1
2 Geochemical and mineralogical characterization of surficial
3 sediments from the Northern Rias: implications for sediment
4 provenance and impact of the source rocks

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Abstract

A multidisciplinary study of the elemental geochemistry and mineralogical characteristics of the marine surficial sediment in the Northern Rias (NW Iberian Peninsula) has been carried out. The linkages between the marine sediment composition and their potential sources were examined.

The influence of the river-borne sediments is only detected in the innermost part of the three Rias. Regional variations of the mineral assemblages are governed by the source-rock composition of the different geological complexes and the relative source-rock contribution controlled by the continental hydrology. Mineralogical composition of the Ortigueira Ria and adjacent shelf surficial sediments are mainly made up of mafic and ultramafic rocks of the Cape *Ortegal* complex indicated by the high content of Mg, Mn and chrysotile and riebeckite minerals. In areas nearby *Ortegal* complex the imprint of heavy minerals present in the surrounding rocks has also been recorded. Barqueiro and Viveiro Rias bed-sediments are influenced by granitic and metamorphic rocks from the Ollo de Sapo complex as revealed by the high contribution of muscovite and quartz.

Mining activities in the continental domain left strong imprints on marine surficial sediments. Pyrite content is high in the innermost areas of the Ortigueira Ria since this mineral is exploited in the Mera River basin, whereas high muscovite percentages characterize the Viveiro Ria owing to the abundance of granitic rocks and its exploitation in the Landro River basin. Quartz content is high nearby Cape Estaca de Bares, induced by the presence of an important excavation of this material.

Keywords: surficial sediment, elemental geochemistry, mineralogy, Ria, land-sea exchange, NW Iberian Peninsula.

1. Background and objectives

The chemical composition of marine surficial sediments is determined by the composition of river-derived material, that is dependant of the catchment petrology (Cho et al., 1999) as well as the biogenic contribution (Lackschewitz et al., 1994). Variations in minerals, lithogenic components, organic material and trace elements abundance, therefore, are a tool for deciphering possible sediment sources and for discriminating physico-chemical processes affecting the geological record.

The characteristics of sediments deposited on coastal areas and continental shelves largely reflect the prevailing geology of e.g. the continental source area, oceanographic and climatic conditions and hydrography. Mineral distributions, especially clay minerals, are standard tracers of the spatial changes of regional geology and watersheds, the weathering characteristics of adjacent continental landmass as well as transport processes (Siddiquie and Mallik, 1972; Moriarty, 1977; Shaw, 1978; Shaw and Bush, 1978; Gardner et al., 1980; Rao and Rao, 1995; Lamy et al., 1998; Stein et al., 1994; Chauhan and Gujar, 1996; Kessarkar et al., 2003; Hillenbrand et al., 2003; Diyu and Thamban, 2006). Moreover, heavy minerals content denotes characteristic mineral suites associated with defined geographic provinces and petrographic features of the source areas (Firek et al., 1977; Achab et al., 2009).

The Galician Rias provide excellent case studies to evaluate the geochemical and mineralogical characteristics of the surficial sediments related to the continental hinterland due to their interplay of terrigenous and marine processes. Many effort has been done in the Galician area dealing with geochemical composition of surficial marine sediments (Rubio et al., 2000; Rubio et al., 2001; Vilas et al., 2005;) but few works regarding the mineralogical composition of the marine sediments have been carried out (Belzunce-Segarra et al., 2002; Oliveira et al., 2002; García et al., 2005). This lack of knowledge is especially acute in the Northern Rias, such as Ortigueira, Barqueiro and Viveiro. Two single studies have been found concerning metal distribution in Ortigueira saltmarshes (Otero et al., 2000) and in the inner part of the three Rias (Lorenzo et al., 2007a). Most of the studies on sedimentological and mineralogical characteristics of the coastal sediments in Northern Rias are also scarce, being most of them restricted to local literature (Asensio-Amor and Teves-Rivas, 1964; Teves-Rivas, 1965; Asensio-Amor and Caraballo Muziotti, 1968a,b; Pérez-Mateos and Caraballo Muziotti, 1969; Pérez-Mateos and Caraballo Muziotti, 1970; Gent et al. 2005).

The main purpose of this study was to investigate the distribution patterns of mineralogical and geochemical parameters in three Northern Rias and relate them with rock sources, fluvial input and marine production. To achieve this goal we have analysed surficial sediments that cover riverine end-members to marine end-members from the continental shelf.

2. Geography and geology of the studied area

The north coast of Galicia shows a rough morphology, with cliffs up to 100 m high made up of igneous, plutonic, mafic, ultramafic and metamorphic rocks. Eastward of 8°W (Cape *Ortegal*), and along the 43.6°N are located the Northern Galician Rias Ortigueira, Barqueiro, and Viveiro (locally named Northern Rias or Rias Altas; Torre-Enciso, 1958). These Rias are coastal inlets with an external open area dominated by marine processes and a partially enclosed estuarine shallow area. Different geological domains with contrasting characteristics can be distinguished in the study area (Fig. 1), the allochthonous Cape *Ortegal* complex with mafic and related lithologies, a relative autochthon composed of the series occupying the Ollo de Sapo Domain, characterized by metamorphic (mainly gneisses) and granite-type rocks eastwards (IGME, 1977; Aparicio et al, 1987; Marcos, 2004) (Fig. 1). The Cape *Ortegal* complex exposes abundant ultramafic rocks, pyroxinites, eclogites, amphibolites, serpentinites as well as metaigneous granulites. It comprises a meta-ophiolite overlain by eclogites and high pressure granulites again overlain by a thick slab of ultramafic rocks (Dallmeyer et al, 1997; Martinez Catalán et al., 1996; Peucat et al., 1990; Gil Ibarguchi et al., 1990; Moreno et al., 2001). The principal minerals in the Cape *Ortegal* complex are pyroxenes, olivine, almandine garnet, Ca-plagioclase and hornblende (Table 2, Mirre, 1990) as well as magnetite, ilmenite, chromite, and Fe-Mg spinel.

The Ortigueira Ria is the westernmost of the Northern Rias characterised by a wide entrance protected by the headland of Cape *Ortegal*. On a plane view, Ortigueira Ria is wedge-shaped open to the northeast covering an area of 90 km² with a longitudinal axis 15 km in length and a maximum width of 13 km with depths varying from a few meters at the innermost part to 60 m at the mouth. Three rivers (the Mera, the Baleo and the Landoi rivers) drain into the Ortigueira Ria with fluvial basins of 126, 53 and 21 km² respectively (Fig. 1). The Mera River is the largest one of these three and its average flow is 6.0 m³s⁻¹ (Station 443; Augas de Galicia, 2010). This river flows along a varied lithology of gneiss, and metasediments from the Ollo de Sapo Domain, as well as mafic rocks located upstream. Moreover, the basin of the Mera River has disused pyrite and chalcopyrite mines (Table 2). It is important to note that the catchment of the Baleo River is almost made up of gneiss and schists with small areas of serpentinitized peridotites whereas the Landoi River basin crosses mainly mafic and ultramafic rocks. Another disused quartz mine is found parallel to the Landoi River (Table 2).

The Barqueiro Ria is located in the north limit of the Iberian Peninsula, westwards of the Cape Estaca de Bares, with its central axis orientated southwest-northeast orientation. It is a small wedge-shaped inlet with ranging depths from 3 to 30 m open to the northeast, covering an area of 10 km², with 7 km long and 2.7 km wide. The freshwater contributor is the Sor River, which has as a fluvial basin covering 202 km² with an average discharge of 15.1 m³s⁻¹ (Station 440; Augas de Galicia, 2010). The surrounding area of Barqueiro Ria is mainly composed by two-mica granite and the presence of white quartz veins NNW-oriented, but the river catchment is mainly composed by gneisses. There are some active quartz mines in the area (Filon de Barqueiro and Mina Sonia, Table 2, Mirre, 1990).

The Viveiro Ria is to the East of Cape Estaca de Bares, opens to the north and it is separated from the Barqueiro Ria by Coelleira Island (Fig. 1). It covers 28 km² with a longitudinal axis of 9 km, with the deepest areas around 50 m. This ria is fed by the Landro River, the catchment of it covers 271 km² and it has a mean discharge of 9.3 m³s⁻¹ (Station 438; Augas de Galicia, 2010), developing an estuary in the inner part of the inlet. The basin

of the Landro River covers a mixed area of gneisses and metasediments of the Ollo de Sapo Domain and granitic rocks being part of the Manto de Mondoñedo Domain. In the Landro River basin there is an active mine for exploiting pegmatites in Silan, and from where muscovite is obtained (Mirre, 1990).

3. Material and methods

Seventy one samples were recovered on July 10-12, 2007 in the Ortigueira, Barqueiro and Viveiro Rias and on May 21, 2008, fifteen sediment samples were collected from the continental shelf (Fig. 1). Sampling surveys were conducted onboard the R/V Mytilus and R/V Lura for stations located at depths greater than 10 m, using a 30-liter Van Veen grab sampler. Sediment sampling from shallower stations was carried out onboard small boats using a 5-liter Van Veen grab sampler. The uppermost sediment layer (0–1 cm) of the total material recovered by the grab sampler was removed with a plastic spatula, stored in pre-cleaned LDPE vials and kept at 4 °C. Afterwards, on laboratory, sub-samples were dried at 40 °C and the coarse fraction was separated by dry sieving through a 2 mm sieve.

Grain-size analysis of the 70 surface samples from the Northern Rias was performed in some aliquots of surficial sediments by dry sieving (Retsch AS-200) grouped into mud, sand and gravel fractions, according to the Udden-Wentworth scale. A more detailed description of grain-size distribution ranging from 2000 to 62 µm (2000-1000, 1000-500, 500-250, 250-125, 125-62) was carried out by dry sieving (Cisa RP.09 sieves) and 20 °C wet sieving (Buchanan, 1984) for 62 to 4 µm fractions (62-31, 31-16, 16-8, 8-4 and <4 µm) in some selected samples along the Ria longitudinal axis.

Duplicate sediment of all samples were analysed for total carbon, particulate organic and inorganic carbon (TC, POC, PIC) and particulate organic nitrogen (PON) in the analytical service of the University of A Coruña using an EA1108 (Carlo Erba Instruments) elemental CNH analyzer after sample digestion with HCl at 80 °C to remove carbonates. PIC concentration was determined by difference between TC and the POC concentrations. Calcium carbonate content (CaCO₃) was calculated by multiplying the TIC by a constant factor of 8.33. Additionally, the POC/PON molar ratio (hereafter C/N ratio) was calculated.

A sub-sample of the <2 mm fraction was ground and homogenised with an agate mortar for metal analysis. Approximately 100 mg of each sediment sample was completely digested with 6 cm³ of HF (40 %) and 1 cm³ of Aqua Regia (HCl-36%: HNO₃-60%; 3:1) in closed Teflon bombs at 100 °C for 1 h (Rantala and Loring, 1975). The contents of the bombs were poured into 100 cm³ flasks containing 5.6 g boric acid and filled up with ultrapure Milli-Q water. Chemical elements were analyzed by flame atomic absorption spectrometry (FAAS) on a Perkin Elmer AA100 with a nitrous oxide-acetylene flame (Al, Si Ca and Mg) and an air-acetylene flame (Fe and Mn). Concentrations were determined in all samples with the standard additions method. For the analysis of U, sediments (≈100 mg) were digested using HF-HNO₃-HCl in the proportions indicated above and the residue obtained was evaporated to near dryness in Teflon vials (*DigiPrep* HotBlock-SCP Science), redissolved with 1 cm³ of double-distilled HNO₃ and 5 cm³ of Milli-Q water, heated for 20 min at 75 °C and diluted to 50 cm³ with Milli-Q water. A quadrupole ICP-MS (Thermo Elemental, X-Series) equipped with a Peltier Impact bead spray chamber and a concentric

Meinhard nebulizer (Caetano et al., 2009) was used. Procedural blanks always accounted for less than 1% of element concentrations in samples. The precision and accuracy of the analytical procedures was controlled through certified reference materials analysis (Table 1).

X-ray diffractions in 33 selected stations of the Northern Galicia Region were performed in ground samples using an automatic Brucker D-5005 X-ray diffractometer in the following conditions: Cu α , 40 kV, 30 mA, and graphite monochromator. Identification and quantification of the different mineralogical species present in the crystalline fraction were carried out following the standard procedure (Chung, 1974). Heavy mineral contents have been investigated in the O33 and C9 sampling stations located near to Cape *Ortegal*. Samples were washed with distillate water to remove sea salts and dried at 50 °C for 24 h. Both samples were sieved through 1000, 500, 300, 200, 100 and 63 micron sieves and a pre-concentration process of heavy minerals for every separated fraction was done using a hand tray owing to the low sample availability. Afterwards, in each fraction, ferromagnetic minerals were separated employing a natural magnet and the remaining minerals were segregated by gravity using Licour de Thoulet dense liquid (3.05 g cm⁻³). Heavy minerals were separated electromagnetically in several paramagnetic and diamagnetic classes using a Frantz Isodynamic LB-1 equipment (inclination and slope of 15 degrees). Finally, heavy minerals of each electromagnetic fraction were separated and identified by hand-picking with a thin brush under stereographic binocular Leica EZ4. Minerals that could not be identified under the stereographic binocular were studied using a JEOL JSM-840 Scanning Electron Microscope (SEM) and the X-ray electron dispersive probe (X-Ray EDS) attached to it. When no clear identification was obtained from the SEM observations X-ray diffraction on these separated heavy minerals was performed.

Redundancy Analysis (RDA) was carried out to identify trends in the scatter of data points that are maximally and linearly related to a set of constraining variables. We consider the mineralogical composition as explanatory variables and the geochemical dataset as independent variables. In addition, R-mode factorial analysis was carried out using the software package SPSS 19.0 (LEAD Technologies) for Windows, using as variables the geochemical composition of surficial sediments.

4. Results

4.1. Sediment composition

The Northern Rias sediments were mainly composed of sandy fractions, only the sedimentary material of the innermost parts was muddy (Fig. 2). Sediments from Ortigueira Ria contained a wide range of CaCO₃ (0.4–35 wt%) being even higher offshore in the continental shelf where values reached 90 wt% in the Station C12. C/N molar ratios (Fig. 3) were higher landwards and closer to the Mera, Landoi and Baleo River mouths reaching 20.4.

As found in the Ortigueira Ria CaCO₃ content in Barqueiro sediments increased towards the continental shelf reaching 78 wt%. POC content was very low (averaging 0.26 wt%)

showing a maximum value of 2.4 wt% in the innermost part (Station B06). PON spatial distribution was similar to the POC, with levels ranging from 0.01 to 0.21 wt%. C/N molar ratios ranged between 4.4 and 15.2, with the higher value found close to the freshwater end-member (Sor River).

Unlike the other Northern Galician Rias, carbonate content in Viveiro Ria was highly variable ranging between 4 and 63 wt%, with higher values found in middle Ria and offshore in the continental shelf. C/N molar ratios (7.6–30.3) also show the higher values in the inner parts of the Ria, close to the Landro River mouth (Fig. 3).

Calcium is the major element of sediments from the three Rias mostly derived from the biogenic carbonate, followed by Si, Al and Fe. Mg showed increased values (up to 13 wt%) in the continental shelf close to Cape *Ortegal* (Fig. 3) and minimum values of 0.5 wt%. A similar spatial distribution was found for Fe (0.4 to 0.6 wt%) and Mg (0.5–13.0 wt%) being higher in sediments near Cape *Ortegal* (5.0–6.0 wt% for Fe; 9.0–13.1 for Mg) and lower near Cape *Estaca de Bares* (1.0–2.0 wt% for Fe; 0.5–2.0 wt% for Mg) and the Viveiro Ria (0.3–1.7 wt% for Fe; 0.6–2.0 wt% for Mg). Calcium distribution was highly irregular and depends on the calcium carbonate concentration (Pearson correlation coefficient $r=0.67$), with higher content in the external areas of the rias and continental shelf reaching 33.4 wt%. Aluminium varied from 0.2% in coarser material to 6.6% in the muddy sediments, although sand nearby the Cape Estaca-de-Bares presented enhanced values (2.7–4.0%).

Increased silicon content (up to 29 wt%) was found in offshore sediments and nearby the Cape *Ortegal* (Fig. 3). Si presents averaging values of 16.7 wt% with an standard deviation of 5.7 wt%.

Iron and Magnesium distributions show similar trends, averaging 2.65 and 3.46 wt% (standard deviation of 1.28 and 2.61) respectively. Both present high values in the Ortigueira Ria and Cape *Ortegal* area (*ca.* 6 and 13 wt% respectively), whereas in the Viveiro and Barqueiro Rias these elements are of minor importance (0.5–2 wt%).

Manganese is a minor component of the Northern Rias sediments with mean values of 0.04 wt% and standard deviation of 0.02 wt%. It reaches maximum values (0.12 wt%) around Cape *Ortegal* area. Values around 0.04 wt% can be also found in the external parts of the Barqueiro Ria.

Uranium shows a distinct distribution pattern (averaging $1.34 \mu\text{g g}^{-1}$), with high values in the innermost areas of the Ortigueira and in the east shore of the Viveiro Ria (6.3 and $7.7 \mu\text{g g}^{-1}$ respectively).

4.2. Mineralogical composition

Muscovite, quartz, albite and illite were the main minerals present in the surficial sediments from the Northern Rias (Fig. 4). Muscovite concentration presented high values eastwards at Barqueiro and Viveiro Rias, decreasing in percentage offshore and was almost absent in Cape *Ortegal* area. In coastal area adjacent to this cape, higher fraction of illite (10–30 wt%) was found in surface sediments, decreasing eastward. Sediments from continental shelf area contained increased amounts of albite (10–50 wt%) that decreased towards the innermost ria areas (0–10 wt%). Quartz spatial distribution presented

maximum values in the surroundings of Cape *Estaca de Bares* and low values westwards of Cape *Ortegal*. Calcite and aragonite percentage increased offshore up to 47 wt% in the adjacent continental shelf. Spatial distribution of montmorillonite was also irregular since it was found only in the Ortigueira Ria and offshore Cape *Estaca de Bares* (10 wt%). Pyrite content in sediments varied from nothing to 2 wt% with no particular trend, but higher values can be found offshore, on the continental shelf and in the innermost part of the Ortigueira Ria (Fig. 4). Chrysotile was found just in some surficial sediment samples from Ortigueira Ria (Station O03) and westwards Cape *Ortegal* (Stations C12, C13, C14). Riebeckite displayed a similar spatial distribution than chrysotile, but with higher percentages (*ca.* 10–20 wt%) (Fig. 4).

A quantitative estimation of the heavy minerals abundance was carried out in sediments from Ortigueira Ria and adjacent coastal area (samples O33 and C9). Offshore sediments contained up to 7.4 wt% of heavy minerals concentrated in the <100 µm fraction whereas Ria ones had lower heavy minerals content (2.1 wt%) concentrated in size fractions between 63 and 200 µm. Al-garnets and pyroxenes were very abundant in all samples, followed by tourmaline, amphiboles, andalusite, biotite and chloritoids (Table 3).

4.3. Statistical analysis

Redundancy analysis (RDA) explicitly models response variables (geochemical composition) as a function of explanatory variables (mineralogical composition). It resulted in the extraction of two factors that explain 75.9% of the variance (Fig. 5a). RDA 1 loads positively in riebeckite, chrysotile, albite and illite together with Mn and Mg, and negatively in muscovite and quartz as well as Al and U. RDA 2 displays high scores for calcite and aragonite together with Ca, and negative scores for illite, Al, Fe and Si.

Factorial analysis was carried out using the geochemical database to reveal the underlying structure that was presumed to exist within a set of multivariate observations (Davis, 2002). R-mode factorial analysis returned two factors which explained 69.7% of the total variance (Fig. 5b). The Factor 1 (contribution to the total variance is 44.8%) loads positively with Fe, Si, POC, PON and Al, and negatively, with carbonate content and Ca.

The second factor explains 24.9% of the total variance. Mg and Mn are the main scores of this factor, loading negatively. U followed in importance loading positively with this factor.

5. Discussion

Seabed sediments of the Northern Rias and shelf are predominantly composed by sand (Fig. 2), due to the high energetic hydrodynamic conditions and the NW swell (Lorenzo et al., 2007b). The origin of the sediment is related to fluvial input, being one of the most relevant sources of fine detrital material in the innermost part of the Rias. Another possible source of supplies is related to the eroded material from exposed coastal cliffs located from Cape *Ortegal* area and adjacent beaches. Organic carbon presents in the sediments has two major sources: the terrigenous-derived organic matter mainly from the

fluvial input; and the organic carbon derived from marine biological productivity. Commonly the second source is more important in the outer regions of the shelves. Although sedimentary C/N values do not always reflect organic matter provenance (Miltner et al., 2005), values of 17.5 is considered to be a mix of marine and terrigenous organic matter whereas marine organic matter is considered to have a C/N ratio of around 6 (Middelburg and Nieuwenhuize, 1998). On the continental shelf C/N values are *ca.* 7 indicating that organic matter is mainly of marine origin. Sediments closer to river mouths evidenced the mixture between the terrigenous and the marine organic matter.

With the exception of Ca, chemical elements in the marine sediments are related to the terrigenous inputs. The carbonate fraction is composed of calcite and aragonite, whereas the main minerals involved in the siliciclastic fraction are quartz, muscovite, illite, albite and montmorillonite. Chrysotile and riebeckite are also related to the siliciclastic fraction, but their content is low (their percentages in most of the samples are below 10 wt%). The continental shelf sediments are characterized by the high abundance of calcite, derived from the high content of biogenic sands (gastropods shells or foraminiferal tests) with low organic matter content. Since the northern Galicia is considerably run down in carbonate rocks and calcium derived minerals in the continental domain (epidote, harzburgite, scapolite, tremolite, actinolite; Table 2), the calcium content of these sediments is predominantly from marine origin. The presence of some minerals in low abundances which contain Ca in their composition in these marine sediments (e.g. ca-pyroxenes; hornblende, actinolite, epidote, grossular, andradite, tourmaline, apatite; Table 3) may explain the discrepancy between the calcium carbonate and Ca percentage distribution. Although aragonite is from biogenic origin no evident relation was found with Ca or calcite distribution. Aragonite is more soluble than calcite and is thermodynamically unstable. Thus a potential increase in aragonite corrosiveness related to early diagenetic trends could mask their spatial distribution. On the other hand, aragonite and calcite-forming species can be located in different ecological domains that explain their differences in spatial distribution.

The RDA analysis (Fig. 5a) has allowed the establishment of four mineralogical assemblages that are related to the different geological units close to the studied area. Al and U are related to the appearance of muscovite, indicating the provenance of these sediments from the granitic massif located in the Viveiro coastal domain. Fe, Mg and Si could be related to the illite concentration since this mineral contains rather moderate amounts of these chemical elements. Moreover, their distribution is linked to Cape *Ortegal* complex, since they appeared in elevated concentrations in the westward area of the Cape *Ortegal*. Calcite and montmorillonite are linked to Ca. The last group is composed by aragonite, pyrite, albite, riebeckite and chrysotile. These minerals are related to Mn and Mg, those metals associated to the presence of the Cape *Ortegal* complex. This assemblage defines the influence on surficial sediments of this particular geological domain in the Ortigueira area.

The main processes that affect the sedimentological, geochemical and mineralogical composition of the surficial sediments from the Northern Rias may be achieved by R-mode factorial analysis (Fig. 5b). Two factors extracted discriminate variables related to the marine-terrigenous influence (Factor 1, 44.8%) and to the main geological domains (Cape *Ortegal* Complex and Ollo de Sapo, Factor 2, 24.9%). In this way, Fe, Al and Si are elements related to siliciclastic and terrigenous-derived material (Factor 1). POC and PON show the

same trend because most of the organic matter is of terrigenous origin, mainly in the innermost part of the Rias. Calcium-derived elements (Ca and CaCO_3) load negatively in this factor since they are related to marine-derived origin. Since the studied area lies in middle latitude setting with both physical and chemical weathering processes, mineral assemblages and metal content in the sediments should reflect the average rock composition in the source areas (Chamley, 1989; Petschick et al., 1996). In this way, Factor 2 is linked to the geological and lithological features of the area (Cape *Ortegal* complex and Ollo de Sapo domain) that trigger the mineralogical and geochemical characteristics of the surficial sediment samples.

Terrigenous particles such as quartz, albite, muscovite and illite are the main constituents of the marine surficial sediments of the Northern Rias (Fig. 4). These minerals have sources in continental soils and weathered rocks such as granitic and gneissic rocks covering the landmass of most parts of Galicia (Fig. 1, Table 2). Since granitic and metamorphic watersheds (Ollo de Sapo) are more abundant in the Barqueiro and Viveiro Rias, the content in Al and Si increases in these Rias. Higher values of quartz in the *Estaca de Bares* area are related with local mining activities (Filon de Barqueiro, Fig. 1). Moreover, muscovite reflects the influence of the metamorphic rocks of the massif as a source of lithoclastic sediments (Shaw and Bush, 1978). However, the high amount of muscovite in the Viveiro Ria can be explained by the riverine supply from granitic rocks in the Landro River watershed as well as a subproduct of the exploitation of the Silan pegmatites vein in a Viveiro treatment plant.

Sediments from the Ortigueira Ria and Cape *Ortegal* area have a different mineralogical composition from those located in the Barqueiro and Viveiro Rias. The massifs of mafic and ultramafic rocks in the Cape *Ortegal* complex are reflected on the chemical composition of the surficial sediments. Thus, the abundance and distribution patterns both in the Ria and shelf of chrysotile and riebeckite are related to the weathering and transport of the rocks present in the Cape *Ortegal* complex to the marine domain. The high contents of Mg, Fe and Mn recorded in the surficial sediments near the Cape *Ortegal* are also related to this geological complex, due to the increased content of these metals in ultramafic and mafic rocks when compared with Al and Si. Additionally, the Fe distribution in the sediments around Cape *Ortegal* may also be influenced by an old pyrite mining industry in the Mera River basin.

The increase of e.g. pyrite, muscovite and quartz in the innermost areas of the Ortigueira, Viveiro Rias and Cape *Estaca de Bares*, respectively, indicates higher terrigenous input, probably linked to mining activities in the hinterland. High pyrite content in the inner parts of the Ortigueira Ria may be interpreted as a result of increasing river supply of pyrite and chalcopryrite from mining activities on land in the Mera River basin (Table 2). This finding is supported by the high Fe content detected in this ria. The increased content of pyrite in the shelf area sediments could be related to relict sandy sediments enriched in pyrite e.g. in foraminifer infillings (Mallik, 1972). Our results do not allow discriminating the authigenic pyrite from that one derived from mining activities since no electron microscopy was performed.

The surficial sediments of the Ortigueira Ria are characterised by the increase in heavy minerals weathered from Cape *Ortegal* complex (Table 3). Heavy minerals are present in higher abundances in the eastern flank of the Cape *Ortegal* and in surficial sediments of

the Ortigueira Ria (Table 3). Garnets are very abundant in sediments supplied by weathering of the rocks from Cape *Ortegal* (Table 2) as pointed out by Pérez-Mateos and Caraballo Muziotti (1969). These authors showed that recent beach sands rich in heavy minerals (e.g. altered olivine grains) occur just on the eastern flank of the Cape *Ortegal*. Heavy minerals in sands eastern of *Estaca de Bares* cape are absent or scarce (Gent et al., 2005). Andalusite is an abundant mineral in sediments from Ortigueira Ria and adjacent coast derived from the metamorphic rocks of the Ollo de Sapo domain while amphiboles and pyroxene (mainly enstatite) are derived from mafic and ultramafic rocks of Cape *Ortegal* (Table 2). The increased abundance of biotite, muscovite and cloritoids was derived from igneous and metamorphic rocks weathering. Tourmaline has also an important contribution and appears due to their presence in gneiss eastern of Ortigueira Ria.

6. Concluding remarks

Mineral and geochemical composition of the Northern Rias and shelf sediments were used to reconstruct the pathways of modern sediment inputs from the continental domain to Rias and inner shelf. Surficial sediments in these Rias integrate several sources (marine/terrigenous), petrological, lithological characteristics of the river basins draining the area and the human activities on land. The influence of the river-borne sediments in only detected in the innermost part of the three rias, whereas shelf sediments are a marine dominated zone.

Mineral assemblages in sediments of the Northern Rias are controlled by source rocks cropping out in the adjacent hinterland. The western part of the Northern Rias sediments is dominated by muscovite and quartz weathered from the Ollo de Sapo complex and granites by the Landro and Sor rivers. The western part of the Northern Rias sediments is characterized by the presence of riebeckite, chrysotile and heavy minerals and high concentrations of Fe and Mg, showing the lithological imprint of minerals contained in the mafic and ultramafic rocks surrounding the area.

The mining activities of pyrite on Mera River basin lead to a signature in the surficial sediments of the Ortigueira Ria. On the contrary, higher pyrite contents offshore could be related to authigenic sources. Exploitation of feldspars in the Landro watershed leads to a high contribution a secondary mineral, muscovite, in the Viveiro Ria. The presence of a quartz vein in Cape *Estaca de Bares* results on a high amount of quartz in this area.

In the northern Galician region the lithological feactures of Cape *Ortegal* complex, Ollo de Sapo domain and granitic massifs have a great influence in the mineralogic and chemical composition of ria and shelf sediments.

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Table 1. Measured average concentrations and standard deviations of studied metals with regard to the certified reference materials (CRM's) from National Research Council of Canada.

CRM		Al (%)	Ca (%)	Fe (%)	Mg (%)	Mn ($\mu\text{g}\cdot\text{g}^{-1}$)	Si (%)	U ($\mu\text{g}\cdot\text{g}^{-1}$)
MAG-1	Certified	8.68 $\pm$ 0.16	0.98 $\pm$ 0.07	4.76 $\pm$ 0.42	1.80 $\pm$ 0.06	760 $\pm$ 70	23.5 $\pm$ 0.45	2.7 $\pm$ 0.3
	Measured	8.50 $\pm$ 0.20	1.09 $\pm$ 0.14	4.73 $\pm$ 0.30	1.63 $\pm$ 0.15	705 $\pm$ 30	23.4 $\pm$ 0.73	2.2 $\pm$ 0.8
PACS-2	Certified	6.62 $\pm$ 0.32	1.96 $\pm$ 0.18	4.09 $\pm$ 0.06	1.47 $\pm$ 0.13	440 $\pm$ 19	28*	2.03 $\pm$ 0.08**
	Measured	6.60 $\pm$ 0.20	1.90 $\pm$ 0.61	4.00 $\pm$ 0.05	1.36 $\pm$ 0.13	426 $\pm$ 9	27 $\pm$ 3	2.08 $\pm$ 0.40

* Informative value

** Monford et al., 2007

Table 2. Minerals in the continental region of the Northern Galician Rias (summarized from Mirre, 1990). The most abundant are highlighted with an asterisk.

Ria	Zone	Mineral
Ortigueira	Cape Ortegal complex	Amphibole*
		Garnet*
		Pyroxene*
		Talc*
		Chromite
		Epidote
		Phlogopite
		Magnesite
		Scapolite
	Cape Ortegal complex and Mera fluvial basin	Chrysotile
		Tremolite-Actinolite
	Mera fluvial basin	Pyrite*
	Cape Ortegal complex and Espasante	Chlorite*
	Cape Ortegal complex and sands of ria beaches	Rutile
	Sands of ria beaches	Ilmenite*
Barqueiro	Cape Ortegal complex, Landoi basin and Cariño ¹	Olivine*
	Ladrido and adjoin fluvial basins (SE ria)	Staurolite
	Landoi vein ² : disused mine	Quartz
	Barqueiro vein ³ : working Sonia mine	Quartz
Viveiro	Estaca de Bares Cape and Sor fluvial basin	Cordierite
	Disused iron mines nearly Viveiro ⁴	Garnet
		Magnetite
		Chlorite: Chamosite*
		Siderite*

* Most abundant minerals

¹ Dunite mine (half a million tons per year are extracted)

² Quartz vein 6 km long parallel to Landoi River

³ Quartz vein 10 km long (Filon Barqueiro)

⁴ Silvarosa old mine, 3 km W Viveiro town, and Galdo old mine, 2 km NW Viveiro town

Table 3. Mineralogical composition of the heavy fraction (very abundant: VA; abundant: A; less abundant: LA and scarce (<5%): S) in the sand fraction (>0.0625 mm) corresponding to stations O33 (Ortigueira Ria) and C9 (Ortigueira shelf).

Mineral	Abundance	Note
Magnetite	S	
Amphibole: Hornblende	A	
Amphibole: Actinolite	A	
Amphibole: Riebeckite	LA	
Andalusite	A	
Chromites	LA	Chromite–Hercynite series
Epidote	S	
Garnet	VA	Garnet group*
Goethite	LA	Biogenic origin
Biotite	A	
Muscovite and Chloritoids	A	Partially changed
Pyroxene: Enstatite	VA	Enstatite-Orthoferrosilite group
Serpentine: Chrysotile	S	
Staurolite	LA	
Tourmaline	A	Schorl (majority) and Dravite
Apatite	S	Organic crystalline debris
Gold	1 grain (>200µm)	
Rutile-Anatase	LA	
Pyrite	S	
Zircon	S	

* Al-garnets such as Spessartine (most abundant), Almandine, Pyrope, and Grossular, and Fe-garnet such as Andradite (less abundant).

Table captions

Table 1. Measured average concentrations and standard deviations of studied metals with regard to the certified reference materials (CRM's) from National Research Council of Canada.

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Figure Captions

Figure 1. Geographical location and main lithological and hydrological features of the studied area. a) Detailed sketch map showing the main geological units and the lithological characteristics of the area. Numbers indicate the main lithological units, 1: Mafic and ultramafic rocks, 2: Quaternary detritics, 3: Vein, 4: Granitic bedrock, 5: Metamorphic bedrock. Dots indicate the position of the surface sediment sampling. White dots specify the samples where mineralogical analyses were conducted. Dotted black lines indicate the longitudinal transects represented in Figures 3 and 4 b) White lines shown the limits of the main riverine basins and rivers draining the Ortigueira, Barqueiro and Viveiro Rias. Data for riverine basins and litology maps was available from the Spatial Data Infrastructure of Galicia <http://sitga.xunta.es/sitganet/index.aspx?lang=gl> reported in the European Datum 1950 UTM projection zone 29N.

Figure 2. Ternary plot showing the content of gravel, sand and mud fractions in the sediments of the Northern Rias.

Figure 3. Contour plots showing the distribution of sediment composition in the northern rias region. Grey bars represent the variation of each analyzed element in three longitudinal transects shown in Figure 1. Dots indicate the sampling stations, which are also shown in Figure 1 (black and white dots).

Figure 4. Contour plots showing the abundance of the minerals, based on XRD determination, found in the surface sediments. Grey bars represent the variation of each mineral in three longitudinal transects shown in Figure 1. Dots indicate the sampling stations, which are also shown in Figure 1 (white dots).

Figure 5. a) Plot showing the loadings obtained by the RDA analysis. Arrows represent the constraining variables, the crosses are the dependent variables and black dots are the samples included in the analysis. b) Scatterplot with the factor loadings extracted using the R-mode factorial analysis with the geochemical variables. Each variable is represented as a point.