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# Fluvial carbonate occurrences in high energy rivers: Examples from the Gállego River Tributaries, Pyrenees, Huesca

*Carbonatos fluviales en ríos de alta energía: algunos afluentes del Río Gállego, Pirineos, Huesca*

**Ana María Alonso-Zarza y Aurélian Rygaloff**

Departamento de Petrología y Geoquímica, Fac. CC. Geológicas, IGEO, CSIC. Universidad Complutense de Madrid, C/ José Antonio Novais, 12, 28040 Madrid, Spain.
alonsoza@ucm.es; aurelien.rygaloff.ar@gmail

**ABSTRACT**

*In this paper we study the carbonate deposits that form on the bed of Oliván and Orós mountain streams, which are tributaries of the Gállego River, in the Pyrenees. The streams drain the terrains formed by the Eocene Flysch, which provide calcium and carbonate to the rivers. These fluvial carbonates although scarce, in comparison with the dominant coarse gravel deposits of the streams, show similarities with fluvial tufa deposits. The main carbonate facies, formed on the bedload and between the large clasts, include: large oncoids, small framestone patches and rudstones of phytoclasts. The carbonate, very well laminated, is composed of calcite and includes vegetal debris and diatoms. The laminae are formed by coarse calcite crystals (bladed, fibrous, fan-like with filaments and bushes) and micrite-microspar. Microbes played an important role in the formation of some of the microstructures, however the main mechanism favoring carbonate precipitation in these mountain, cold-streams is mechanical* $CO_2$ *degassing.*

**Key-words:** *Pyrenees, streams, fluvial carbonate, biogenic, mechanical degassing.*

**RESUMEN**

*En este trabajo estudiamos los depósitos carbonáticos que se forman en el lecho de dos arroyos de montaña, Oliván y Orós, afluentes del Río Gállego, en los Pirineos. Los arroyos drenan los terrenos formados por el flysch eoceno, cargándose en calcio y carbonato. Estos carbonatos fluviales, escasos en relación con los depósitos de gravas gruesas que cubren el lecho del río, tienen muchos rasgos en común con los de las tobas fluviales. Las principales facies carbonáticas que se forman sobre la carga de fondo y entre los clastos grandes son: grandes oncoides, pequeños parches de framestones y rudstones de fitoclastos. El carbonato, muy bien laminado, está formado por calcita e incluye numerosos restos vegetales y diatomeas. Las láminas están formadas por grandes cristales de calcita (bladed, fibrosa, en forma de abanicos y de arbustos) y micrita-microesparita. Los microbios tuvieron un papel importante en la formación de algunas de las microestructuras pero el principal mecanismo que favorece la precipitación de calcita en estos ríos fríos de montaña es la desgasificación mecánica de* $CO_2$

**Palabras clave:** *Pirineos, arroyos, carbonatos fluviales, biogénico, desgasificación mecánica.*

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## Introduction

Fluvial carbonates are forming at present in relatively wide climatic conditions in temperate to tropical environments (Arenas-Abad *et al*., 2010; Capezzuoli *et al*., 2014). They usually are included in the term tufa or meteogene travertines (Pentecost and Viles, 1994; Ford and Pedley, 1996). Their depositional models are relatively well understood and include fluvial and fluvio-lacustrine environments with or without barriers, and a variety of fluvio-palustrine settings (Arenas-Abad *et al*., 2010). In these cases, carbonate depositions within the rivers give place to relatively thick sedimentary sequences (dm to m) but of relatively reduced extent in comparison with lacustrine carbonates. A different situation occurs in high energy mountain rivers draining carbonate catchments. In these cases, carbonate precipitation within the rivers occurs as thin (mm-cm) carbonate coatings on the bedload and also as small framestone patches. The formation at present day of these types of carbonates is relatively common in rivers draining carbonate terrains; however, they have been rarely studied in both recent and ancient coarse fluvial or alluvial deposits. In this paper we describe carbonate deposits forming at present in the tributaries of the Gállego River. Our aim is to understand the conditions favoring the formation of these deposits.

## Geological setting

The Oliván and Orós streams are situated in the northern area of the Gállego River, corresponding to the Intermediate Depression of the Central Spanish Pyrenees in the Eocene Flysch sector. The Gállego River drains mostly perpendicular to the Pyrenees except in an intermediate sector in which it parallels the External Sierras. Several lateral morraines and frontal arcs are preserved north to Sabiñánigo, indicating that the Gállego glacier probably reached this locality (Sancho *et al*., 2004; Palacios *et al*., 2015) (Fig. 1). The studied carbonates come from Orós and Oliván streams, all tributaries from the East of the Gállego River (Fig.1).

These streams contain naturally formed cascades, such as Cascada de Orós, and pools forming part of the gorges carved by glacial and fluvial erosive activity which resulted in very strong slope-gradients and so high water velocity, before spreading in their alluvial fans which connect with the Gállego Valley (Gómez-Villar and García-Ruiz, 2000) (Fig. 1). Due to the strong gradients and for prevention successive dams were built in both streams.

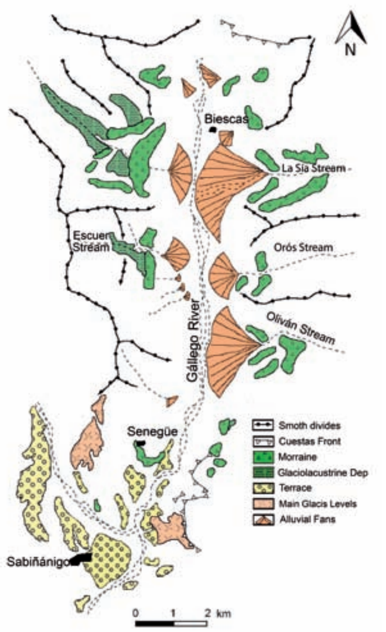


**Fig. 1.- Geomorphology of the study area showing the location of the Oliván and Orós streams (modified from García-Ruíz *et al.*, 2005).**

*Fig. 1.- Geomorfología del área estudiada mostrando la localización de los arroyos de Oliván y Orós (modificado de García-Ruiz* et al.*, 2005).*

The water velocity is highly variable depending on the sites (> 1.2 m/s below small natural dams to 0.1 m/s in the quieter areas), and the depth varies depending on the season and on the stream area, but is usually between 0.1 to 1 m. Mean water temperatures vary from 6°C in Oliván and 8°C in Orós on 20$^{th}$ March 2016 to 20°C in both streams on 20$^{th}$ August 2016. PH is very similar in both streams 8.3, showing no significant changes from March to August 2016. At present the clastic dominated deposits of the streams are formed mostly by pebbles, cobbles and boulders sourced from the Eocene Flysch (Fig. 2). The natural cascades (Orós) and the dams also show cm-thick carbonate crusts.

## Methods

Twenty samples were taken in Orós and Oliván streams during August 2009 including the most representative carbonate river bed deposits. Due to their fragility, before cutting and polishing, samples were embedded in resin containing Epofer EX 401 and Epofer 432 in a vacuum system. Conventional optical petrography studies were performed on 16 thin sections. Mineralogical characterization of the whole-rock was carried out with a Phillips PW-1710 X-ray diffraction (XRD) system operating at 40 kV and 30 mA. SEM observations were carried out on gold-coated samples using a JEOL JSM-820 of the CAI of geological techniques of Complutense University of Madrid (Spain) working at 20 kV.

## Description

Many of the clasts of Oliván and Orós bedload are coated by carbonate crusts (Figs. 3 and 4). These crusts occur all along the river channel and give a notably white/beige color to the riverbed which contrasts with the dark color of the clasts (Fig. 4). The carbonate crusts form concentric layers ranging from less than 1 mm to a few cm in thickness (Fig. 4). Carbonate also agglutinates sand grains and vegetal debris and contributes to form small barrages within the streams (Fig. 5). The carbonate precipitate is beige in color and has a rough surface with millimetric lumps visible at naked eye. Carbonate crusts forms also on the riverbed in rapids on cascades and barriers.

*Facies*

The carbonate deposits of the Orós and Oliván Ravines can be grouped in to 3 facies.

1. Coated clasts and phytoclasts forming oncoids. The oncoids with a pebble to boulder nuclei have mm to cm thick laminated coatings. The coatings are usually asymmetric, thicker in the upper part of the clast (Fig. 4). The lamination is very irregular. In the oncoids whose nuclei are vegetal fragments (phytoclasts) the carbonate coating is continuous and relatively symmetric around the vegetal structure
   The thickness of the coating is 1 mm to 1.5 cm and usually follows the shape of the vegetal nuclei. In some cases, the coatings are so thick that it is not possible to recognize the morphology of the nuclei. The vegetal debris are varied and include pine spines, pine fruits, herbs,

**Fig. 2.- Orós Stream, entrenched in the Flysch with high energy water and very large clasts (see the sitting person for scale).**

*Fig. 2.- Arroyo de Orós, encajado en el Flysch Eoceno, se observa la alta energía del agua y los grandes clastos. Para la escala ver la persona sentada.*

   leaves and different types of vegetation fragments. These oncoids are smaller than the formed on clasts.
2. Framestone patches formed by "in situ" coated vegetal. Different types of herbaceous vegetation, mostly stems, but also some roots appear coated by mm-thick laminae of carbonate with a constant thickness. These patches occur in relatively protected areas of the rivers mostly trapped between the largest coated clasts, but they can also form small cascades in the stream (Fig. 5).
3. Rudstones of coated phytoclasts consist of leaves, stems and sand grains joined together by calcium carbonate (Fig. 6). The coated stems are oriented and/or imbricated. The phytoclasts are mm to cm in section and several cm in length. As in other facies the vegetal remains are in cases well preserved. These rudstones occur in protected areas of the river bed, commonly near the river banks or in relatively quiet pools.

## Mineralogy and Petrology

All the carbonate coatings are composed of calcite (> 95%) with minor traces of quartz. Diatoms and vegetal debris are


**Fig. 3.- Coated clasts showing irregular surfaces and some microbial mats (arrow).**

*Fig. 3.- Clastos con cubiertas irregulares y algunas películas microbianas (flecha).*

common in all the described facies. There are strong similarities between the calcite laminated coatings of the different facies, so here we describe the different types of laminae that form the coatings independently of the facies where they are found. The laminae are very irregular, but in general well defined (Figs. 7 and 8).


**Fig. 4.- Hand sample of one coated clast (oncoid), showing the irregular carbonate lamination.**

*Fig. 4.- Muestra de mano de uno de los clastos con cubiertas (oncolito). Se observa la laminación irregular.*

**Fig. 5.- Framestone patches developed at the front of a small cascade in the Orós stream.**

*Fig. 5.- Pequeño framestone desarrollado en el frente de una pequeña cascada en el Arroyo de Orós.*

There are four different types of crystals/laminae:

1. *Coarse calcite laminae/crystals*. These laminae are usually the thickest with widths of about 1 mm. In cases the laminae formed by different types of crystals show optical continuity.

a) Bladed calcite crystals about 0.5 to 1 mm long and up to 0.2 mm wide. They have well defined exfoliation lines, are transparent and commonly they are either dissolved, micritised or both. They form very irregular laminae.

b) Fibrous, very regular and tabular laminae of fibrous/palisadic crystals, with well-defined growth bands. These bands are relatively rare and thin (about 0.1 mm wide).

c) Irregular bands formed by crystals (about 0.5 mm long and 0.2 mm wide) containing fan-like networks of micritic filaments. These crystals have euhedral terminations, and coalesce each other forming irregular bands (Fig. 9).

d) Bushes of about 1 mm long and up to 0.8 mm across. The bushes contain a large number of microbial filaments of about 10 microns across. The filaments show a fan arrangement and are included within larger subeuhedral individual crystals that coalesce to form the bushes.


**Fig. 6.- Phytoclastic rudstone with large vegetal debris (arrow).**

*Fig. 6.- Rudstone de fitoclastos con grandes restos vegetales (flecha).*

2. *Micrite/microspar laminae* have very different thickness from 0.1 to 1.5 mm. Under the microscope they are seen as dark very irregular laminae of two different types.

a) Thin (0.1 mm), dark "true" micritic laminae occur as the first coating of either clasts or vegetal fragments or intercalated between any other laminae. Their porosity is relatively low. The micrite crystals are very small, difficult to see even under high magnification, probably they are less than 2 microns across.

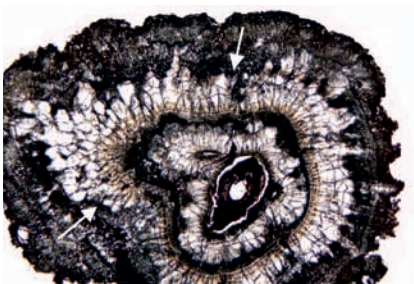

**Fig. 7.- Phytoclast showing irregular micritic and bladed calcite crystal laminae. Some bladed crystals are micritised (arrows).**

*Fig. 7.- Fitoclasto con cubiertas irregulares. Alternan láminas micríticas con láminas de cristales bladed, algunos micritizados (flechas).*

b) Micrite to microspar laminae are very porous, under the microscope, grey in color. The crystal size varies from 2 to 60 μ across. These crystals are arranged following irregular lines and leaving pores between the different lines. Some filaments are observed, and the crystals seem to be fixed on them (Fig. 10). These laminae may contain a variety of vegetal debris and sometimes microspar is the only type of coating they have. In occasions, the microspar does not occur in laminae but as a matrix between the vegetal structures.

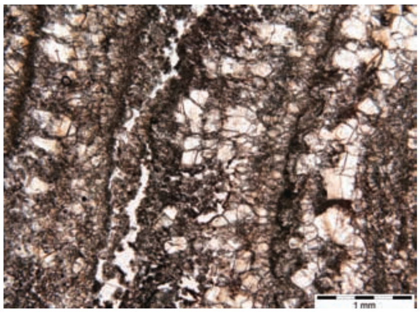

**Fig. 8.- Thin section image of the irregular lamination composed by laminae of bladed crystals of different size.**

*Fig. 8.- Imagen de microscopio óptico de la laminación irregular formada por láminas de cristales bladed de distintos tamaños.*

## Interpretation and Discussion

Carbonate precipitation in these mountain cold high-energy rivers is not uncommon, but rarely studied probably because the dominant sedimentation within these streams is detrital and the amount of carbonate that is precipitated in these rivers is scarce in comparison with the common fluvial carbonates or tufas (e.g. Arenas *et al.*, 2014; Cappezzuoli *et al.*, 2014; García-Gar-

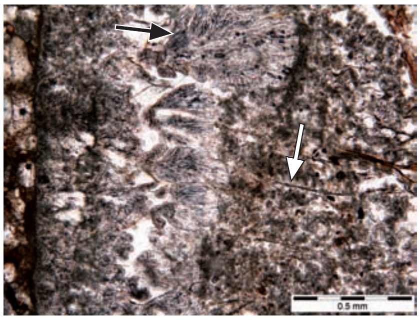

**Fig. 9.- Alternation of microspar laminae with microbial filaments (white arrow) and lamina of large crystals containing fan-like networks of filaments (black arrow).**

*Fig. 9.- Alternancia de láminas micro-esparíticas con muchos filamentos microbianos (flecha blanca) y láminas formadas por cristales que contienen filamentos formando abanicos (flecha negra).*

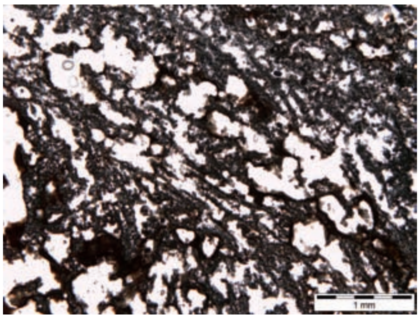

**Fig. 10.- Porous micritic lamina. The micrite form on a network of filaments.**

***Fig. 10.- Láminas micríticas porosas. La micrita se forma sobre una malla de filamentos.***

cía *et al*., 2014). The formation of carbonates in these cold environments requires high calcium and carbonate supplies sourced by dissolution of the Eocene Flysch carbonate-rich rocks and accounts for the high and suitable pH of the water, in the range of those of the common-temperate tufa forming environments (Arp *et al*., 2001; Manzo *et al*., 2012). In recent times most authors indicate that in these settings the driven mechanism for carbonate precipitation is mechanical degassing (Turner and Jones, 2005; Arenas *et al*., 2014), whereas photosynthesis has a minor role. The well-defined lamination, the facies, texture and composition of the laminae, are very similar to tufas, which may help to understand the mechanisms and controls on carbonate precipitation in these settings.

The presence of microbial biofilms in the riverbed and clasts is a key for carbonate precipitation in freshwater riverine settings. In the study case the influence of microbes is seen not only in the fine crystalline laminae (micrite and microspar), but also in some of the coarse crystals. The dark colour, the size and the common organization on lines/ filaments of the micrite/microspar crystals are similar to the micro-peloids associated with EPS (Extracellular Polymeric Substances) obtained in *in vitro* flume experiments by Pedley *et al*. (2009). These micro-peloids may latter overgrow to form euhedral crystals far from the influence of the EPS. The importance of microbes is also seen in the formation of the crystals containing fans of micritic filaments and the bushes. In both cases it is clear that the initial precipitation occurred on the microbes, it is uncertain whether they played an active role, but at least they were the template for precipitation. Farther from the influence of the microbe templates the crystals continued growing abiotically forming euhedral faces (cements), as described by Pedley *et al*. (2009). No clear biogenic features are found in the other two types of coarse crystal laminae (fibrous and bladed), suggesting mostly abiotic precipitation, probably in periods of higher water flow and reduced biofilm layer (Manzo *et al*., 2012). The fact that these crystals show clear dissolution features and show important degradation by micritization also suggest that these laminae may be indicative of lower degree of saturation and slower precipitation rates, favoring the formation of the large crystals (autumn till early spring). On the contrary, the micrite/microspar laminae and the large crystals containing filaments would form under slow discharge and well-developed biofilms (late spring-summer).

## Conclusions

The Orós and Olivan streams contain, although in relatively small amount, carbonate precipitated similarly to that found in fluviatile tufas. The main facies coated clasts, small framestones and phytoclastic rudstones are composed of laminae with different textures. Micrite and microsparite laminae as well as coarse bushes and crystals containing microbial filaments point out the importance of microbes in the formation of these accumulations, on the contrary bladed and fibrous crystals are more probably abiotic precipitates. The alternation of the different laminae reflects changes in environmental conditions, probably seasonally. However, a more precise study is needed to confirm this. The high turbulent regime of these streams makes difficult the preservation of all the laminae. The accumulation of carbonate in these high-energy streams is the result of suitable pH and concentrations of calcium and carbonate sourced from the hinterland. Although $CO_2$ mechanical degassing due to turbulence is the main responsible for precipitation, the microbial biofilms also contributed to carbonate precipitation either actively or acting as templates.

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