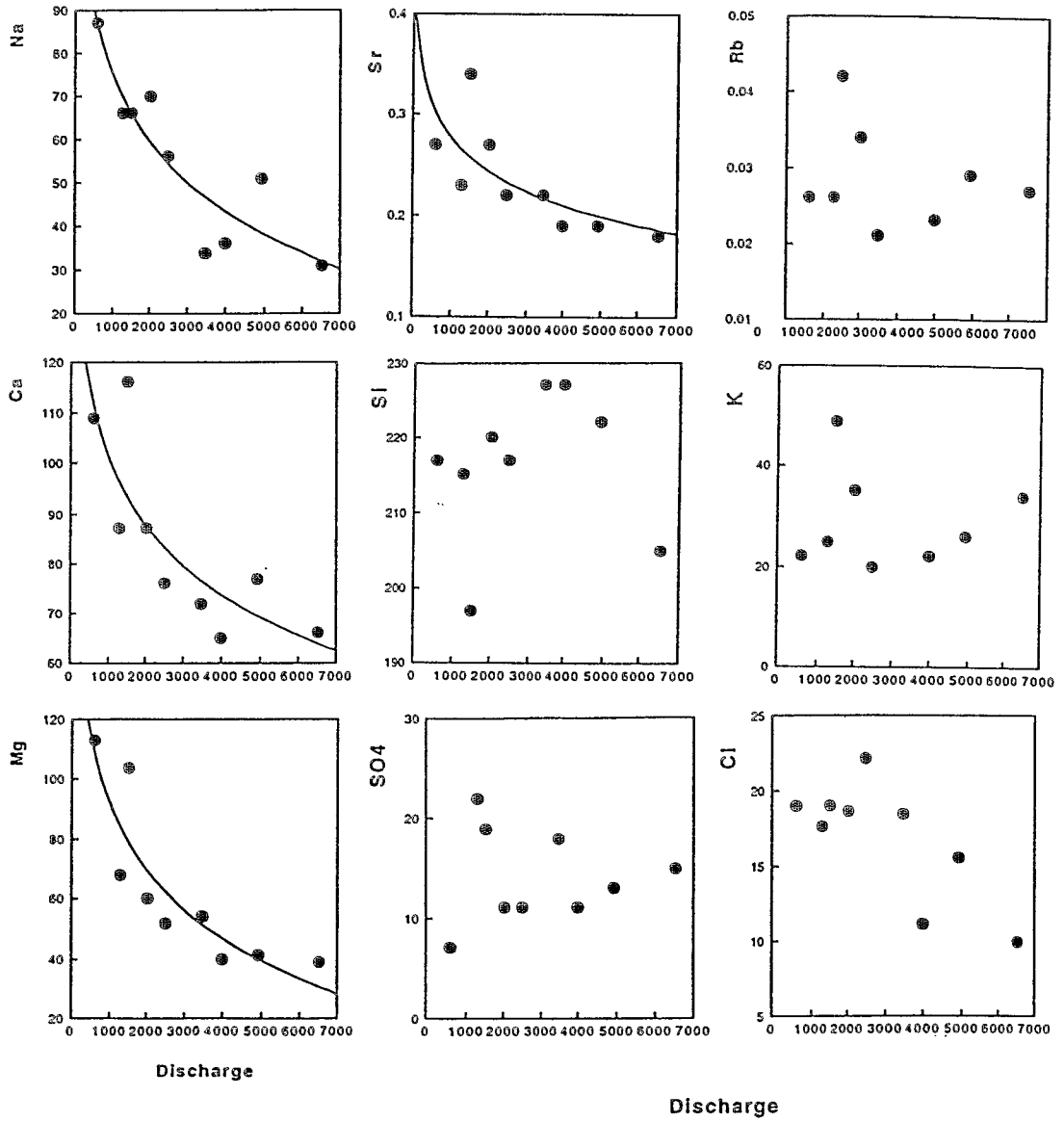
Figure 4
Relationship between dissolved major and trace element concentrations and discharge of the Oubangui river water samples.

Table 1

87Sr/86Sr ratios, major and trace ion compositions (in 10-6 moles/l for Ca, Na, K, Mg Si, Cl, SO4, Sr and HCO3) of dissolved solids for samples from the Oubangui watersheds. Monthly mean discharge for the Oubangui river in m3/s; Σ + and Σ - in 10-6 eq/l.

Sample	87Sr/86Sr	2 $\Sigma \pm$	Cl	SO4	Ca	Na	Mg	K	Si	Rb	Sr	Discharge	HCO3	Σ +	Σ -
OUBANGUI															
Oubangui 06/89	0.719315	3.2E-05	18	19	115	66	104	49	197	0.04	0.343	1520	460	553	516
Oubangui 07/89	0.719274	4.9E-05	18	11	87	70	60	35	220	0.03	0.272	2020	350	399	390
Oubangui 08/89	0.719889	0.00003	15	18	72	34	54	76	227	0.07	0.220	3470	250	362	301
Oubangui 09/89	0.720849	4.9E-05	11	11	65	36	40	22	227	0.02	0.191	4000	250	268	283
Oubangui 10/89	0.720325	2.7E-05	10	15	66	31	39	34	205	0.03	0.179	6530	210	265	250
Oubangui 02/11/89	0.719682	2.9E-05	22	13	65	50	41	28	222	0,03	0.169	4920	238	290	286
Oubangui 18/11/89	0.719128	5.5E-05	24	13	77	51	-	26	-	0.03	0.188	-	-	-	-
Oubangui 12/89	0.718993	3.6E-05	22	11	76	56	52	20	217	0.02	0.224	2500	300	332	344
Oubangui 01/90	0.718927	0.00003	22	22	87	66	68	25	215	0.03	0.233	1300	400	401	444
Oubangui 02/90	0.718656	0,00003	24	7	109	87	113	22	217	0.03	0.272	630	460	553	498
SPRINGS															
Mpoko 02/89	0.728293	0.00003	-	-	25	16	14	-	-	-	0.061	-	-	-	-
Mpoko 1 11/89	0.728657	0.00006	-	-	52	67	62	-	-	-	0.194	-	-	-	-
Mpoko 2 11/89	0.719676	3.1E-05	-	-	115	74	82	-	-	-	0.221	-	-	-	-
O.R.S.T.O.M. 11/89	0.719199	2.8E-05	-	-	262	55	21	-	-	-	0.41	-	-	-	-
DRILL															
02/89	0.740882	4.7E-05	61	3	780	856	270	-	-	-	2,195	-	-	-	-
07/89	0.740996	3.5E-05	35	2	775	819	268	-	-	-	2,16	-	-	-	-
02/90	-	-	-	-	771	810	265	-	-	-	-	-	-	-	-
TRIBUTARIES															
Mpoko 11/88	0.726345	2.6E-05	23	12	134	82	104	-	-	-	0.215	-	-	-	-
Mpoko 02/89	0.721992	3.1E-05	23	13	367	65	255	-	-	-	0.313	-	-	-	-
Mpoko 11/89	0.724202	2.4E-05	8	7	157	87	107	80	-	0.05	0.249	-	545	595	567
Mbali 11/88	0.716879	2.9E-05	23	7	86	24	65	-	-	-	0.19	-	-	-	-
Mbali 02/89	0.714546	0.00003	22	14	290	34	206	-	-	-	0.288	-	-	-	-
Mbali 11/89	0.716332	2.1E-05	12	5	130	42	78	138	-	0.07	0.239	-	479	596	501
Mandjo 02/89	0.711884	3.8E-05		-	579	25	353	-	-	-	0.82	-	-	-	-
Mandjo 11/89	0.713782	3.1E-05	9	7	284	25	131	-	-	-	0.399	-	-	-	-
Bili 11/89	0.725484	3.1E-05	21	21	48	66	49	-	-	-	0.169	-	-	-	-
Tomi 11/89	0.726559	2.7E-05	8	19	175	110	124	-	-	-	0.248	-	-	-	-
Uele 11/89	0.717353	5.4E-05	21	20	55	105	53	-	-	-	0.187	-	-	-	-
Kotto 11/89	0.720056	4.6E-05	8	11	67	39	53	-	-	-		-	-	-	-
Bamba 11/89	0.728124	2.5E-05	16	22	120	100	112	-	-	-	0.199	-	-	-	-
Oumba 11/89	0.723665	2.6E-05	8	5	257	56	210	-	-	-	0.207	-	-	-	-
Ombella 11/89	0.722831	2.6E-05	9	21	450	78	278	-	-	-	0.372	-	-	-	-
Oubangui 11/89	0.721671	2.8E-05	12	17	70	49	68	-	-	-	0.17	-	-	-	-
Mbomou 11/89	0.721261	1.9E-05	12	11	71	46	68	-	-	-	0.154	-	-	-	-
Ouaka 11/89	0.725455	3.3E-05	6	14	30	44	39	-	-	-	0.118	-	-	-	-

Shallow groundwaters located in the soil zone exhibit concentration that fluctuate widely. Sometimes, these concentrations are lower or identical than those of rivers. The isotopic composition of these samples are higher than rivers and less than deep groundwaters.
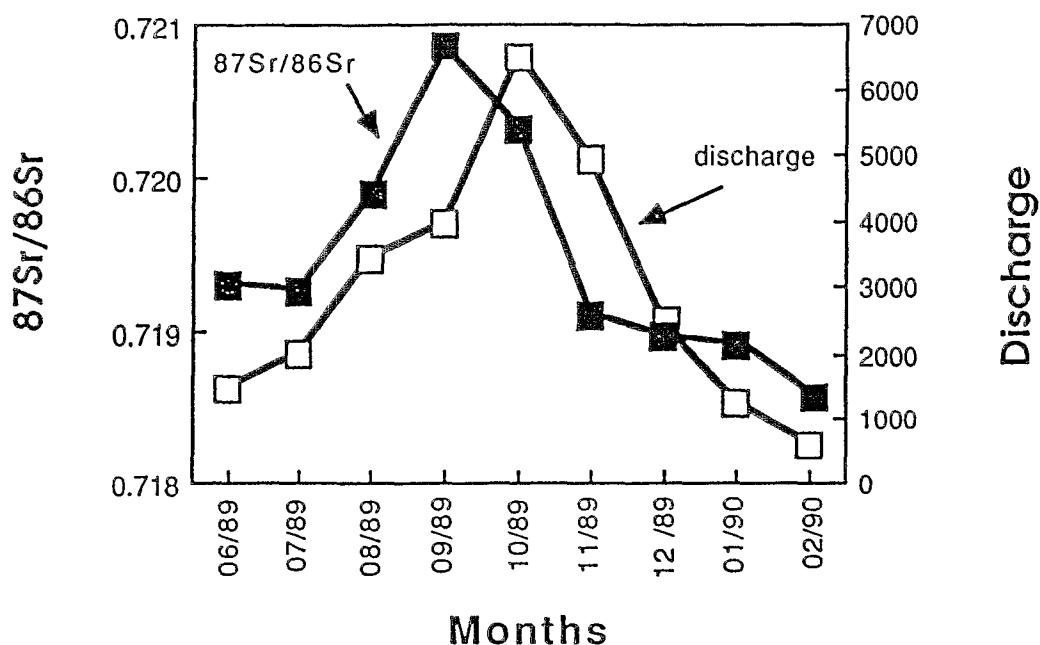

Figure 5
Correlation between 87Sr/86Sr ratios of dissolved solids and discharge of the Oubangui river water samples.

4.2.Results on suspended matter and soils samples.

The suspended matter content (in mg. 1-1) of the Oubangui river at Bangui station ranges between 2 mg. 1-1 on moderate peak discharge from 50 mg.l-1 on high water period (Olivry et al. 1987). The mineralogical study of the suspended load (Barusseau et al., 1989) indicates that kaolinite is dominating (60-80%), illite content is constant (10-15%), the smectite existence is short-lived on low water discharges with negligible content. The 20% remaining are constituted by amorphous phases (oxi-hydroxides, organic matter). For the moment, no temporal variations of the argilaceous suite have been showed.

The data we obtain are reported in Table 2. The ten samples analysed comprehend high and low water periods. The K, Rb, Sr measured concentrations on the suspended load fluctuate correlatively with the water discharge. The very weak content of suspended matter analysed implies heavy error on the concentration determinations. We will not discuss concentration variations but the concentration ratios fluctuations (like Rb/Sr).

Large fluctuations were found for the 87Sr/86Sr ratios higher than analytical errors and are around 2. 10-2 between the lower value (0.723) and the highest value (0.741) (Table 2). The strontium isotopic ratio is relatively constant (0.735-0.740) during the increase of water discharge and decrease rapidly during moderate peak flow. The lower 87Sr/86Sr value is observed in March on lower water discharge.

The 87Sr/86Sr ratios are correlated with the suspended matter content. The more the suspended matter increases, the more the strontium isotopic ratio increases and reversely. Good correlation is also observed between 87Sr/86Sr and 87Rb/86Sr ratios.

On the two soil samples collected on the Oubangui basin, the exchangeable Sr exhibits a 87Sr/86Sr close to 0.7299. The insoluble fraction of the soils exhibits a strontium isotopic ratio close to 0.770.

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5 - DISCUSSION

5.1. Discussion on the dissolved load

We first point out the existence of content and isotopic variations proportionally with the water discharge. These fluctuations are more perceptible on the Oubangui river because of the continuous monthly sampling (Fig. 4) but an identical reasoning may be made on small watershed of this basin.

The dissolved elements content in riverwater consist of two principal sources: rock weathering and atmospheric inputs. Several studies (Meybeck, 1979, Stallard and Edmond, 1981) have shown that the atmospheric inputs of chemical constituents to river water can be substantial. These inputs consist of 3 components : marine, terrestrial and anthropogenic. On our studied basin, the anthropogenic source is negligible. Classically, for each element X, the atmospheric inputs have been estimated by reference to the chloride content. The approach to determine the input would be to use either X/Cl ratios in seawater for estimated marine component (Stallard and Edmond, 1981); or, X/Cl ratios in rainwater for estimated the total input (Meybeck, 1979). Recent studies on the Congo basin (Négrel, 1992) have shown the importance of the continental elements originating from the outside of the basin. This study has shown that the rain correction is the best quantification of the atmospheric inputs. So, we corrected the element content for rainfall input and the methodology for this correction is as following :

$$Xatm = Clr \times \frac{X}{Cl} p$$

Where Xatm represent the element originate from the rain input; Clr represent the chloride content of the river water; X/Cl*p is the ratio observed in average rainwater (Négrel, 1992). Similar equation can be write for all the elements. The results we obtain for Na, Ca and Sr are presented in Table 3. For all the rivers from the Oubangui basin, the rainfall input range between 6 to 56% for Na; 1 to 27% for Ca; 0.4 to 6.1% for Mg and 2.1 to 11% for Sr.

The correlation between element contents and water discharge cannot be explained simply by dilution of the basic flow by an input of rain water. If we consider a dilution of the base flow by rain water, only the concentrations should fluctuate and the dissolved solid exportation rate may be constant. After correction of the rainfall input, the dissolved solid exportation rate for each element (Ca, Na, Mg, Sr and Rb) can be calculated (Fig. 8). This exportation rate increase with the increasing discharge. This increasing clearly show that on peak discharge, in spite of the concentration decrease, the chemical weathering is increasing. The variations of the 87Sr/86Sr ratios as a discharge function confirm this hypothesis. The increasing of the 87Sr/86Sr ratios during peak discharge is opposed with a dilution model by rain water because the strontium isotopic compositions of rain water on the Oubangui basin is around 0.7104 (Négrel, 1992) and are in all the case lower than the Oubangui river data. As a summary, the decreasing of the corrected concentrations cannot be explained by dilution but by mixing between two different components. One exhibit low element contents associated with high 87Sr/86Sr ratio, this component dominate on peak discharge. The second component exhibit high element contents associated with low 87Sr/86Sr ratio. This component dominate on moderate discharge.

For K and Si contents, there is no seasonal variations because K is a very biogenic element and is used by growing vegetation (Berner and Berner, 1987) and Si is affected by the presence of diatoms in rivers (Berner and Berner, 1987).

5.1.1. Small watersheds: origin and contribution of the different components

After correction of the rainfall input, the major and trace element concentrations are representing the rocks weathering. The two main lithologies submitted to weathering are carbonate and silicate rocks. At the first order, the isotopic and cations variations may be linked with a two components mixing. On the small watersheds, the correlations isotopes-element ratios allow to characterise the two components. On the figure 9, the different curves represented the possible mixing. These curves are definable by the r parameter. This parameter is expressed by the ratio (Sr1/Sr2) / (Na1/Na2) and (Na1/Na2) / (Ca1/Ca2). The dispersion with regard to the ideal mixing curves is explained by either r variation or by end members variations.
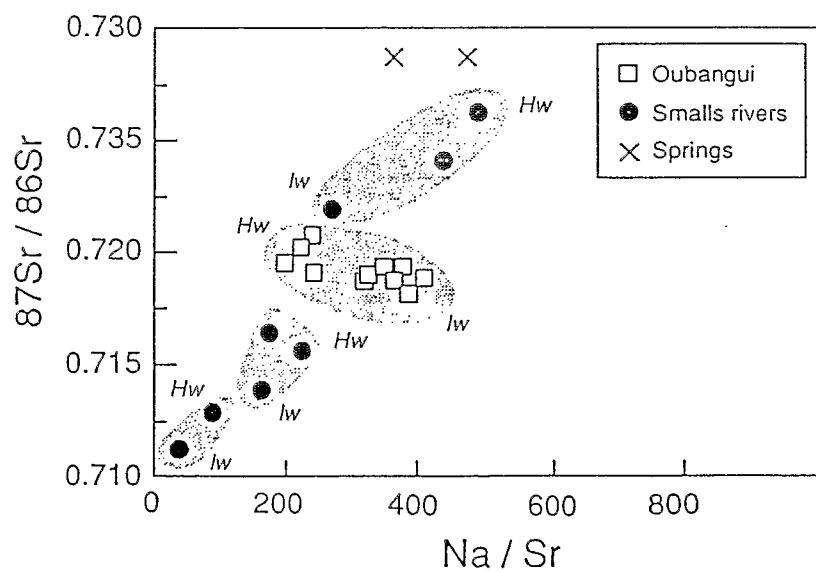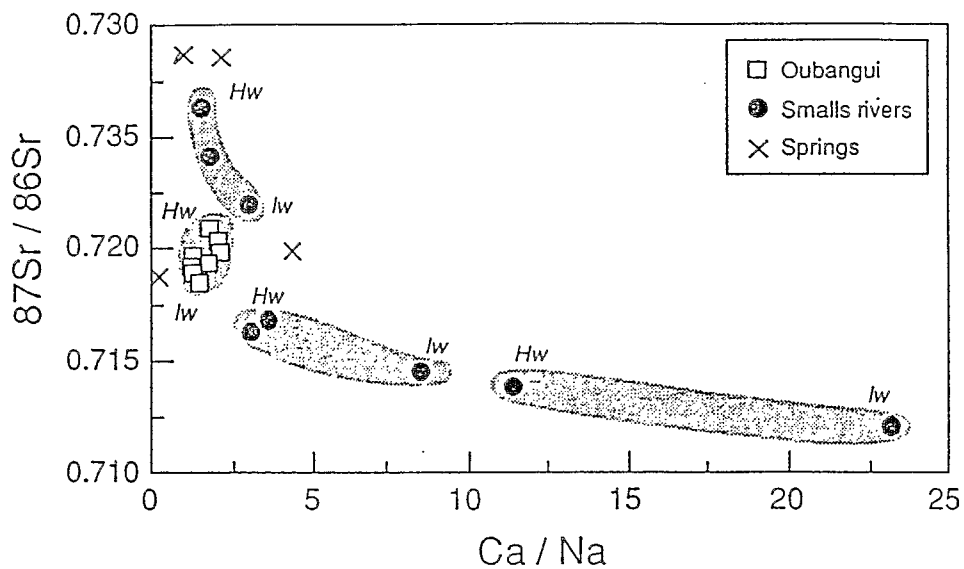
Figure 6

Correlation between dissolved solids 87Sr/86Sr ratios and dissolved solids cation ratios (Ca/Na and Na/Sr) of the Oubangui, Mbali, Mpoko and Mondjo river water samples. Hw and lw represented respectively high water period and low water period.

Table 2

87Sr/86Sr ratios, 87Rb/86Sr ratios, K, Rb, Sr concentrations (in 10-6 moles/l) of suspended solids for samples from the Oubangui river.

Sample	W m3/s	S. M mg/l	87Sr/86Sr	2 Σ ±	Sr ppm	Rb ppm	87Rb/86Sr
10/88	10000	33.5	0.738393	8E-05	42	66	4.436
11/88	6550	33.7	0.73393	7E-05	51	58	3.21
12/88	3700	23.7	0.741235	0.0003	37	63	4.806
1/89	2000	13	0.731945	4E-05	66	63	2.694
2/89	850	3.4	0.72892	0.003	44	54	3.464
3/89	500	2.4	0.723033	6E-05	45	56	3.513
6/89	1520	22	0.73788	0.0004	104	500	3.57
7/89	2020	36	0.74009	7E-05	150	255	4.798
8/89	3470	45	0.739096	4E-05	167	225	3.803
9/89	4000	50	0.7433	8E-05	110	184	4.721

Table 3

Results of the rainfall inputs for Na, Ca ,Mg and Sr on the Oubangui river samples.

Sample	Na	Ca	Mg	Sr

OUBANGUI

Sample	Na	Ca	Mg	Sr
06/89	24%	11%	14%	4.7%
07/89	22%	15%	24%	5.9%
08/89	38%	15%	22%	6.7%
09/89	27%	12%	22%	5.1%
10/89	28%	11%	21%	5.0%
11/89	39%	21%	43%	9.0%
12/89	34%	21%	34%	8.8%
01/90	29%	18%	26%	8.4%
02/90	23%	15%	17%	7.5%

TRIBUTARIES

Sample	Na	Ca	Mg	Sr
Mpoko 11/89	23%	10%	18%	8.2%
Mpoko 02/89	20%	7%	7%	6.5%
Mbali 11/89	46%	12%	27%	8.2%
Mbali 02/89	56%	5%	9%	6.8%
Bili 11/89	28%	31%	35%	11%
Tomi 11/89	6%	3%	5%	2.9%
Uele 11/89	17%	27%	32%	10%
Kotto 11/89	18%	9%	12%	4.7%
Bamba 11/89	14%	10%	11%	7.2%
Oumba 11/89	12%	2%	3%	3.4%
Ombella 11/89	10%	1%	3%	2.1%
Mbomou 11/89	23%	12%	12%	6.9%
Ouaka 11/89	12%	14%	12%	4.5%

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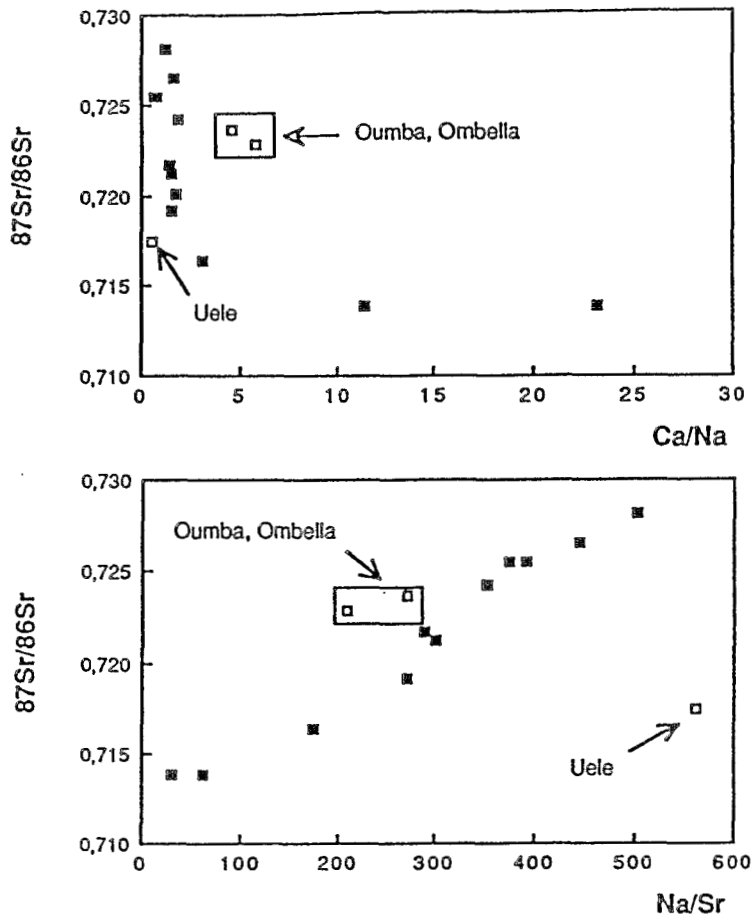
Figure 7
Correlation between dissolved solids 87Sr/86Sr ratios and dissolved solids cation ratios
(Ca/Na; Na/Sr) of the Oubangui tributaries samples on peak discharge.

The chemical and isotopic characteristics of the first component (87Sr/86Sr close to 0.711, high Ca/Na, low Na/Sr ratios) implies that this component is located in the carbonate rocks. The obviousness of a Precambrian carbonate sequence in Central Africa has been made at the end of the XIX century. This sequence has been recognised by structural test hole (Boulvert and Salomon, 1988; Poidevin, 1976) because the carbonate are not exposed and are shielded by allogenic ferralitic soils as on the Mondjo basin (Boulvert and Salomon, 1988). Recent studies on the Oubangui basin (Boulvert and Salomon, 1988) overlay the carbonate extension. This sequence is thickly (close to 100 m) and highly karstified (Boulvert, personal communication). The characteristics of the second component (high 87Sr/86Sr, Na/Sr ratio and low Ca/Na ratio) may be linked with silicate weathering. Either the weathering of the basement (with granites, gneisses, sandstones and shales), or the weathering of sedimentary cover soils and decayed rocks.

The isotopic and chemical characteristics of the carbonate end-member are supposed to be constant because carbonate rocks are principally constituted by CaCO3 mineral where partitioning between cation and trace elements are known. For the silicate end-member, its characteristics are quite differents and are related with the mineralogical composition of the altered rocks. The use of temporal variations on small watersheds allows the determination of these characteristics because the mixing proportions between carbonate and silicate end-members fluctuate as a time function. At the second order, the correlation isotopic-cation ratios are not evident because some cations like Na are very dependent to the atmospheric correction. The use of Ca/Sr ratio is better because Ca and Sr are less dependent to the atmospheric correction.

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Correlation between 87Sr/86Sr ratios and Ca/Sr ratios on three rivers (Mbali, Mondjo and Mpoko river) for peak and moderate flow are represented in figure 10. In this figure, the carbonate end-member characteristics may be constrained easily. The Ca/Sr ratio of rivers which drains carbonate range between 1200 (Turekian and Wedepohl, 1961) to 2000 (Meybeck, 1988). We choose a Ca/Sr ratio of 1700 for the carbonate end-member. For the isotopic ratio, because carbonate rocks do not content Rb, their low Rb/Sr preserve the original 87Sr/86Sr value. In Central Africa, carbonate sequence are not exposed but in Congo Republic, a river (Nyari river) drains an identical Precambrian carbonate sequence and exhibit a 87Sr/86Sr ratio close to 0.708 (Négrel, 1992). The mixing line between this carbonate component and silicate component shows the existence of at least two silicate end-members with different 87Sr/86Sr ratios (the 87Sr/86Sr ratios for the silicate end-members are given by the intersect at Ca/Sr = 0). The first silicate end-member located on the Mpoko basin is radiogenic (87Sr/86Sr close to 0.736). The second located on the Mbali and Mondjo basin (these two rivers belonged the same watershed) is less radiogenic (87Sr/86Sr close to 0.720). the existence of these two silicate components is related to rocks heterogeneities between the two watersheds because the age of the bedrocks is equal (500-600 M.a.).

The surface water samples collected on peak discharge on all of the Oubangui tributaries are plotted with the temporal variations on the three rivers (fig 10). Oubangui tributaries are represented in white square while temporal variations are represented in black square. The Oubangui tributaries water samples are in general agreement with a two component mixing model.

It is impossible to interpreted more the results because of the mis reading of the silicate end-member isotopic characteristics.

### 5.1.2. Isotopes-elements correlations on the Oubangui river. Origin of the different sources

We saw above that on small watersheds, the correlation between 87Sr/86Sr ratios and major and trace element ratios can be interpreted as a mixing of at least two different water pools. Comparatively, the correlation between cation and 87Sr/86Sr ratios (Fig. 6) on the Oubangui river and on rivers draining small watershed fluctuate inversely while the isotopic ratios increase with the increasing discharge. The Ca/Na ratio decrease and Na/Sr ratios increase on the Oubangui river, inversely on the small watershed (Mbali, Mpoko, Mondjo), the Ca/Na ratios increase and the Na/Sr ratios decrease.

The hypothesis which could be suggested to explain this inverse fluctuation concerns the hydrological functioning and the geological story. The three small rivers represent only the North zone weathering while the Oubangui monthly sampling represents the chronological evolution of the mixing between water coming from the East part of the basin (Zaire Rep.) and the water coming from the North zone (Central African Rep.). The oriental part of the basin is constituted by the association Mbomou-Uele rivers and dominates during low water period. During this period, the Uele river is the main tributary of the Oubangui river (Boulvert, 1987; Dugas and Thiebaux, 1989). On the opposite, during the wet period because of the dyssimmetry of the basin, the main part of the Oubangui river alimentation is located in the North zone. The low 87Sr/86Sr ratio on moderate peak load can be related with the preponderance of the Uele river. The Uele river drains the upper-Zaire granite-gneiss basement which is 2200 to 3000 M.a. old (Cahen, 1984). On the opposite, the rivers of the north zone drain gneiss and granites which are 500 M.a. old. The age difference between the North zone and the East part of the basin, implies that the isotopic ratio of silicate component in the north zone will be more radiogenic than in the oriental part of the basin.

5.2. Discussion on suspended load

The results obtained on the suspended load show firstly that the 87Sr/86Sr ratio of suspended loads is always higher than those obtained for dissolved load. Secondly that the 87Sr/86Sr ratios of the suspended load fluctuate highly correlatively with the hydrological event.

The suspended load is mainly constituted by clay minerals. Numerous studies on clays (Clauer, 1976) have shown two origins for Sr. The first origin is adsorbed and is isotopically equilibrated with dissolved load, the second one is constitutive and the 87Sr/86Sr ratio is always higher than absorbed Sr.
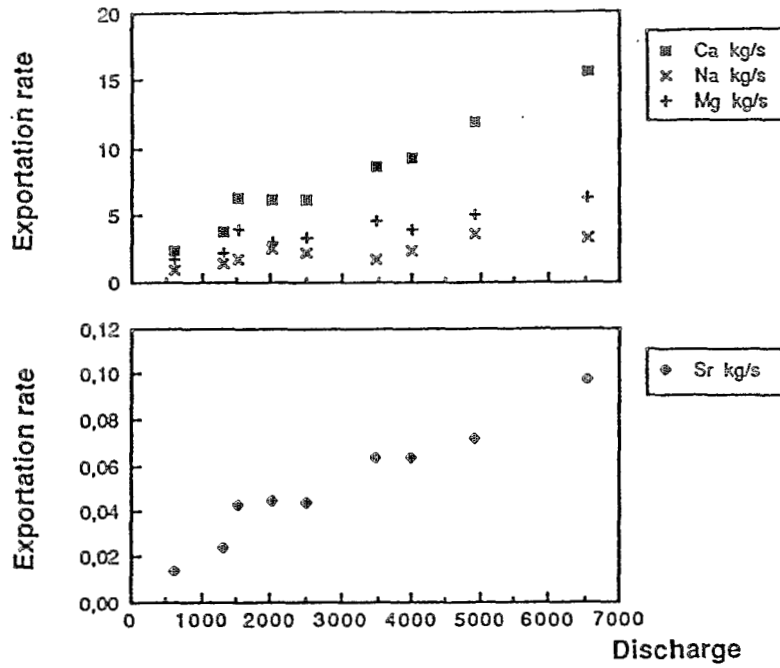
Figure 8

Dissolved solids exportation rate versus discharge for the Oubangui monthly samples.
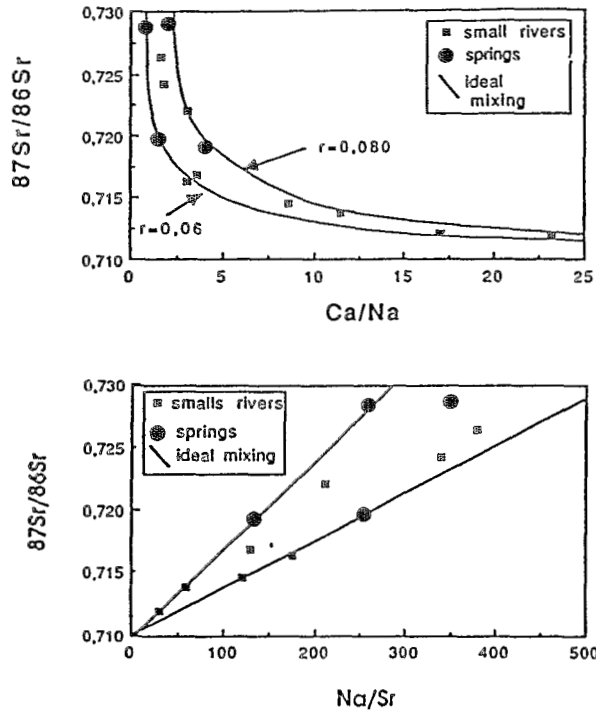
Figure 9

Correlation between dissolved solids 87Sr/86Sr ratios and dissolved solids cation ratios (Ca/Na and Na/Sr) of the small watersheds between low water period and peak discharge.
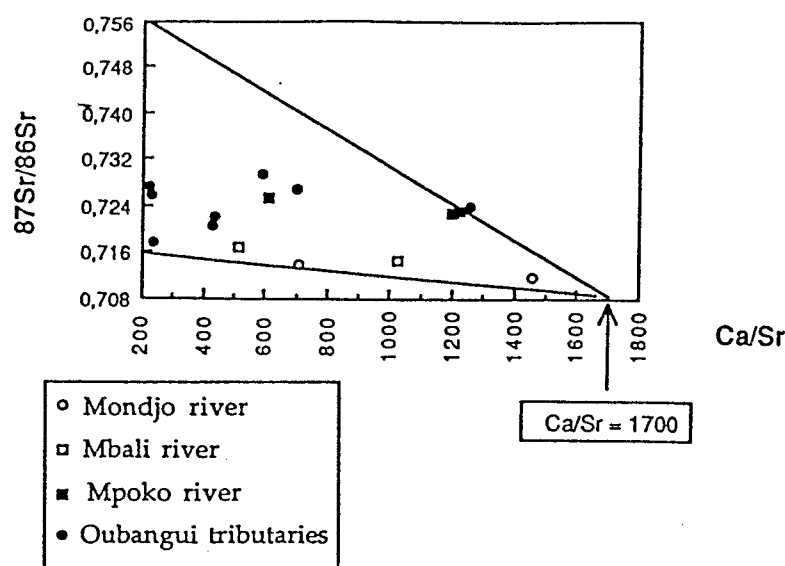
Figure 10

Correlation between dissolved solids 87Sr/86Sr ratios and dissolved solids cation ratios (Ca/Sr) of the Oubangui tributaries samples on peak discharge and on the Mbali, Mpoko and Mondjo river water samples between peak and moderate discharge.

Because the bulk load (dissolved + suspended) is not constant, the isotopic variations cannot be related with both phase fluctuations. While neither the petrologic characteristics, nor the clay family abundance fluctuates, the existence of at least two population is proposed. The first population have low 87Sr/86Sr ratio and is associated with low water period while the second population exhibits higher 87Sr/86Sr ratio and is associated with high water period and high suspended load content. The origin and history of these two population are related to the hydrological functioning of the river. Two hypotheses can be proposed.

The first hypothesis is related to the hydrological functioning of this basin (see § 5.1.2). During the dry period, the Uele river is the main tributary of the Oubangui river. We saw above that on the Uele basin the rock minerals can exhibit low 87Sr/86Sr ratios, and clay minerals resulting from these rocks weathering are in equilibrium with low radiogenic dissolved strontium (87Sr/86Sr on suspended matter : 0.72284, Négrel and Dupré, in prep.; 87Sr/86Sr on dissolved load : 0.71735). On high water period, the North zone of the Oubangui basin becomes dominant in the water alimentation. The clay minerals originating from this area result from the weathering of primary minerals with high Sr isotopic ratios. Also, the dissolved 87Sr/86Sr is higher than can the Uele basin.

The second hypothesis is superimposed to the first one and is linked with the weathering profile functioning. During moderate peak discharge, the water and clay minerals originate from the base of the profile. On high water period, the runoff predominates and clay minerals originate from the top of the weathering profile. Between the top and the base of the weathering profile, the coexistence of clay minerals resulting from the weathering of same rocks but genetically differents have been shown (Muller, 1990). At the base of the profile, the isotopic characteristics of clays are in relation with the dissolved Sr of the aquifer (neoformation, requilibration). This Sr results from the weathering of whole rocks. Inversely at the top of the profile, the isotopic characteristics may be higher because of the weathering of residual minerals.

The existence of two clay populations in a weathering profile is corroborated by the analysis of two clay samples from the Oubangui basin. The first sample originates from the top of the

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profile. The exchangeable Sr exhibits a 87Sr/86Sr ratio close to 0.729 (with a dissolved load close to 0.725) and a 87Sr/86Sr ratio close to 0.770 for the insoluble residue. The second sample originate at the base of the profile (the sampling was made by drilling). The exchangeable Sr exhibits a 87Sr/86Sr ratio close to 0.714 (with a dissolved load close to 0.715) and close to 0.719 for the insoluble residue. These ratio are in agreement with this hypothesis.

6 - SUMMARY

This study using strontium isotopic ratios on dissolved and suspended loads provides more informations about the functioning of a large tropical basin (Oubangui river in Central African Republic). The following conclusions result from this study :

1) The general decrease of major and trace element concentrations (Cl, Ca, Na, Mg, Sr) associated with the increasing discharge cannot be explained simply by dilution of the basic flow by an input of rain water.

2) On small watersheds, the coupled variations of isotopic ratios and major and trace cation ratios (Na/Sr, Ca/Na) results from the mixing of at least two different water pools. The first pool is located in calcareous rocks which are not exposed and the second one in silicate formations. A two component mixing model shows a predominance of the silicate formations during the rainy season.

3) On the Oubangui river, the existence of a third pole is clearly shown on low water period. This third pole originate in the hydrological functioning of this basin because on low water period, the Uele river is the principal tributary of the Oubangui river.

4) For summarising, on the Oubangui basin, the seasonal variations are the consequence of geological heterogeneities and hydrological functioning while on the small watersheds, the temporal variation are related to the weathering processes.

5) For the suspended load, the results show that the suspended load carried by the Oubangui river during the year have not a single origin. We proposed that the clay minerals came from different levels of the weathering profile or different areas, and contributed differently as a function of time. The isotopic heterogeneity originates in the existence of waters in the soils zone of different isotopic composition.

ACKNOWLEDGEMENTS :

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