δ^{13}C tracing of dissolved inorganic carbon sources in Patagonian rivers (Argentina)

F. Brunet,[1] D. Gaiero,[2] J. L. Probst,[1]* P. J. Depetris,[2] F. Gauthier Lafaye[3] and P. Stille[3]

[1] *Laboratoire des Mécanismes de Transfert en Géologie (LMTG), UMR no. 5563 CNRS–IRD–Université Paul Sabatier, 14 avenue Edouard Belin, Toulouse 31400, France*
[2] *Centro de Investigaciones Geoquímicas y de Procesos de la Superficie (CIGeS), FCEFyN, Universidad Nacional de Córdoba, Avenida Vélez Sarsfield 1611, X5016GCA Córdoba, Argentina*
[3] *Centre de Géochimie de la Surface (CGS), UMR no. 7517 CNRS–Université Louis Pasteur, 1 rue Blessig, 67084 Strasbourg Cedex, France*

Abstract:

The main Patagonian rivers (Colorado, Negro, Chubut, Deseado, Coyle, Chico, Santa Cruz and Gallegos) were sampled between September 1995 and November 1998 to determine their chemical and isotopic compositions, the origins of the suspended and dissolved river loads and their inputs to the South Atlantic Ocean. This paper focuses on the dissolved inorganic carbon (DIC) transport and its δ^{13}C isotopic signature. The $\delta^{13}C_{DIC}$ values vary between $-12\cdot8$ and $-1\cdot8$‰ and allow one to distinguish two river groups: (i) the Colorado, Negro, Chubut and Santa Cruz, which display the highest values and the lowest seasonal variations; (ii) the Deseado, Coyle, Chico and Gallegos, which show the lowest values and the highest seasonal variations. For the first group, $\delta^{13}C_{DIC}$ is mainly controlled by important exchanges between the river waters and atmospheric CO_2, due to the presence of lakes and dams. For the second group, $\delta^{13}C_{DIC}$ also appears to be controlled by the oxidation of organic carbon, showing a negative relationship between $\delta^{13}C_{DIC}$ and the dissolved organic carbon. These biogeochemical processes interfere with the contribution of carbonate and silicate weathering to the riverine DIC and do not allow use of $\delta^{13}C_{DIC}$ alone to distinguish these contributions.

The annual DIC flux exported by Patagonian Rivers to the South Atlantic Ocean averages 621×10^9 g. of C, i.e. a specific yield of $2\cdot7$ g m^{-2} year^{-1}. The mean $\delta^{13}C_{DIC}$ can be estimated to $-4\cdot9$‰, which is high compared with other rivers of the world.

KEY WORDS   dissolved inorganic carbon; flux; Patagonia; river; isotopic signature; tracing; dissolved organic carbon; strontium isotopes; rock weathering; atmospheric CO_2; biospheric CO_2

INTRODUCTION

The significance of rock weathering and river transport in the global carbon cycle has already been discussed by many workers (e.g. Berner *et al*., 1983; Meybeck, 1987; Amiotte-Suchet and Probst, 1993a,b, 1995; Ludwig *et al*., 1998, 1999; Amiotte-Suchet *et al*., 2003). Recently, it has been demonstrated that riverine inputs of carbon to the ocean have to be taken into account in the regional distribution of sources and sinks of CO_2 in the ocean (Aumont *et al*., 2001). The river transport of carbon also contributes to transform this carbon and to degas CO_2 to the atmosphere (Devol *et al*., 1987). Rivers transport on average 1 gigaton ($0\cdot8$ to $1\cdot2$ Gt according to literature estimates) of carbon per year to the oceans (Ludwig *et al*., 1996a,b). This carbon is discharged as dissolved organic carbon (DOC, 25%), particulate organic carbon (POC, 20%), dissolved inorganic carbon (DIC, 38%) and particulate inorganic carbon (PIC, 17%). Some 70% (DOC, POC and two-thirds of the DIC) of this riverine carbon flux originates from the atmospheric/soil CO_2, and 30% (PIC and one-third of the DIC) originates from the physical and chemical erosion of carbonate rocks. DOC and POC have two main sources, the soil organic matter and the phytoplankton production in the river itself.

PIC originates mainly from physical erosion of carbonates, even if in some rivers part of the PIC can be produced by calcite precipitation in the river water column. DIC, which is the most important carbon fraction, originates from three main sources: atmospheric CO_2, carbonate dissolution and organic matter oxidation in the soils or in the river itself. Geochemical modelling (Amiotte-Suchet and Probst, 1995; Gaillardet *et al.*, 1997; Probst *et al.*, 1997) and geochemical tracers (Négrel *et al.*, 1993; Probst *et al.*, 1994; Gaillardet *et al.*, 1999; Mortatti and Probst, 2003) have been used to distinguish DIC originating from atmospheric/soil CO_2 and from carbonate dissolution. Nevertheless, each DIC source has a different $\delta^{13}C$ isotopic signature (-26 to $-9‰$ for soil organic matter according to whether C_3 or C_4 plants (Mariotti, 1991), -8 to $-6‰$ for atmospheric CO_2 (Cerling *et al.*, 1991) and around $0‰$ for carbonate rocks (Keith and Weber, 1964)), but few studies have been devoted to the use of carbon isotopes to trace the different DIC sources, to follow the riverine DIC transport into the ocean and to assess the carbon transformation in the river itself (Hitchon and Krouse, 1972; Dandurand *et al.*, 1982; Kendall *et al.*, 1992, 1995; Pawellek and Veizer, 1994; Cameron *et al.*, 1995; Flintrop *et al.*, 1996; Taylor and Fox, 1996; Yang *et al.*, 1996; Amiotte-Suchet *et al.*, 1999; Aucour *et al.*, 1999; Barth and Veizer, 1999; Telmer and Veizer, 1999).

Indeed DIC, DOC and POC release in the upper parts of the drainage basin can be transformed during their transfer from the soils to the river and even in the river itself. Consequently, the isotopic signature of DIC ($\delta^{13}C_{DIC}$) can vary greatly in the river water from upstream to downstream because DIC content and its isotopic signature are controlled by several biogeochemical processes, such as organic matter oxidation, photosynthesis and respiration of phytoplankton and exchange with the atmosphere. Oxidation and respiration lead to increasing DIC content by CO_2 production and to decreasing $\delta^{13}C_{DIC}$. The atmospheric CO_2 exchange depends on the CO_2 partial pressure (pCO_2) in the river water column. Generally, the river water degasses CO_2 to the atmosphere because the river water pCO_2 ($10^{-2.5}$ atm) is greater than the atmospheric pCO_2 ($10^{-3.5}$ atm). Consequently, the isotopic signature of DIC tends to reach equilibrium with atmospheric CO_2.

Patagonian river inputs to the southern part of the South Atlantic Ocean are the major sources of land materials discharged into the ocean, south to latitude $40°$. These river inputs play an important role in the biogeochemistry of this oceanic region, which is a confluence zone of different oceanic currents, and should have an important effect upon marine production in the Patagonian coastal environment. Nevertheless, very few measurements on the chemical and isotopic composition of Patagonian river waters are available. Moreover, their suspended and dissolved river loads and their inputs to the South Atlantic Ocean were not known until we decided in 1995 to study the geochemistry of Patagonian rivers within the framework of the European project PARAT. This paper is focused on the DIC transport by the major Patagonian rivers and its $\delta^{13}C_{DIC}$ isotopic signature. The main scientific questions this paper tries to address are the following:

- What are the DIC content and the $\delta^{13}C_{DIC}$ isotopic signature of the major Patagonian rivers?
- What are the main carbon sources controlling the DIC riverine transport and what are the main biogeochemical processes controlling the $\delta^{13}C_{DIC}$ isotopic signature?
- What is the amount of DIC discharged into the South Atlantic Ocean by Patagonian rivers and what is its average $\delta^{13}C_{DIC}$ isotopic signature?

STUDY AREA CHARACTERISTICS

The eight rivers studied here have the particularity to have their source in the Andean cordillera, and they cross the Patagonian plateau to reach the South Atlantic Ocean (Figure 1). The drainage basins of these rivers can be divided into two parts:

1. A band of 50 km along the Andes (corresponding only to 15% of the total basin areas) with steep slopes and heavy rainfall (more than 800 mm of rainwater). The vegetation is mainly forest (i.e. C_3 plants). The geological substratum of this area is constituted by volcanic rocks (basalts, rhyolites, andesites), continental
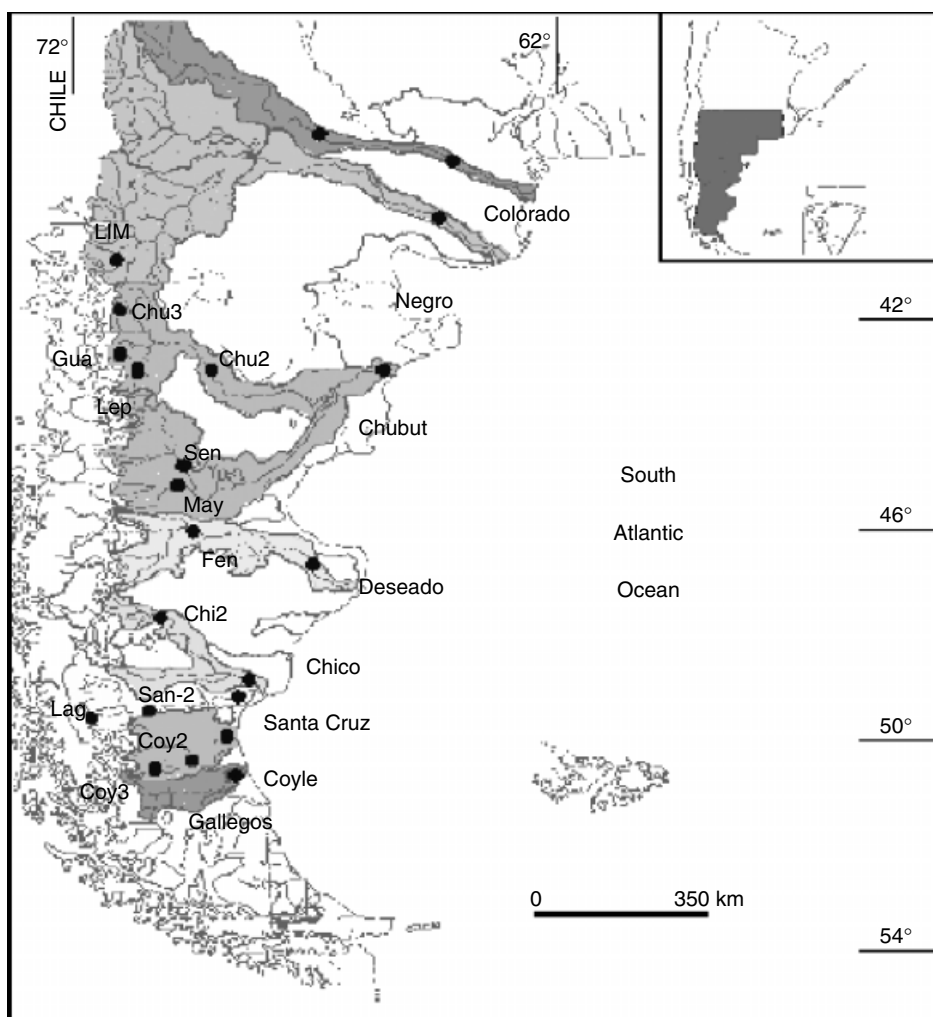
Figure 1. Location map of Patagonian river basins and sampling stations

and, to a lesser extent, marine sedimentary rocks with very few carbonates. Metamorphic and plutonic rocks are in relatively minor proportions.

2. A large area that corresponds to the Patagonian plateau (85% of the total basin areas). The rivers cross this plateau from west to east. It is a semi-arid area (precipitation is below 150 mm year^{-1}) and there is no contribution of water in this region. The vegetation is very limited and corresponds to grassy steppe (C$_3$ plants). This region is geologically dominated by alluvial sediments in the plain and marine sedimentary rocks and basaltic plates.

The eight main Patagonian rivers drain 30% of the total Patagonian territory; the remaining 70% corresponds to endorheic basins and smaller coastal drainage basins.

These river basins exhibit a spectrum of human impact even though the population densities are very low (<10 km^{-2}). Reservoirs and lakes are present in the Colorado, Negro and Chubut rivers. The main pollution problems are related to sewage effluents, agricultural runoff, oil extraction and transportation, and metal wastes located near harbours. Environmentally important are the extensively farmed Negro and, to a

lesser extent, the Chubut and Colorado river valleys. Mining activities have minor importance. Coal mining developed in the headwaters of the Gallegos River (Rio Turbio) has generated abundant debris that is eventually wind-transported or is directly introduced into the river water.

CLIMATE AND HYDROLOGY

Climate in the Patagonian plateau is temperate semi-arid in the north (mean annual temperature $T = 14$ to $16\,°C$) and gradually becomes temperate-cold arid to semi-arid in the south ($T = 6$ to $8\,°C$). Rainfall P in most of the plateau is 200 mm year^{-1} or less. In contrast, climate is temperate humid to sub-humid in the northern and central Patagonian Andes ($T = 6$ to $8\,°C$ and $P \approx 800$ mm) and becomes temperate-cold humid to sub-humid in the southern portion ($T < 6\,°C$, $P \approx 1000$ mm). The Andes intercept the prevailing and strong westerlies, causing orographically enhanced rainfall on their western side, while the eastern side of the mountain chain is in the rainshadow. Only a narrow strip along the Andes (about 15% of the total area) has a rainfall higher than 800 mm year^{-1}. Hence, the Andean west-to-east precipitation gradient is ~8 mm km^{-1}.

The eight main Patagonian rivers (Colorado, Negro, Chubut, Deseado, Chico, Santa Cruz, Coyle and Gallegos) jointly deliver a freshwater volume of 50 to 60 km^3 (according to the period) to the southwest Atlantic Ocean coastal zone per year. The River Negro (44%), the Santa Cruz (43%) and the Colorado (6%) account for most of the total mean annual Patagonian discharge (Table I). Their combined total mean runoff averages 250 mm year^{-1}, reflecting the actual semi-arid hydrological conditions of the Patagonian plateau.

Monthly discharge variations are only available for the Colorado, Negro, Chubut, Santa Cruz and Gallegos. As seen in Figure 2, the seasonal variations of Patagonian river discharges are very different from one river to another. The Santa Cruz presents the most regular variations, showing the highest discharges during the southern summer (due to snowmelt) and the early autumn (due to rainfall). For the other Patagonian rivers, the monthly variations are different from one year to another. For the Colorado, the high water period starts at the end of the winter–beginning of spring (due to snowmelt occurring in the Andes) and continues until the end of summer (due to rainfall), except for the year 1998. The highest Negro discharges are controlled by the autumn and winter rainfall and by the spring snowmelt, except at the end of 1996. The Chubut variations are similar to the Negro, except during the winter (no rainfall). Nevertheless, the years 1997 and 1998 are atypical because the Chubut discharge variations are very low. The most southern Patagonian river, the Gallegos, shows the dominance of spring snowmelt water.

Evidently, the climatic variability in the headwaters is reflected in the specific water yield, e.g. very low values in the semi-arid Deseado, Coyle and Chubut and excess water in the upper catchments of the Santa Cruz and Gallegos. Inspection of Table I also shows that, on the basis of runoff, it is possible to distinguish three types of river in Patagonia: (i) those with low runoff (<100 mm year^{-1}), like the Chubut, Deseado,

Table I. Drainage area and major hydrological parameters in Patagonian rivers

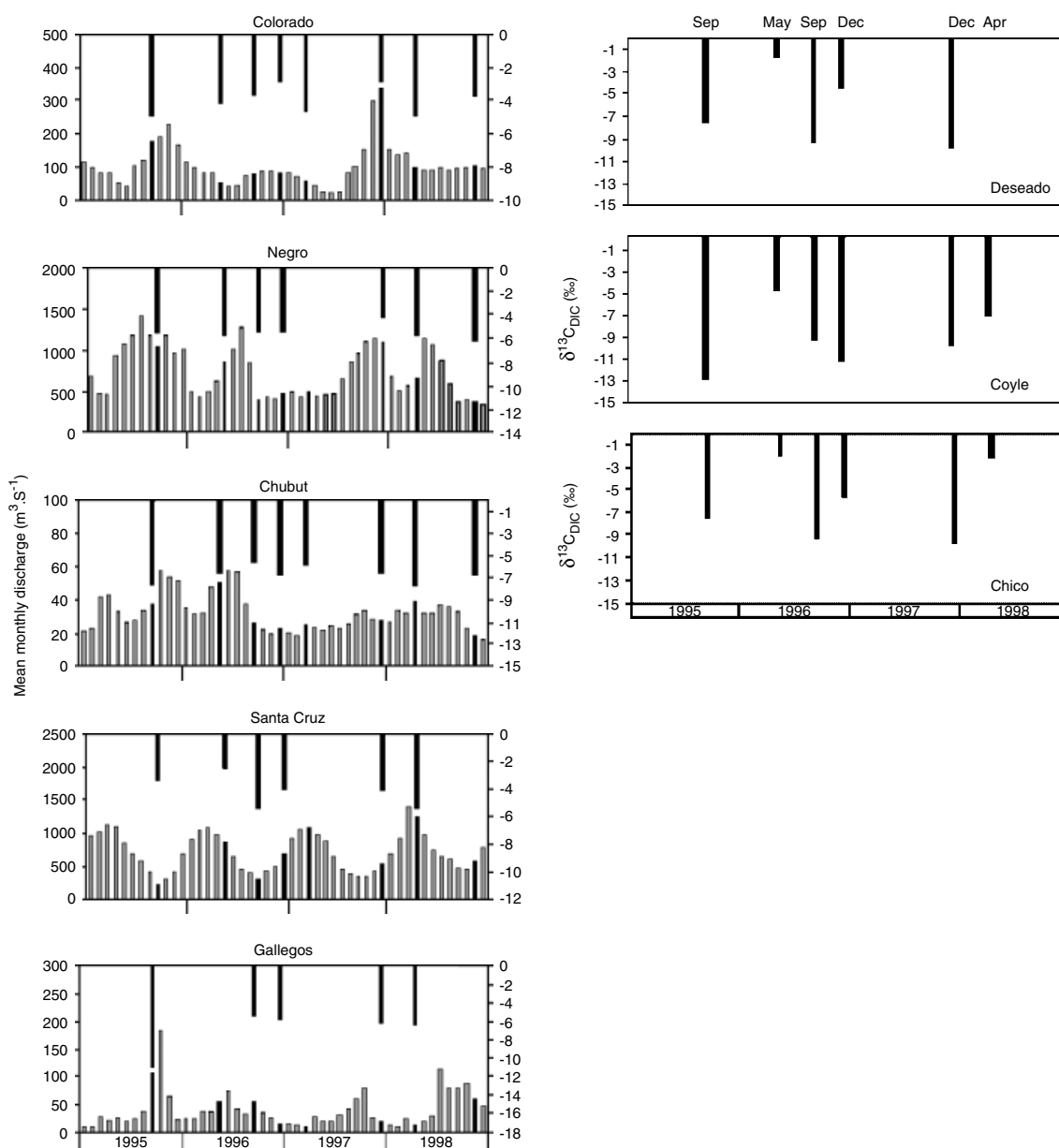| River	Total area (km^2)	Drainage area (km^2)	Mean discharge (m^3 s^{-1})	Runoff (mm year^{-1})	Population (inhabitant/km^{-2})
Colorado	69 000	22 300	105	148	1
Negro	95 000	95 000	742	246	7·1
Chubut	57 400	31 680	32	32	3·5
Deseado	14 450	14 400	5	11	0·4
Chico	16 800	16 800	30	56	1·5
Santa Cruz	24 510	15 550	713	1446	0·2
Coyle	14 600	14 600	5	19	0·1
Gallegos	5100	610	40	2068	1·3

Figure 2. Mean monthly discharge and $\delta^{13}C_{DIC}$ variations for the Patagonian rivers during the sampling period 1995–98. In the discharge variations, dark bars identify samplings. Discharge data are not available for the Rivers Deseado, Chico and Coyle

Chico and Coyle; (ii) those with intermediate runoff (100–300 mm year^{-1}), like the Negro and Colorado; and (iii) those with high runoff (>1000 mm year^{-1}), namely the Santa Cruz and Gallegos.

Andean Patagonia is characterized by a long string (which begins south of 36°S and continues down to Tierra del Fuego) of hundreds of lakes of glacial origin and variable size. Shared between Argentina and Chile, the largest lake discharges to the Pacific seaboard and bears the name Buenos Aires (in the Argentine territory) and General Carrera (in Chile); it is 170 km long, 50 km wide, and has an area of 2240 km². Lake Nahuel

Huapi, in the River Negro headwaters, is a more appropriate example of Patagonian oligotrophic proglacial lakes: with clear, nutrient-poor waters, it has an area of 557 km^2, a water volume of about 88 km^3, and a mean depth of 157 m (Markert *et al.*, 1997). Some rivers hold oligotrophic or ultra-oligotrophic proglacial lakes in their drainage basins (e.g. the Santa Cruz river drainage basin has 13 lakes, with a combined surface area of 2.6×10^3 km^2), others only have reservoirs (e.g. the River Chubut has a 70 km^2 reservoir lake), still others have both kinds of water body (e.g. the River Limay drainage basin, tributary of the River Negro, holds 29 lakes and four reservoirs). In every case the net effect of such lakes or reservoirs is a persistent modulation of the discharge series, which in some cases may be quite pronounced, as in the River Santa Cruz.

SAMPLING AND METHODS

The eight major rivers of Patagonia (south of Argentina) were sampled during eight missions between September 1995 and November 1998 within the framework of the PARAT project (project of the European Community–International Cooperation with Developing Countries). For each river basin, the main channel downstream at the mouth was sampled during most of the missions. Moreover, samples were collected on the main channel upstream near the Andes and on the major tributaries of some rivers during the missions of May 1996, December 1996 or March 1997 according to the station (see Table II and Figure 1).

Water samples were collected at the middle of the river from a bridge; the pH, temperature, conductivity and alkalinity were measured in the field. The river water samples were filtered in the field through a 0·45 μm Millipore filter. For each river, we analysed the major anions on a filtrate without any treatment and the major cations on a filtrate acidified with ultrapure HCl to pH 1–2. Samples for Sr isotope were also acidified with ultrapure HCl. For DOC analyses, the filtrate was treated with 1 ml of HgCl$_2$ at 1‰ to stop any microbiological activity, and stocked in a 60 ml glass bottle (the bottles had been cleaned and pyrolysed at 500 °C for 2 h). The samples for isotopic analysis of DIC were collected in 250 ml polyethylene bottles and poisoned with 1 ml of HgCl$_2$ at 5‰ to prevent any microbial activity. Bottles were carefully sealed, taking care that no trapped air remained in contact with the sample. Samples were kept between 0 and 5 °C prior to analysis. The major cations (Ca^{2+}, Mg^{2+}, Na$^+$, K$^+$) were analysed by atomic absorption spectrometry on a Perkin Elmer spectrometer with an air–C$_2$H$_2$ gaseous mixture. La was added (0·5%) to the sample for Ca^{2+} and Mg^{2+} analysis. The measurement is made with an accuracy of 1 μmol l^{-1}. The major anions (Cl$^-$, SO$_4^{2-}$, NO$_3^-$) were analysed by liquid chromatography on a Dionex 400 chromatograph. The detection limit is 1 μmol l^{-1}. Alkalinity was measured by titration with the Gran method. The DOC was analysed by combustion at 680 °C on platinum catalyst, after acidification, CO$_2$ degassing and detection by non-dispersive infrared analysis on a Shimadzu TOC 5000 analyser. The δ^{13}C of DIC was measured following the procedure of Kroopnick *et al.* (1970). The sample is acidified inside a vacuum line with concentrated phosphoric acid (H$_3$PO$_4$). The evolved CO$_2$ is purified and trapped with liquid nitrogen in a glass tube. The ^{13}C/^{12}C isotopic ratio of the CO$_2$ extracted from the DIC was then analysed on a VG OPTIMA mass spectrometer. The results are reported as δ values with reference to the Vienna Pee Dee Belemnite (VPDB; Craig, 1954) with an analytical precision of ±0·2‰.

Sr isotopic ratios and concentrations were analysed on a VG Sector multicollector mass spectrometer. Sr was deposited on W single filaments with Ta$_2$O$_5$ as activator. The NBS 987 standard yielded an ^{87}Sr/^{86}Sr value of 0·710 27 ± 1 (2σ mean, $n = 18$).

ISOTOPIC CONSTRAINT FOR RIVERINE DIC

Figure 3 summarizes the theoretical contributions of the different carbon sources with their respective ranges of δ^{13}C values to the δ^{13}C isotopic signature of the riverine DIC.

Table II. Periods of sampling on the eight Patagonian rivers and on their tributaries during the period 1995–98

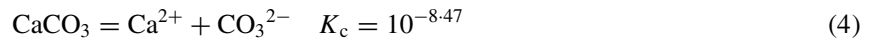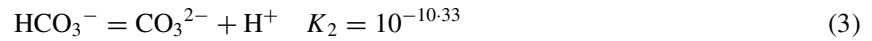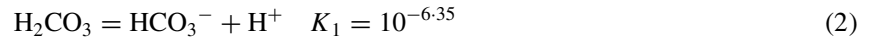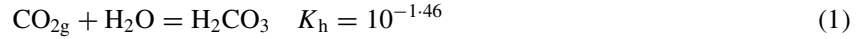| River (sampling station)	Code in Figure 1	Sampling period							
		Sep 95	May 96	Sep 95	Dec 96	Mar 97	Dec 97	Apr 98	Nov 98
Colorado basin									
Colorado (Rio Colorado)	COL1	X	X	X	X	X	X	X	X
Negro Basin									
Negro (Gral. Conesa)	NEG1	X	X	X	X		X	X	X
Neuquen (Neuquen)	NEU					X			
Limay (Bariloche)	LIM					X			
Chubut basin									
Chubut (Trelew)	CHU1	X	X	X	X	X	X	X	X
Chubut (Paso de Indios)	CHU2				X				
Chubut (El Maiten)	CHU3					X			
Mayo (Rio Mayo)	MAY				X				
Senguer (RP no. 22)	SEN				X				
Lepa (RN no. 40)	LEP					X			
Gualjaina (Gualjaina)	GUA					X			
Deseado basin									
Deseado (Jaramillo)	DES1	X	X	X	X		X	X	
Fenix (Perito Moreno)	FEN				X				
Chico basin									
Chico (Rio Chico)	CHI1	X	X	X	X		X	X	
Chico (Tamel Aike)	CHI2				X				
Santa Cruz basin									
Santa Cruz (Cte. Piedrabuena)	SAN1	X	X	X	X		X	X	
Santa Cruz (Ch. Fhur)	SAN2				X				
Lago del Desierto	LAG				X				
Coyle basin									
Coyle (RN no. 3)	COY1	X	X	X	X		X	X	
Coyle (Esperanza)	COY2				X				
Coyle (Gdor. Mayer)	COY3		X		X				
Gallegos basin									
Gallegos (Guer Aike)	GAL1	X	X	X	X		X	X	
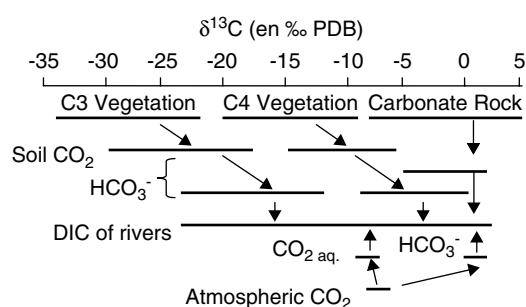
Figure 3. $\delta^{13}C_{DIC}$ theoretical variations of the different riverine DIC sources and their contribution to the river $\delta^{13}C_{DIC}$ after fractionation

The carbonate system

The DIC is composed of aqueous carbon dioxide ($CO_{2\ aq}$), carbonic acid (H_2CO_3), bicarbonate (HCO_3^{-}) and carbonate (CO_3^{2-}) ions. These aqueous compounds can be in contact with gaseous carbon dioxide ($CO_{2\ g}$) and/or carbonate minerals, such as calcite ($CaCO_3$). The carbonate system is controlled by the following four

equations (Stumm and Morgan, 1996):

$$CO_{2g} + H_2O = H_2CO_3 \quad K_h = 10^{-1.46} \tag{1}$$

$$H_2CO_3 = HCO_3^- + H^+ \quad K_1 = 10^{-6.35} \tag{2}$$

$$HCO_3^- = CO_3^{2-} + H^+ \quad K_2 = 10^{-10.33} \tag{3}$$

$$CaCO_3 = Ca^{2+} + CO_3^{2-} \quad K_c = 10^{-8.47} \tag{4}$$

where K_h, K_1, K_2 and K_c are the equilibrium constants of the carbonate system. These constants are temperature dependent. The above values are given for a temperature of 25 °C.

Generally, in river water, pH values range between 5·5 (which corresponds to the equilibrium with the atmospheric CO_2) and 8·3 (which is close to the pH for calcite precipitation). In this pH range, bicarbonate ions are the dominant DIC species. The (pCO_2 in the river is calculated from the pH, the temperature and the alkalinity concentration in the river water.
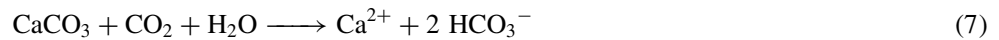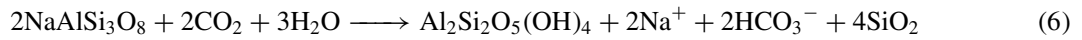
Soil CO_2 and C_3 or C_4 plants

The isotopic signature of the soil CO_2 is directly in relation to the vegetation that covers the area. Soil CO_2 is produced by the decay of organic matter and roots respiration:

$$CH_2O + O_2 \longleftrightarrow CO_2 + H_2O \tag{5}$$

We can distinguish two main types of vegetation, i.e. C_3 and C_4 plants, which differ in the pathway of photosynthesis. The C_3 plants absorb atmospheric CO_2 with a fractionation of about 20‰, leading to their isotopic signature being close to $-26‰$ (Mariotti, 1991). For the C_4 plants, the fractionation during CO_2 absorption is close to 4‰; consequently, their $\delta^{13}C$ range is between -19 and $-9‰$, with an average of $-12‰$ (Mariotti, 1991). During the processes of organic matter degradation and root respiration, there is no or very low fractionation. But Cerling *et al.* (1991) show an enrichment of soil gases in $^{13}CO_2$ by $+4·4‰$ caused by the difference of the diffusion coefficient of the two carbon isotopes (^{12}C and ^{13}C). As a result, the soil CO_2 has a $\delta^{13}C$ with an average of $-21‰$ with C_3 plants and of $-8‰$ with C_4 plants.

Rock weathering

The soil CO_2 plays a major role in the weathering of silicates (e.g. the hydrolysis of albite, Equation (6)) and carbonates (e.g. the dissolution of calcite, Equation (7)):

$$2NaAlSi_3O_8 + 2CO_2 + 3H_2O \longrightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4SiO_2 \tag{6}$$

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2\,HCO_3^- \tag{7}$$

During these weathering reactions, the CO_2 is transformed into bicarbonate ions (HCO_3^-) and released into the river water. During this change of carbon species, fractionation also occurs. The factor of enrichment between the different species is well known (Mook *et al.*, 1974; Zhang *et al.*, 1995; Szaran, 1998) and is temperature dependent (see Table III).

As seen in Equation (7), only half of the HCO_3^- comes from the soil CO_2 and the other half is supplied by carbonate dissolution from the rock. The $\delta^{13}C$ of the bicarbonate ions released into the solution is a mixing between the isotopic signature of the soil CO_2 ($-21‰$, in the case of a C_3 vegetation) and the isotopic signature of the carbonate rocks (0‰). Nevertheless, carbonate rocks can also be weathered by acids other than H_2CO_3, such as acids contained in the rainwater, like H_2SO_4 or HNO_3. In this case, all the riverine DIC comes from the carbonate dissolution, and it has the same isotopic signature (0‰).

Table III. Equations of the relationship between the isotopic enrichment factor ε between the different carbonate species and the temperature (°C) (from Zhang *et al.* (1995))

Equation[a]	ε (‰)	
	5 °C	25 °C
Fractionation between CO_2 gas and CO_2 aq		
$\varepsilon\ CO_2\ _{gas}\ (CO_2\ _{aq}) = (0.0049 \pm 0.0015)T - 1.31 \pm 0.005$	-1.29	-1.19
Fractionation between CO_2 gas and bicarbonates		
$\varepsilon\ CO_2\ _{gas}\ (HCO_3^-) = (-0.1141 \pm 0.0028)T + 10.78 \pm 0.04$	10.2	7.9
Fractionation between CO_2 gas and carbonates		
$\varepsilon\ CO_2\ _{gas}(CO_3^{2-}) = (-0.052 \pm 0.021)T + 7.22 \pm 0.38$	7	6

[a] Temperature T (°C).

Concerning the CO_2 inputs from the atmosphere, there is a similar fractionation to that occurring in the soil during its incorporation as bicarbonate of $+8.5$‰ (for a temperature of 20 °C). The $\delta^{13}C$ of atmospheric CO_2 can vary between -8 and -6‰ (Cerling *et al.*, 1991), with an average value of -7.8‰ (Mariotti, 1991).

RESULTS AND DISCUSSION

DIC and DOC variations in Patagonian rivers

DIC concentration in a river water is mainly controlled by lithology (presence or not of carbonates), discharge and temperature variations, and biogeochemical processes, such as organic matter oxidation.

As seen in Figure 4a, DIC concentrations measured in Patagonian rivers present a general decreasing trend with runoff—as already observed for the Amazon and its tributaries (Probst *et al.*, 1994), even if this relationship cannot be observed of each river, contrary to what has already been observed for some other major rivers of the world (e.g. see the Ubangui and Congo (Probst *et al.* 1992). Such a relationship indicates that, when the runoff increases, the riverine DIC content is progressively diluted by increasing inputs of rainwater and snow and glacier melt waters, which have very low DIC contents. The largest Patagonian rivers (mainly those with proglacial or reservoir lakes in their respective basins) depict a weak seasonal effect in their DIC concentrations and appear to be uncorrelated with mean monthly discharges. In most rivers, DIC speciation (about 90%) is accounted for by carbonate alkalinity (HCO_3^- and CO_3^{2-}; Table IV). Exceptions are the Rivers Santa Cruz and Gallegos, where a high proportion of DIC is accounted for by H_2CO_3. This is probably linked to the contributions of high pCO_2 waters circulating under glaciers and snow covers in the upper river basin (see the 'Relationship with pCO_2' section).

Riverine DOC can originate from autochthonous origin (phytoplankton production in the river itself) and from allochthonous origin (erosion of soil organic matter). DOC concentrations present a general decreasing trend with runoff (Figure 4b), except for the Gallegos, in which the DOC content is mainly of allochthonous origin.

Figure 5 further shows the significance of hydrological conditions in the joint control of DIC and DOC, and also the diverse behaviour of those rivers containing coal beds (Gallegos) and marshes and peat (Coyle) in their basins. In these rivers, small increments of DIC are associated with large increments of DOC concentrations and, as already seen in Figure 4b for the Gallegos (discharge data are not available for the Coyle), the DOC concentrations increase with discharge, which points to an allochthonous origin of the organic carbon.

Contribution of rock weathering to riverine DIC

As seen previously, it is very important to determine the contributions of silicate weathering and of carbonate dissolution to the total riverine DIC because for silicate weathering all DIC originated from
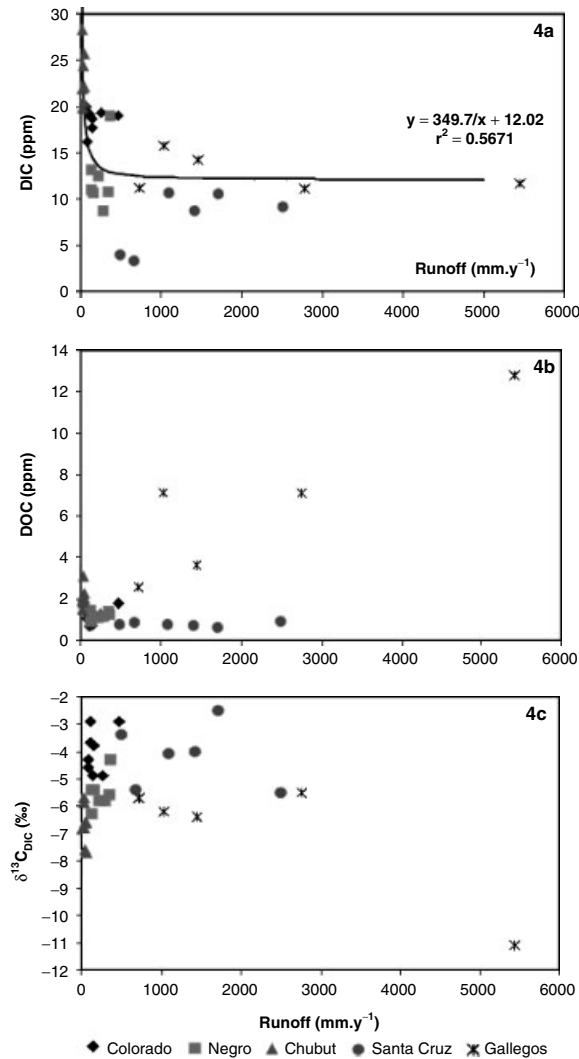
Figure 4. Relationships between the DIC concentrations (a), DOC contents (b), $\delta^{13}C_{DIC}$ (c) and the runoff intensity for five Patagonian rivers (Colorado, Negro, Chubut, Santa Cruz and Gallegos)

the soil CO_2 (see Equation (6)) and for carbonate dissolution half the DIC is supplied by carbonates (see Equation (7)), and their respective $\delta^{13}C$ isotopic signatures are very different. Thus, we used an independent tracer, i.e. Sr isotopes, to show the contribution of carbonates (around 0·708), which have an $^{87}Sr/^{86}Sr$ composition significantly different from that of basalts (around 0·704) and of metamorphic and plutonic rocks (>0·715) (Faure, 1986). Moreover, the riverine Sr isotopic signature is not influenced by biogeochemical processes such as organic matter oxidation and CO_2 degassing. Patagonian rivers drain a wide variety of igneous, sedimentary and metamorphic rocks, and their water can be regarded as a series of three-component mixtures (Figure 6). With the exception of the Rivers Santa Cruz and Chico, the $^{87}Sr/^{86}Sr$ compositions of most river waters appear as mixtures of two-component end-members, represented by basic to intermediate volcanic rocks at one extreme, and carbonates and evaporites at the other. This is better observed in the inset in Figure 5. The Sr isotopic composition of the River Negro is located in

Table IV. Physico-chemical and isotopic compositions of the Patagonian rivers at the outlet of each drainage basin

Season	T (°C)	pH	Runoff (μmol year⁻¹)	H₂CO₃ (μmol l⁻¹)	HCO₃⁻ (μmol l⁻¹)	CO₃²⁻ (μmol l⁻¹)	log[pCO₂ (atm)]	DIC (mg l⁻¹)	DOC (mg l⁻¹)	SI calcite	δ¹³C_DIC (‰)	Sr (ppb)	⁴⁷Sr/⁴⁴Sr
Colorado (at Rio Colorado)													
Sep 95	15·7	7·96	256	42	1559	6	−3·02	19·29	1·28	0·19	−4·9	816	0·706 965
May 96	6·3	7·96	78	56	1602	4	−3·04	19·94	1·08	0·03	−4·3	762	0·706 957
Sep 96	14·6	7·8	112	64	1533	4	−2·86	19·21	1·24	−0·02	−3·7	761	0·706 954
Dec 96	21·3	8·53	116	11	1547	23	−3·66	18·97	0·7	0·82	−2·9	818	0·706 944
Mar 97	20·4	8·15	86	22	1315	8	−3·24	16·15	1·26	0·44	−4·6	1090	0·7069
Dec 97	20·4	8·28	472	20	1552	12	−3·30	19·01	1·77	0·60	−2·9		
Apr 98	15·4	8·32	144	18	1448	11	−3·40	17·73	1·35	0·55	−4·9		
Nov 98	20	7·98	151	38	1509	6	−3·01	18·63	0·74	0·27	−3·8		
Negro (at Gral. Conesa)													
Sep 95	13·3	7·54	348	65	829	1	−2·87	10·74	1·41	−1·21	−5·6	94	0·706 399
May 96	8	8·00	287	22	709	2	−3·42	8·79	1·18	−1·02	−5·8	64	0·706 957
Sep 96	13·8	7·28	130	114	803	1	−2·62	11·00	1·43	−1·47	−5·4	97	0·706 39
Dec 96	22·6	8·54	158	6	868	13	−3·80	10·65	1·12	−0·07	−5·4	93	0·706 28
Dec 97	18·3	6·48	383	715	869	0	−1·76	19·01	1·26	−2·13	−4·3		
Apr 98	16·6	8·21	220	16	1018	6	−3·43	12·49	1·1	−0·30	−5·8		
Nov 98	20	7·57	130	67	1027	2	−2·77	13·14	0·9	−0·96	−6·3		
Chubut (at Trelew)													
Sep 95	9	8·11	37	39	1667	7	−3·16	20·55	1·97	−0·25	−7·6	84	0·706 344
May 96	8·8	7·54	50	147	1696	2	−2·58	22·14	2·3	−0·82	−6·6	77	0·706 34
Sep 96	7·4	6·75	26	920	1669	0	−1·80	31·08	1·93	−1·60	−5·7	87	0·706 388
Dec 96	20·3	8·5	23	14	1785	24	−3·46	21·86	1·48	0·41	−6·8	110	0·706 638
Mar 97	17	7·67	25	85	1565	3	−2·70	19·83	1·82	−0·60	−5·9		
Dec 97	17	7·2	37	281	1753	1	−2·19	24·42	3·1	−1·00	−6·6		
Apr 98	16	7·53	51	151	1985	3	−2·47	25·67	2·04	−0·59	−7·7		
Nov 98	20	7·94	19	63	2284	8	−2·79	28·27	2·11	−0·00	−6·8		
Deseado (at Jaramillo)													
Sep 95	8·1	8·8	11	22	4632	90	−3·41	56·93	10·27	0·9	−7·6	169	0·706 174
May 96	10·9	8·62	11	35	6149	71	−3·17	63·06	6·36	1·2	−1·8	2573	0·707 224
Sep 96	2·6	8·42	11						8·55	0·21	−9·4	130	0·706 213
Dec 96	17·8	9·35	11	5	4315	384	−3·94	56·44	8·9	1·47	−4·6	409	0·706 821
Dec 97	19·6	8·51	11	26	3469	47	−3·18	42·5		0·67	−9·8		
Apr 98	10	8·8	11	12	2673	55	−3·64	32·87	3·96	0·04			
Coyle (at RN N°3)													
Sep 95	7·4	7·55	19	114	1307	1	−2·71	17·07	6·51	−1·07	−12·8	72	0·705 593
May 96	10	8·23	19	30	1722	9	−3·26	21·12	3·42	−0·18	−5	77	0·705 594
Sep 96	16	7·74	19	89	1892	4	−2·70	23·82	3·91	−0·46	−4·6	100	0·705 607
Dec 96	15·7	10·2	19	0	882	527	−5·60	16·91	7·03	1·37	−11·2	82	0·705 601
Dec 97	15	7·8	19	50	1206	3	−2·96	15·10	5·673	−0·82	−9·4		
Apr 98	8	8·47	19	20	1906	17	−3·46	23·32	4·06	0·11	−7·1		

Table IV. (*Continued*)

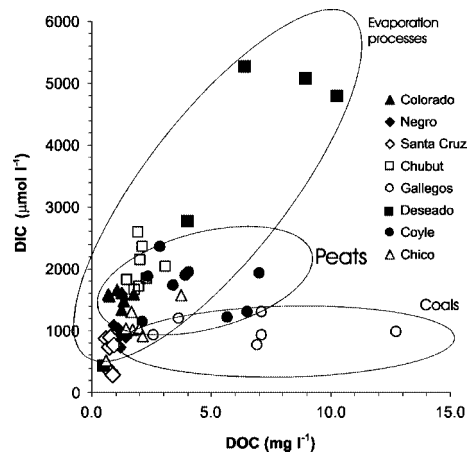| Season	T (°C)	pH	Runoff (μmol year⁻¹)	H₂CO₃ (μmol l⁻¹)	HCO₃⁻ (μmol l⁻¹)	CO₃²⁻ (μmol l⁻¹)	log[pCO₂ (atm)]	DIC (mg l⁻¹)	DOC (mg l⁻¹)	SI calcite	δ¹³C_DIC (‰)	Sr (ppb)	⁸⁷Sr/⁸⁶Sr
Chico (at Rio Chico)													
Sep 95	7·5	8·2	56	30	1556	7	−3·29	19·12	3·74	−0·30	−7·2	85	0·709 025
May 96	7·7	7·43	56	115	1008	1	−2·70	13·49	1·72	−1·29	−1·9	72	0·709 874
Sep 96	5·1	7	56	430	1309	0	−2·17	20·87	1·66	−1·57	−1·8	88	0·709 946
Dec 96	13·8	8·18	56	18	1020	6	−3·42	12·52	1·99	−0·51	−5·7	56	0·709 87
Dec 97	15·2	6·8	56	376	903	0	−2·08	15·35	2·12	−1·92	−4·4		
Apr 98	7·2	8·46	56	11	1023	9	−3·73	12·51	1·45	−0·24	−2·1		
Santa Cruz (at Cte. Pledrabuena)													
Sep 95	7·8	7·13	493	62	271	0	−2·97	3·99	0·78	−2·57	−3·4	33	0·709 687
May 96	7·4	6·1	1710	626	254	0	−1·97	10·56	0·61	−2·64	−2·5	26	0·711 227
Sep 96	7·2	6·25	669	179	102	0	−2·52	3·38	0·89	−3·79	−5·4	27	0·710 922
Dec 96	12·7	6·26	1416	438	289	0	−2·05	8·73	0·72	−3·30	−4	33	0·711 234
Dec 97	15·5	8·1	1093	601	290	0	−1·87	10·7	0·79	−3·38	−4·1		
Apr 98	9·9	6·15	2503	518	250	0	−2·02	9·22	0·94	−3·52	−5·5		
Gallegos (at Guer Aike)													
Sep 95	6·4	6·96	5428	254	730	0	−2·38	11·81	12·72	−2·07	−11·1	58	0·705 049
May 96	2·3	6·9	2800	239	536	0	−2·47	9·29	6·9	−2·49		40	0·704 77
Sep 96	4·8	6·65	2761	393	531	0	−2·21	11·09	7·1	−2·64	−5·5	48	0·704 851
Dec 96	12·6	7·44	724	84	838	1	−2·77	11·08	2·59	−1·44	−5·7	62	0·704 784
Dec 97	15·9	6·41	1034	659	653	0	−1·83	15·74	7·12	−2·60	−6·2		
Apr 98	6·6	8·05	1448	32	1153	4	−3·27	14·27	3·65	−2·60	−6·4		

Figure 5. Relationship between riverine DIC and DOC contents in the Patagonian rivers
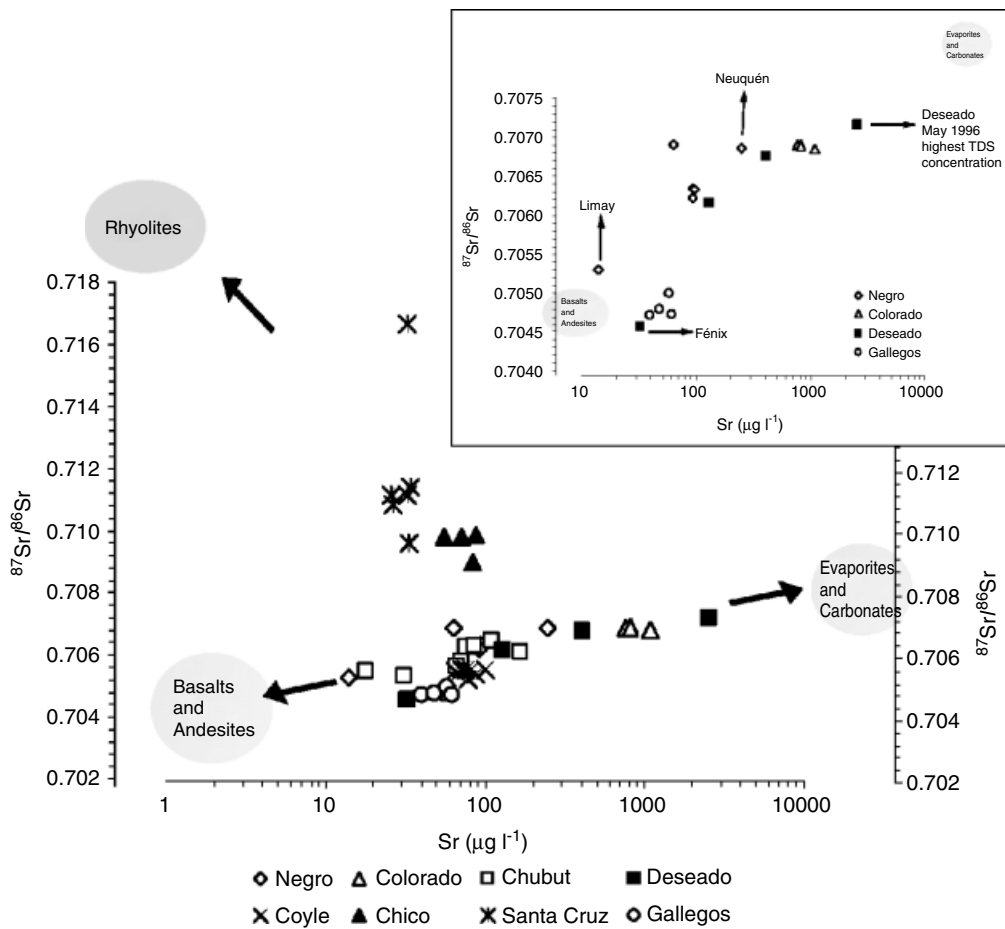

Figure 6. $^{87}Sr/^{86}Sr$ versus Sr in the Patagonian rivers. The contributions of the different rock poles are represented by shaded areas according to the data of Faure (1986)

an intermediate position between the two end-members represented by their tributaries (i.e. Rivers Limay and Neuquén). The drainage basin of the River Limay is dominated by basalts and andesites with an significant proportion of granitic rocks (DNSG, 1997). Although, basalts and andesites are important in the headwaters of the Neuquén, a high $^{87}Sr/^{86}Sr$ ratio and Sr concentrations point to the importance of evaporites and carbonate rocks (i.e. Mendoza, Cuyo and the Lotena Group (DNSG, 1997) which represent about 10% of the total lithology of the drainage basin. Next to the River Neuquén, the River Colorado shares a similar lithology. In the Colorado, however, the waters reflect an Sr isotopic composition dominated by carbonate and evaporite signatures, compared with the River Negro. A less radiogenic end-member is found in the river waters of the Gallegos and in the Andean tributary of the Deseado (i.e. River Fénix; see inset in Figure 6). The dominant rocks in the Gallegos drainage basin are Pliocene–Recent basalts and glacial deposits most probably derived from basaltic rocks. Thus, the four water samples of the River Gallegos exhibit a mean Sr isotopic composition ($^{87}Sr/^{86}Sr = 0.704\,863 \pm 0.000\,129$) slightly higher than the mean composition found in local basaltic rocks ($^{87}Sr/^{86}Sr = 0.703\,267 \pm 0.000\,091$) (D'Orazio *et al.*, 2000).

The isotopic water composition of the River Deseado is variable and suggests a dependence on water discharge. Probably, during low stand (i.e. high total dissolved solids concentration), waters draining terrains with carbonates and evaporites dominate over waters draining basic rocks (i.e. River Fénix).

The Santa Cruz and Chico river water samples are located in the middle position in the series of three-component mixtures. Clearly, the presence of rhyolites in the headwaters of the Lago del Desierto (a tributary of the River Santa Cruz), point to such rocks as important Sr contributors. Near the continental outlet, the River Santa Cruz water presents intermediate $^{87}Sr/^{86}Sr$ ratios combined with low Sr concentrations, also suggesting a contribution from basic rocks. In the River Chico water, a similar intermediate $^{87}Sr/^{86}Sr$ ratio but with a high Sr concentration could indicate that, together with basic and felsic volcanic rocks, carbonates and evaporites also contribute to this river.

Consequently, these results show that the Patagonian river water composition is controlled by a carbonate and evaporite end-member and two silicate end-members (rhyolites and basalts) that have different $^{87}Sr/^{86}Sr$ ratios and which could control the $\delta^{13}C_{DIC}$ (see below).

$\delta^{13}C$ values of DIC in Patagonian rivers

Temporal and spatial variations. The $\delta^{13}C_{DIC}$ of Patagonian rivers ranges from $-12 \cdot 8$ to $-1 \cdot 8‰$ at the outlet (Table IV and Figure 2). On average, Patagonian rivers have a signal higher than other world rivers (see Table V). In spite of these large variations we can class the Patagonian rivers into two groups:

1. The Colorado, Negro, Chubut, and Santa Cruz have the highest $\delta^{13}C_{DIC}$ values and they present low temporal variations of the signal (less than 3‰). These rivers are, in terms of discharge, the most important in Patagonia; they are supplied by lakes at the source and glaciers for the River Santa Cruz. They are also impacted by dams (Rivers Colorado, Negro and Chubut). The high $\delta^{13}C_{DIC}$ values can be explained by the presence of lakes and dams that increase the residence time of water and improve the exchanges with the atmospheric CO_2, as already shown by Yang *et al.* (1996) for the St Lawrence River. Moreover, in these rivers, the DOC content is very low (<2 mg l^{-1}). Consequently, the contribution of DOC oxidation in the river itself to produce DIC must be very low and cannot affect the $\delta^{13}C_{DIC}$.
2. The Rivers Deseado, Chico, Coyle and Gallegos have lower $\delta^{13}C_{DIC}$ values than the first group and they present important temporal variations (between $4 \cdot 4$ and $8 \cdot 2‰$), even though these variations are not seasonal (see below). We also note that these rivers present a more significant DOC content, which could contribute to lowering the $\delta^{13}C_{DIC}$, as already shown by Barth and Veizer (1999) for the St Lawrence river basin. These rivers are smaller than the rivers of the first group, and there is no or few lakes and dams. Consequently, the atmospheric exchanges are not as great as for rivers of the first group and their contribution to the $\delta^{13}C_{DIC}$ is much less important.

Table V. Average values and ranges of $\delta^{13}C_{DIC}$ in some world rivers (after literature data) compared with Patagonian rivers (this study)

River	$\delta^{13}C_{DIC}$			Reference
	Mean	Max.	Min.	
Kalamazoo (USA)	−10·42	−8·7	−13·7	Alekwana and Krishnamurthy (1998)
Owens Creek (USA)		−9	−15	Kendall et al. (1992)
Shelter Run (USA)		−11	−20	Kendall et al. (1992)
Fraser (Canada)	−6·04	−3·57	−10·2	Cameron et al. (1995)
St Lawrence (Canada)	−5·12	+0·7	−16·5	Yang et al. (1996)
	−4·66	+0·3	−13·7	Barth et al. (1998)
	−4	+2·2	−13·3	Barth and Veizer (1999)
	−5·9	+0·11	−14·21	Hèlle et al. (2002)
Ottawa (Canada)	−10·43	−7·3	−17·4	Telmer and Veizer (1999)
Mackenzie (Canada)	−11·82	−5·7	−24·4	Hitchon and Krouse (1972)
Amazon (Brazil)		−11·8	−28·5	Longinelli and Edmond (1983)
Orinoco (Venezuela)		−11·3	−20·1	Tan and Edmond (1993)
Strengbach (France)	−16·68	−9·3	−24·4	Amiotte-Suchet et al. (1999)
Rhöne (France)	−8·91	−2·2	−13	Aucour et al. (1999)
Rhine (Germany)	−8·8	−4·4	−14·4	Buhl et al. (1991)
	−10·14	−4	−17·1	Flintrop et al. (1996)
Danube (Austria)	−6·92	+0·3	−11·4	Pawellek and Veizer (1994)
Ganges Brahmaputra (India)		+3·9	−12·7	Galy and France-Lanord (1999)
Indus (Pakistan)	−3·21	+0·6	−9·6	Karim and Veizer (2000)
Waimakariri (New Zealand)	−7·62	−5·28	−15·94	Taylor and Fox (1996)
Patagonian rivers				This study
Colorado	−4	−2·9	−4·9	
Negro	−5·49	−4·3	−6·3	
Chubut	−7·34	−5·7	−10	
Deseado	−6·32	−1·8	−9·8	
Chico	−4·56	−1·8	−8·8	
Santa Cruz	−4·25	−2·5	−5·5	
Coyle	−7·97	−5	−12·8	
Gallegos	−6·98	−5·5	−11·1	

At first view, the temporal variations are not seasonal (extreme values are obtained for the same period, September 1995 and 1996 for the Chico, Chubut, Coyle and Gallegos) and the available discharge data confirm this. For the rivers for which the discharge data are available (Colorado, Negro, Chubut, Santa Cruz and Gallegos) there is no relationship between $\delta^{13}C_{DIC}$ and runoff (Figure 4c), except perhaps the Gallegos, for which the lowest $\delta^{13}C_{DIC}$ value corresponds to the highest discharge in September 1995. Indeed, for the River Gallegos, the DOC content increases when the runoff increases (Figure 4b) and the $\delta^{13}C_{DIC}$ could decrease due to respiration processes. In the same way, for the Santa Cruz, the two lowest $\delta^{13}C_{DIC}$ (−5·4‰ in September 1996 and −5·5‰ in April 1998) correspond respectively to a low water period and to a high flow period (Figure 2).

Some samples were also collected in the upper parts of some Patagonian river basins (Negro, Chubut, Deseado, Chico, Santa Cruz and Coyle), on the main channels and on the different tributaries during May 1996, December 1996 and March 1997 (Table II). As seen in Table VI, the $\delta^{13}C_{DIC}$ values measured in the upper basins are close to the values measured in the main channel at the outlet. For the first group of rivers, the upstream−downstream variations are very low (<2‰; Negro and Santa Cruz), except for the Chubut. For this river, the values measured in the upper catchment are lower (−6 to −10‰) than those measured at the outlet (−5·9 to −6·8‰). Consequently, the Chubut tributaries (Mayo, Senguer, Lepa, Gualjaina) and the

Table VI. Physico-chemical and isotopic compositions of the Patagonian rivers and of their tributaries in the upper drainage basins

Basin	River	Season	pH	Alkalinity (μmol l^{-1})	log[pCO$_2$ (atm)]	DIC (mg l^{-1})	DOC (mg l^{-1})	δ^{13}C$_{DIC}$ (‰)	Sr (ppb)	^{47}Sr/^{44}Sr
Negro	Limay	Mar 97	6·24	292	−2·00	8·59	0·98	−5·3	14	0·706 921
Chubut	Chubut (at P de Indios)	Dec 96	8·6	1392	−3·70	16·56	1·63	−7·2	67	0·705 692
	Chubut (at El Maiten)	Dec 96	8·53	1751	−3·55	20·94	1·58	−8·4	59	0·704 848
	Mayo (at Rio Mayo)	Dec 96	7·72	288	−3·50	3·62	0·65	−6	18	0·705 566
	Senguer (RP no. 22)	Mar 97	7·45	566	−2·95	7·44	1·47	−8·2	31	0·705 385
	Lepa (at RN no. 4D)	Mar 97	7·97	1490	−3·04	18·33	3·85	−10		
	Gualjaina (Gualjaina)	Mar 97	7·72	2039	−2·65	25·63	3·64	−9·2		
Deseado	Fenix (Perito Moreno)	Dec 96	6·4	453	−2·00	11·50	0·47	−4·7	33	0·704 63
Coyle	Coyle (at Gdor. Mayer)	May 96	7·96	2350	−2·89	29·21	2·87	−6·7	88	0·705 443
	Coyle (at Gdor. Mayer)	Dec 96	9·17	1869	−4·17	21·27	2·36	−6·9	79	0·705 295
	Coyle (at Esperanza)	Dec 96	8·83	1144	−4·01	13·42	2·1	−8	65	0·705 55
Chico	Chico (at Tamel Aike)	Dec 96	6·6	526	−2·12	10·56	0·58	−8·8		
Santa Cruz	Santa Cruz (at Ch. Fhur)	Dec 96	6·79	288	−2·57	4·94	0·22	−3·8	34	0·711 457
	Lago del Desierto	Dec 96	6·77	385	−2·42	6·66	0·75	−5·3	33	0·716 705

upper Chubut could be associated with rivers of the second group. For the second group rivers, the spatial variations are more important (about 3‰ for the Chico and the Coyle), except for the Deseado, which presents the same value. All these upstream–downstream variations are difficult to explain because the variations are very low and because discharge data do not exist for these rivers.

Relationship with ^{87}Sr/^{86}Sr. As shown above, we can use the ^{87}Sr/^{86}Sr isotopic composition of the river water to determine the contribution of carbonate and silicate (rhyolites and basalts) weathering, as this isotopic tracer is conservative and as there is no interaction with atmospheric CO$_2$ exchange or with respiration processes. By plotting the ^{87}Sr/^{86}Sr ratio versus the δ^{13}C$_{DIC}$ (Figure 7) it becomes evident that the δ^{13}C$_{DIC}$ does not allow one to identify these two contributions clearly. This is because each river that presents relatively constant values of ^{87}Sr/^{86}Sr ratio exhibits large variations of δ^{13}C$_{DIC}$ due to biogeochemical processes, which interfere with the δ^{13}C$_{DIC}$ signature of DIC released by carbonate and silicate weathering. Nevertheless, if we plot the average values for each river, then (except for the Rivers Santa Cruz and Chico) a positive trend appears in going from a low ^{87}Sr/^{86}Sr ratio and δ^{13}C$_{DIC}$ end-member corresponding to a basaltic rock weathering to a higher ^{87}Sr/^{86}Sr ratio and δ^{13}C$_{DIC}$ end-member corresponding to carbonate dissolution. Santa Cruz and Chico river values cannot be included in this pattern. This is because, as seen in the ^{87}Sr/^{86}Sr versus Sr diagram (Figure 6), the carbonate contributions are very low and the waters of these two rivers result more from a mixing between two silicate rock end-members (basalts and rhyolites).

Relationship with pCO$_2$. As seen in Figure 8, the River Colorado has an average pCO$_2$ value of 800 ppm, and presents low variations. In contrast, the Santa Cruz exhibits a high pCO$_2$ value (on average 9000 ppm). This high value can be attributed to the river water being supplied by glacier melt, which releases high pCO$_2$ waters. The other Patagonian rivers show pCO$_2$ values that are, on average, 10 times higher than the atmospheric pCO$_2$ and present significant variations.

All the Patagonian rivers, except the Santa Cruz, present the lowest pCO$_2$ during the mission of December 1996 (Figure 8). For the Colorado, Negro, Deseado and Coyle, these pCO$_2$ values are even below the atmospheric pCO$_2$, and are probably a consequence of a period of high photosynthesis activity in the river water column. During the following summer (mission of December 1997) we observed the highest values.
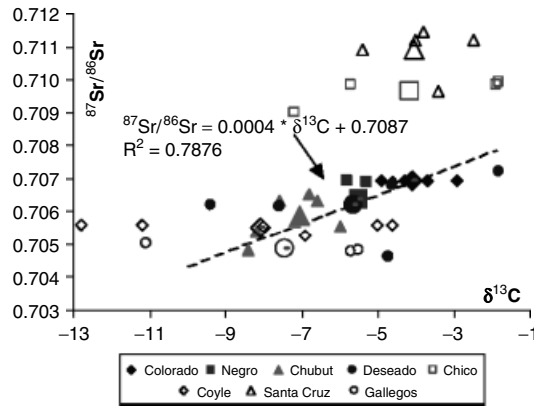
Figure 7. Relationship between Sr isotopic ratio $^{87}Sr/^{86}Sr$ and the $\delta^{13}C_{DIC}$. The largest symbols represent the average value for each river. The equation is calculated with the average value of each river, except Chico and Santa Cruz (see text)
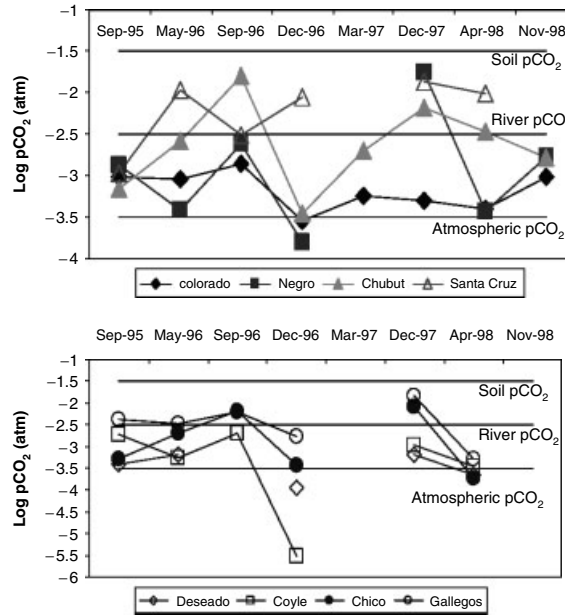

Figure 8. Temporal variations of pCO_2 calculated at the Patagonian river mouths during the eight sampling missions with references to the mean pCO_2 of the atmosphere, soils and river waters

This increase is due to a drop in the pH in the rivers in comparison with the values of the other missions. Moreover, monthly discharges of Patagonian rivers in December 1997 are higher than in December 1996 (see Figure 2).

The $\delta^{13}C$ of DIC can be expressed as a function of aqueous CO_2 ($H_2CO_3^*$), bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}) with their respective $\delta^{13}C$ values ($\delta^{13}C_{H_2CO_3^*}$, $\delta^{13}C_{HCO_3^-}$ and $\delta^{13}C_{CO_3^{2-}}$):

$$[DIC]\delta^{13}C_{DIC} = \delta^{13}C_{H_2CO_3^*}[H_2CO_3^*] + \delta^{13}C_{HCO_3^-}[H_2CO_3^-] + \delta^{13}C_{CO_3^{2-}}[CO_3^{2-}] \qquad (8)$$

For the Patagonian rivers we can neglect the carbonate ions (CO_3^{2-}) term, except for four samples (one on the River Deseado and three on the River Coyle where carbonate ions represent 15·9% and 54·5%, 10·6%

and 5·3% respectively of the total DIC). These samples correspond to the mission of December 1996. For the others, carbonate ions represent less than 5% of the total alkalinity. Then Equation (8) can be written as follows:

$$[DIC]\delta^{13}C_{DIC} = \delta^{13}C_{H_2CO_3^*}[H_2CO_3^*] + \delta^{13}C_{HCO_3^-}[HCO_3^-] \tag{9}$$

If one considers that $\delta^{13}C_{H_2CO_3^*}$ and $\delta^{13}C_{HCO_3^-}$ of the river water are in isotopic equilibrium with the isotopic signature ($\delta^{13}C_{CO_2\ gas}$) of the soil CO_2 (mixing of biogenic and atmospheric CO_2):

$$\delta^{13}C_{H_2CO_3^*} = \delta^{13}C_{CO_2\ gas} + \varepsilon_1 \tag{10}$$

$$\delta^{13}C_{HCO_3^-} = \delta^{13}C_{CO_2\ gas} + \varepsilon_2 \tag{11}$$

with $\varepsilon_1 = \varepsilon CO_2\ _{gas}(H_2CO_3^*)$ and $\varepsilon_2 = \varepsilon CO_2\ _{gas}(HCO_3^-)$ (see values in Table III), one can write Equation (9) as follows:

$$\delta^{13}C_{DIC} = \delta^{13}C_{CO_2\ gas} + \frac{\varepsilon_1}{1 + [HCO_3^-]/[H_2CO_3^*]} + \varepsilon_2(1 + [H_2CO_3^*]/[HCO_3^-]) \tag{12}$$

showing that the variation of the $\delta^{13}C_{DIC}$ is controlled by the ratio $[H_2CO_3^*]/[HCO_3^-]$ in the solution, as already proposed by Amiotte-Suchet *et al.* (1999).

The plot of the $\delta^{13}C_{DIC}$ versus the ratio $[H_2CO_3^*]/[HCO_3^-]$ is given in Figure 9. The dotted curves represent different theoretical patterns of riverine $\delta^{13}C_{DIC}$ in isotopic equilibrium with different soil CO_2 isotopic signatures ($\delta^{13}C_{CO_2\ gas}$). These curves are calculated from Equation (12) for different $\delta^{13}C_{CO_2\ gas}$. The first remark is that the riverine $\delta^{13}C_{DIC}$ is not in equilibrium with a constant value of the soil $\delta^{13}C_{CO_2\ gas}$ because the different clusters of points intersect the different theoretical curves. The $\delta^{13}C_{CO_2\ gas}$ values vary from -21 to $-4‰$, showing that the soil CO_2 is a mixing of biogenic CO_2 ($\delta^{13}C_{CO_2\ gas} = -20$ to $-26‰$ for C_3 plants) and atmospheric CO_2 ($\delta^{13}C_{CO_2\ gas} = -8‰$) and that the proportion of biogenic and atmospheric CO_2 is variable according to the river and to the season. This result is different to what was observed by Amiotte-Suchet *et al.* (1999) on a small granitic catchment in the Vosges Mountains (France), where the $\delta^{13}C_{DIC}$ was in equilibrium with a constant value of $\delta^{13}C_{CO_2\ gas}$.

In Figure 9, one can distinguish two groups of points:

1. Samples (mainly from the Rivers Santa Cruz and the Negro) presenting large variations (0 to 2·1) of the ratio $[H_2CO_3^*]/[HCO_3^-]$ and high values of $\delta^{13}C_{DIC}$ ($-1·5$ to $-6‰$) that tend to equilibrium with the
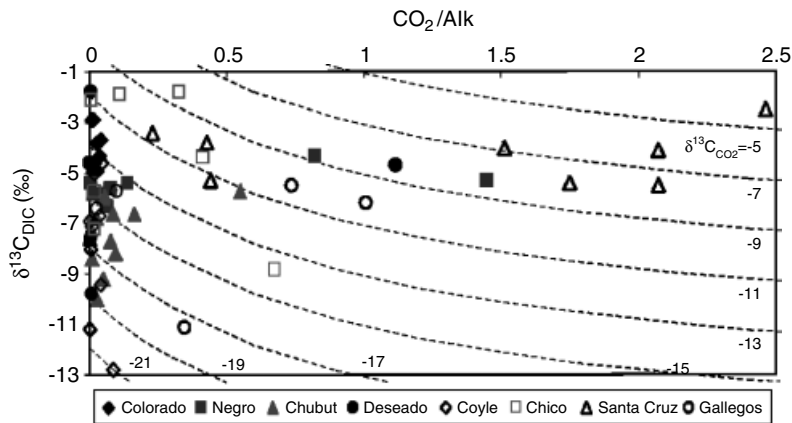

Figure 9. Relationship between $\delta^{13}C_{DIC}$ measured in the Patagonian rivers and the calculated ratio H_2CO_3/Alkalinity. The dotted curves represent different theoretical patterns of riverine $\delta^{13}C_{DIC}$ calculated for different soil $\delta^{13}C_{CO_2\ gas}$

atmospheric CO_2 after fractionation (around $-5‰$). This result shows the role of glaciers in river water supply and also the role of the atmospheric exchanges, which increase the riverine $\delta^{13}C_{DIC}$.

2. The second group, with a very low ratio $[H_2CO_3^*]/[HCO_3^-]$ (<0.3), exhibits greater variations of the $\delta^{13}C_{DIC}$ (-1.5 to $-13‰$) with lower values than for the first group, indicating different biogeochemical processes in the river. The variable $\delta^{13}C$ value of soil gaseous CO_2 is a consequence of variable mixing between biogenic CO_2 (which decreases $\delta^{13}C_{DIC}$) and atmospheric CO_2 (which increases $\delta^{13}C_{DIC}$).

Role of DOC. DOC in river can have two distinct origins: allochthonous, i.e. DOC supplied by the erosion of soil organic matter (mainly fulvic and humic acids) and autochthonous, i.e. DOC produced by photosynthesis in the river water. The autochthonous fraction is generally more labile than the DOC coming from soil leaching. Soil organic matter has an isotopic signature of about $-26‰$ for C_3 plants. The C/N ratio can be used to determine the origins of the organic matter. Meybeck (1982) showed that C/N >8 represents material coming from soil and lower values seem to indicate a riverine phytoplanktonic source. Patagonian rivers exhibit a C/N <4, except for the Gallegos, which has a ratio close to 10 (Depetris *et al*., 2005) due to the inputs of coalmine wastes. This result indicates that DOC of Patagonian rivers is dominated by respiratory processes. That means that riverine DOC is labile and it can be easily transformed into DIC by oxidation processes.

The plot of the evolution of $\delta^{13}C_{DIC}$ versus DOC content shows two different trends (Figure 10), one for low DOC content (<2 mg l^{-1}) and the other for high DOC content ($2-12$ mg l^{-1}). For low DOC content we observe the highest $\delta^{13}C_{DIC}$ values. These values reflect a control of the riverine $\delta^{13}C_{DIC}$ by atmospheric CO_2, and DOC content has no influence on the isotopic signature of the DIC pool. This is the case for the Rivers Colorado, the Negro and the Santa Cruz. In contrast, for the other rivers, the $\delta^{13}C_{DIC}$ decreases when the DOC content increases, indicating that the riverine isotopic signature of DIC could be controlled by the DOC content in the river. We can consider two hypotheses to explain this pattern:

1. Organic carbon oxidation in the river can contribute to a decrease in the riverine $\delta^{13}C_{DIC}$. Furthermore, the C/N ratio of Patagonian rivers (see above) shows that part of this carbon is labile. This decreasing pattern has already been observed by Barth and Veizer (1999) on the St Lawrence river basin.
2. The high DOC content associated with low $\delta^{13}C_{DIC}$ in the river could reflect the contribution of drainage areas with significant soil organic matter. The DIC supplied by these organic-rich areas is largely produced by CO_2 released by the degradation of this soil organic carbon. Then, the riverine $\delta^{13}C_{DIC}$ coming from
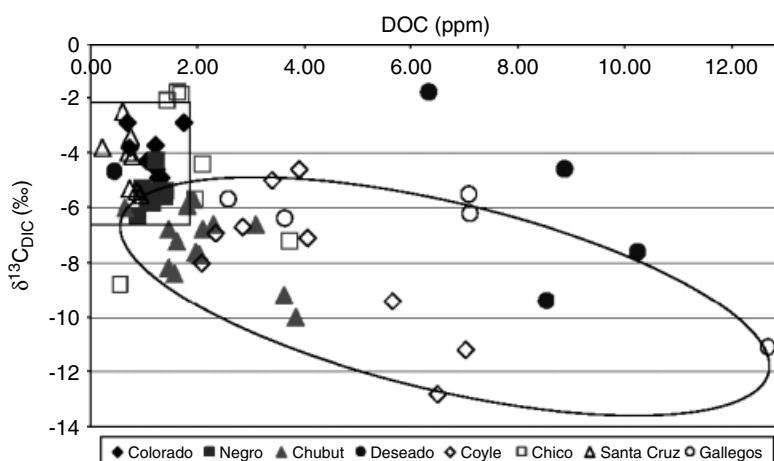

Figure 10. Relationship between $\delta^{13}C_{DIC}$ and DOC content in the Patagonian rivers

these areas could be in equilibrium with the signature of the soil CO_2 (vegetation of Patagonia is mainly of C_3 type, $\delta^{13}C_{\text{soil } CO_2} = -20\permil$).

These two hypotheses have to be confirmed by further measurements and tested in different basins where one of the two situations (respiration in the river/contribution of organic-rich soil areas) is clearly dominant.

Budget to the ocean. For Patagonian rivers j with available discharge data (Colorado, Negro, Chubut, Santa Cruz and Gallegos), the annual average fluxes F_j of carbon have been calculated at the mouth using the discharge weighted concentration C_m and the annual mean discharge Q_{ma} for the period 1995–98 as follows:

$$F_j = C_m Q_{ma} \tag{13}$$

with

$$C_m = \frac{\sum\limits_{i=1}^{8} C_i Q_{m_i}}{\sum\limits_{i=1}^{8} Q_{m_i}} \tag{14}$$

where C_i is the instantaneous concentration of the different carbon forms and Q_{m_i} is the corresponding mean monthly discharge of each sampling period i.

For the other three rivers (Deseado, Chico and Coyle) the mean monthly discharges are not available, and one has only the mean annual discharge. Consequently, for these rivers, the mean annual fluxes have been calculated simply by multiplying the mean arithmetic concentration for the eight sampling missions by the mean annual discharge.

The total DIC flux delivered by all Patagonian rivers to the South Atlantic Ocean is the sum of each individual river flux F_j. The results obtained for the different rivers and for the different carbon fractions (DIC, PIC, DOC and POC) are reported in Table VII. DIC is the major carbon fraction for all rivers, representing 49% (for the Gallegos) to 89% (for the Colorado) of the total carbon. Almost 80% of total DIC exported from Patagonia to the South Atlantic Ocean is produced by the two largest drainage basins, the Negro and Santa Cruz river basins. Patagonian rivers export 621×10^9 g, 68×10^9 g and 45×10^9 g of carbon per year in the form of DIC, DOC and POC respectively to the South Atlantic Ocean (Table VII). These results are comparable to the estimation of Ludwig *et al.* (1996a, 1996b), who used a modelling approach (GEM-Corg). For DIC, this Patagonian flux represents only 3·6% of the total riverine flux exported to the South Atlantic Ocean by South American and African rivers. The DIC specific yield of Patagonian rivers (2·7 g m^{-2} year^{-1}) is close to that of the Río de la Plata (2·2 g m^{-2} year^{-1}; Kempe *et al.*, 1991) and to that of the tropical River Amazon (2·85 g m^{-2} year^{-1}; Mortatti and Probst, 2003).

The average isotopic signature of the eight Patagonian rivers ($j = 1$ to 8) can be estimated to be $-4·9\permil$ by weighting the $\delta^{13}C_{\text{DIC}}$ isotopic signature ($\delta^{13}C_j$) of each river j by its annual average DIC flux F_j as follows:

$$\delta^{13}C = \frac{\sum\limits_{j=1}^{8} F_j \delta^{13}C_j}{\sum\limits_{j=1}^{8} F_j} \tag{15}$$

Table VII. Fluxes of DIC, DOC, POC and PIC exported to the South Atlantic Ocean by the Patagonian rivers and percentages of each carbon fraction with respect to the total carbon

	DIC		DOC		POC		PIC	
	Flux (10^3 t year^{-1})	TC (%)	Flux (10^3 t year^{-1})	TC (%)	Flux (10^3 t year^{-1})	TC (%)	Flux (10^3 t year^{-1})	TC (%)
Colorado	62	89	4	6	3	4	1	1
Negro	297	85	29	8	19	5	3	1
Chubut	24	88	2	7	1	4	0·3	1
Deseado	7	73	1·2	13	1	10	0·4	4
Chico	15	68	2	9	4	18	1·2	5
Santa Cruz	198	86	18	8	13	6	1·4	1
Coyle	3	77	0·8	21	0·1	3	0	0
Gallegos	15	49	11	36	4	13	0·7	2
Patagonia	621	84	68	9	45·1	6	8	1

with average $\delta^{13}C_j$ being calculated for each river j using the eight sampling missions ($i = 1$ to 8) in the same way:

$$\delta^{13}C_j = \frac{\sum_{i=1}^{8} F_i \delta^{13}C_i}{\sum_{i=1}^{8} F_i} \tag{16}$$

Today, a value close to $-10‰$ for the input of DIC from the continent is used in oceanic carbon cycle modelling to simulate the $\delta^{13}C_{DIC}$ evolution in the world ocean. In spite of this small contribution at a global scale, this new result is interesting because of the geographical position of Patagonia. Indeed, this part of the South Atlantic Ocean is a zone of convergence of major oceanic currents. This oceanic zone is also a sink of atmospheric CO_2 and has been investigated in the framework of the CONFLUENCE project in order to study the mixing of oceanic and continental water masses off the Argentine coast. Our study will bring new data of the DIC isotopic composition originating from the continent, and will allow a better understanding of the carbon transfer of this coastal zone.

At a global scale, this result shows also that the $\delta^{13}C$ signature of DIC terrestrial flux used in the oceanic carbon cycle model is probably underestimated.

CONCLUSIONS

This study of Patagonian rivers using an isotopic approach illustrates the role of atmospheric exchange and of organic carbon oxidation in the isotopic signature of DIC in rivers. The largest Patagonian rivers (Colorado, Negro, Chubut and Santa Cruz) with reservoir lakes and supply by glaciers exhibit high values of $\delta^{13}C_{DIC}$ due to significant CO_2 degassing to the atmosphere. A similar result has already been obtained for the St Lawrence River by Barth and Veizer (1999).

The variations of $\delta^{13}C_{DIC}$ and DOC content in the other rivers show the control of organic carbon oxidation on the isotopic signature of the riverine inorganic carbon pool. This control takes place in the soil and also in the river. High DOC contents are attributed to the leaching of drainage areas enriched in soil organic matter and where riverine DIC originates mainly from CO_2 produced by degradation of organic carbon and presents a very negative $\delta^{13}C$ isotopic signature. In the Patagonian rivers studied, one can see that the DOC is relatively labile and can be oxidized in the river water column to produce aqueous CO_2 with low $\delta^{13}C$ values.

These biogeochemical processes interfere with the DIC contribution of carbonate and silicate weathering and, hence, do not allow the use of the $\delta^{13}C_{DIC}$ riverine signature alone for these rivers to distinguish the DIC released by carbonate dissolution.

In terms of budget to the ocean, the Patagonian DIC flux is estimated to be 621×10^9 g. of carbon per year, of which 80% is discharged by the two largest rivers, the Rivers Negro and Santa Cruz. The DIC specific yield average for the whole of Patagonia is $2 \cdot 7$ g m^{-2} year^{-1}, which is comparable to other world rivers. However, its $\delta^{13}C$ isotopic signature, which averages $-4 \cdot 9\%_0$, is very high compared with other world rivers, suggesting that one probably has to revise the average value of $-10\%_0$ considered today as representative of the DIC river inputs in oceanic carbon cycle modelling.

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