GEOLOGICA CARPATHICA – SERIES CLAYS, 5, 1 – 2, BRATISLAVA, JUNE – DECEMBER 1996
33 – 38

PROVENANCE AND EVOLUTION OF SUSPENDED CLAY MINERALS IN THE RIO TINTO (TINTO RIVER), SW SPAIN

EMILIO GALAN[1], ANA REQUENA[2] and JUAN CARLOS FERNANDEZ-CALIANI[3]

[1]Dpto. Cristalografía y Mineralogía, Fac. Química, Univ. Sevilla, 41071-Sevilla, Spain
[2]Dpto. Ingeniería Minera, Esc. Politécnica Superior, Univ. Huelva, 21819-Huelva, Spain
[3]Dpto. Geología, Fac. Ciencias Experimentales, Univ. Huelva, 21819-Huelva, Spain

(Manuscript received October 1, 1996; accepted in revised form February 19, 1997)

Abstract: The Río Tinto (Tinto river), SW Spain, is one of the most polluted fluvial environment of the world as a consequence of the intense mining and smelting activities developed in its upstream area since prehistoric times. The load suspended in this river is largely composed of clay minerals (mica, kaolinite and chlorite) and inorganic amorphous components (allophane and iron oxide gels) with significant amounts of quartz, feldspars, and locally jarosite, hematite and carbonates. Although clay degradation occurs by the effect of acid mine-drainage, the spatial distribution of clay minerals and associated mineral and amorphous phases is in good agreement with the composition of the rocks and soils drained by the river. Therefore, the mineral assemblages reflect the inherited detrital character of the suspended sediments.

Key words: suspended clay minerals, acid mine-drainage, Río Tinto, Spain.

Introduction

The Tinto river, so-called because of its wine-red colour, has its origin in one of the most important metallogenic province of Europe -the Iberian Pyrite Belt- which comprises great massive sulphide deposits mined since prehistoric times (e.g. Strauss & Madel 1974). The river flows through the Pyrite Belt draining different geologic formations of Devonian and Carboniferous age (Schermerhorn 1971), consisting predominantly of slates and volcanic-sedimentary rocks in which the orebodies are interbedded. Locally, sulphide oxidation has produced a gossan environment submitted to erosion by the water flow. In its lower course, the river and its major tributary, namely Candón stream, drain Cenozoic sedimentary formations made up mainly of limestones and marls belonging to the Guadalquivir Basin (Viguier 1974). Finally, the Tinto discharges into the Atlantic ocean after its confluence with the Odiel river, forming the Huelva estuary on the southwest coast of Spain (Fig. 1). The whole lenght of this river is approximately 90 km, and its catchment cover a surface of 1,676 km^2. According to García-Vargas et al. (1980), the annual discharge averages 1,153,100 m^3, and suspended solid quantities in the river range from 0.5 to 1.3 g/l in conditions of high water flow.

Because of natural processes and particularly as a result of the large scale mining and smelting operations occurred at the head of the stream, waters are very acidic (the pH reaches values as low as 2) and they are extremely polluted by sulphates and heavy metals, especially Fe, Cu, Zn, Pb, and Mn, due to acid mine-drainage (García-Vargas et al., op.cit.; Cabrera et al. 1992; Nelson & Lamothe 1993; and other unpublished reports). Heavy metals and suspended particles are released by the aerobic leaching and erosion processes that take place on the outcropping orebodies and waste dumps located on the river banks. Although active and past mining activities only affect the uppermost course, they produce a large environmental impact throughout the river basin, which is considerated as one of the most polluted fluvial environment of the world. In comparison with other European contaminated rivers (including the Rhin, Danube and Elbe), the average content of toxic metals in bottom sediment found in the Tinto river is four times greater (Nelson & Lamothe, op.cit.).

It is well known that the highest amounts of toxic metals transported in suspension by the rivers are bonded in the fine-grained fractions (Borovec 1994, 1996), which are largely enriched in phyllosilicates (Konta 1985, 1991). Relationships between clay mineral composition and heavy metal content of suspended sediments in the Tinto river have been recently reported by Fernández-Caliani et al. (1996). The aim of this work is focused on determining the provenance, composition and distribution pattern of suspended clays in order to understand the factors controlling the origin and evolution of clay minerals in this very acidic aquatic environment.

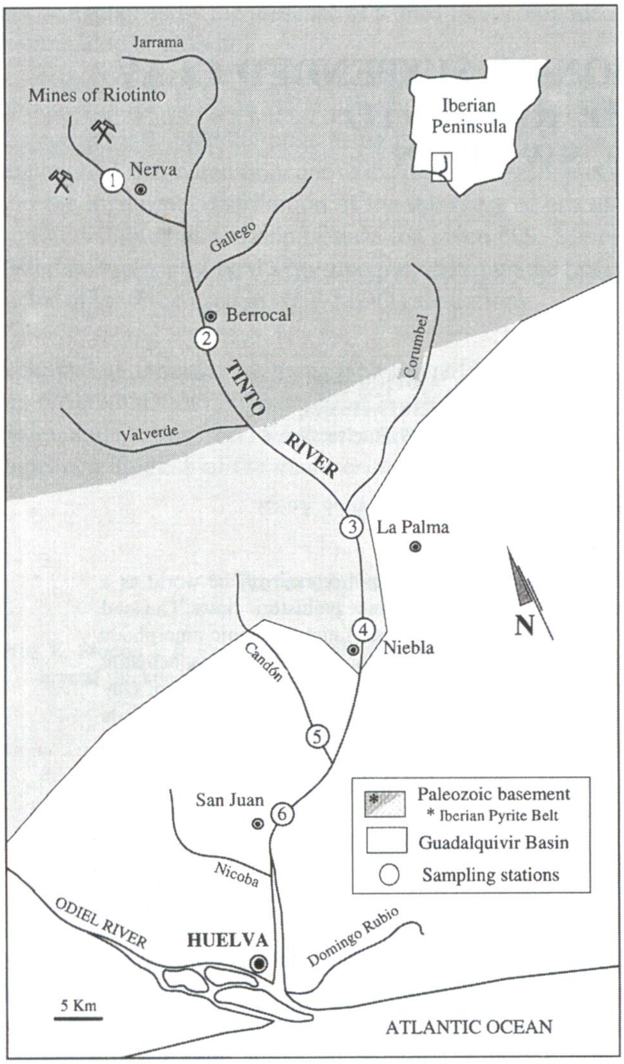

Fig. 1. Location map of the Tinto river and sampling stations sites.

Sampling and analytical methods

Sampling was done during a rainstorm period (winter of 1995), when there is a greater concentration of suspended matter in river, and the sediments were obtained by water sampling followed by filtration in situ over 0.4 µm pore-size filter, according to methodology compiled by Eisma (1993). Five water samples were collected at different sampling stations (Nerva, Berrocal, La Palma, Niebla, San Juan) evenly distributed along the river course, and one from the Candón stream, an unpolluted tributary (Fig. 1).

Each sample was divided into two parts. The first one was air-dried and sieved for analyses by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The second part was dispersed in distilled water for particle-size analysis by means of a Sedigraph equipment.

Mineral compositions of the whole sediment and fine fractions were determined on a Philips diffractometer with automatic slit, using nickel-filtered Cu-Kα radiation at 20 mA, 40 kV, and a scanning speed of 1° 2θ per minute. For clay mineral analysis, the <2 µm and 2–20 µm fractions were separated by centrifugation, and well oriented aggregates were prepared by sedimentation of clay suspension on glass slides. Previously, the samples were treated with hydrogen peroxide to destroy the organic matter and with acetic acid to remove the carbonates.

Identification of the clay minerals was carried out following the routine procedures, which involved the standard pretreatments of solvation with ethylene glycol (EG) and dimethylsulfoxide (DMSO), and heating at 550° C. Furthermore, the freshwater clays collected from the Candón stream were treated with acidic water of the Tinto river in order to evaluate the effect of the acid mine-drainage on the clay minerals stability.

The relative abundance of the mineral phases present in both bulk sample and fine fractions was calculated by measuring the intensity of diagnostic diffraction peaks, taking into account the relative intensities proposed by Schultz (1964) and Martín Pozas (1968). Correction factors were applied for a diffractometer with automatic slit.

Results

Particulate load suspended in the Tinto river is largely composed of silt-clay sediments (Fig. 2). The dominant grain size of mineral particles is less than 10 mm, and the clay fraction (< 2 µm) represents between 20 and 50 % of the bulk samples. Very small colloidal particles of less than 0.1 mm could be present in high percentage. Clay-size particles are less abundant in the

Table 1: Quantitative mineral composition (% wt) of suspended sediments in the Tinto river.

Mineral Composition	Sampling stations					
	Nerva	Berrocal	La Palma	Niebla	Candón	San Juan
Bulk Sample						
Quartz	22	16	18	19	18	40
Phyllosilicates	52	62	72	78	64	31
Feldspars	<5	8	10	<5	<5	17
Jarosite	10	<5				
Hematite	13	12				
Pyrite	<5					
Calcite					14	12
2-20 µm fraction						
Micas	79	55	65	77	67	80
Kaolinite	15	45	35	23	21	20
Chlorite	6					
Smectites					12	
<2 µm fraction						
Illite	72	67	73	75	22	87
Kaolinite	25	33	27	25	8	13
Chlorite	<5					
Smectites					70	

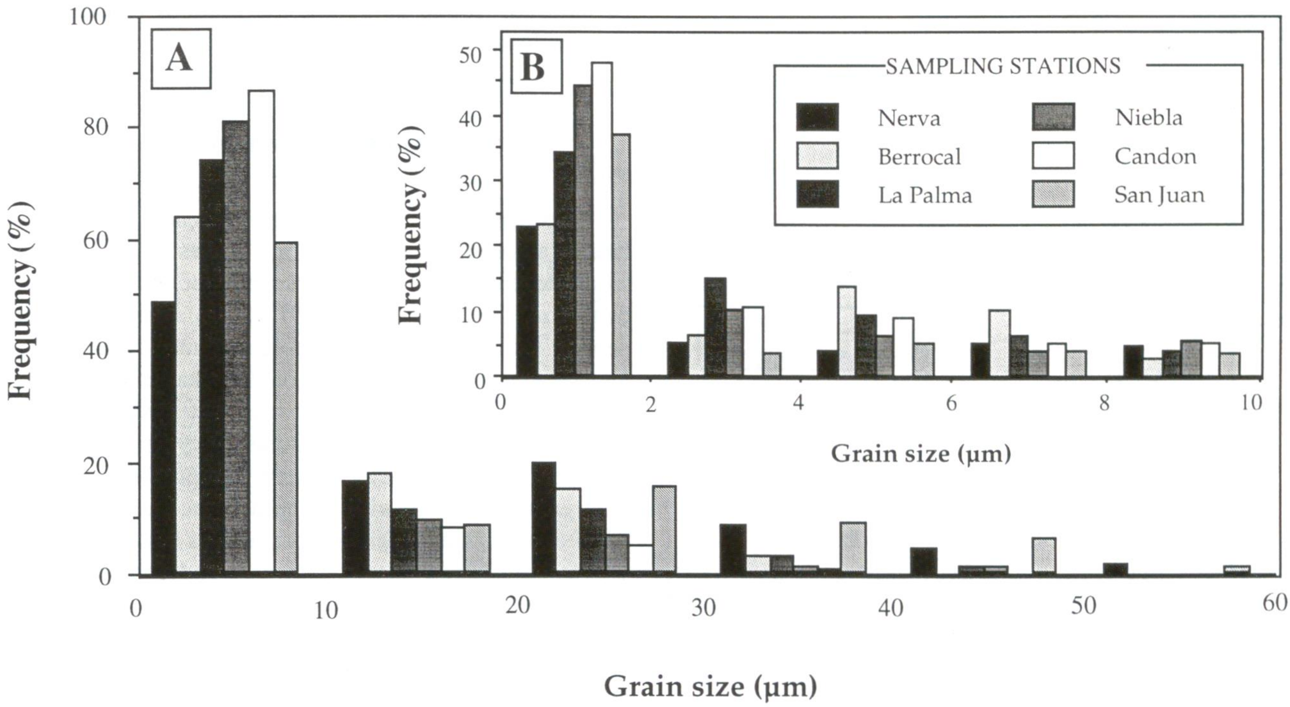

Fig. 2. Bar graphs showing the grain-size frequency of particles carried in suspension by the river. A) bulk sample; B) <10 mm fraction.

sediments collected at Nerva and Berrocal localities than in the sampling stations located downstream, as headwaters are vigorous and can transport fine-grained sand, as well as some organic debris supplied by terrestrial erosion.

Table 1 gives the mineralogical composition of suspended sediments for all the samples, and figure 3 depicts a generalized spatial variation of the mineral abundance.

Clay minerals, quartz and feldspars, in this order of abundance, are the basic and omnipresent mineral phases identified from the crystalline suspended matter. Indeed, most of bulk samples are essentially composed of very thin flakes of phyllosilicates (50–80 %), with minor amounts of quartz (15–25 %) and feldspars (<10 %). The phyllosilicates/quartz+feldspars ratio shows a little variation along the river, except for the sediments carried in suspension near to the mouth, and collected at San Juan sampling station. In this estuarine zone, quartz (40 %) domines over phyllosilicates (30 %), and consequently the ratio is inverted. Locally, significant amounts of jarosite (5–10 %) and hematite (12–15 %) are present in the upper course, while carbonates (12 %) occur as suspended particles when going downstream. Because of strong turbulence even heavy mineral, such as pyrite, can be also found in suspension. Moreover, poorly crystallized phases (allophane and iron oxide gels) have been detected by XRD in all studied samples.

Clay fraction is clearly dominated by illite (65–90 %) with considerable quantities of kaolinite (10–35 %), excepting the Candón samples which correspond to smectite-rich sediments. Effectively, smectites are present in the clays suspended in the Candón stream, reaching percentages as high as 70 % of the < 2 µm fraction. However, sediments transported in suspension by the Tinto river are devoid of smectites.

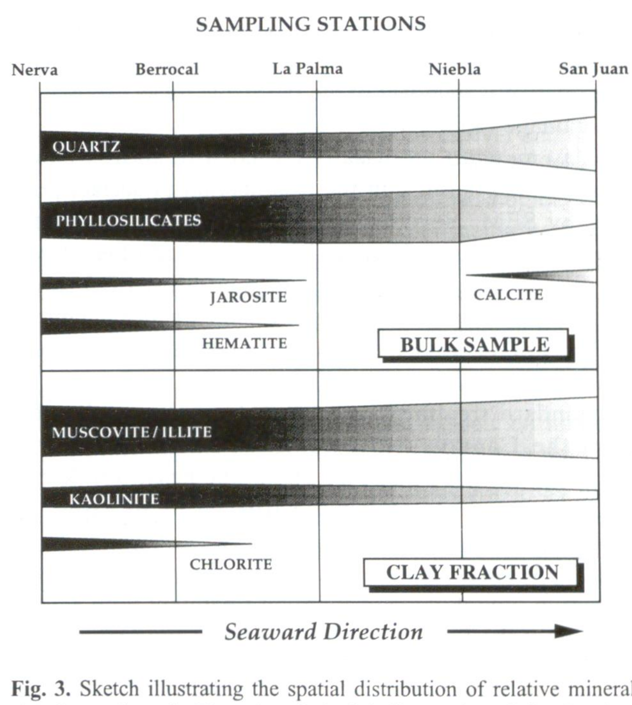

Fig. 3. Sketch illustrating the spatial distribution of relative mineral abundance along the Tinto river, in both bulk sample and clay fraction.

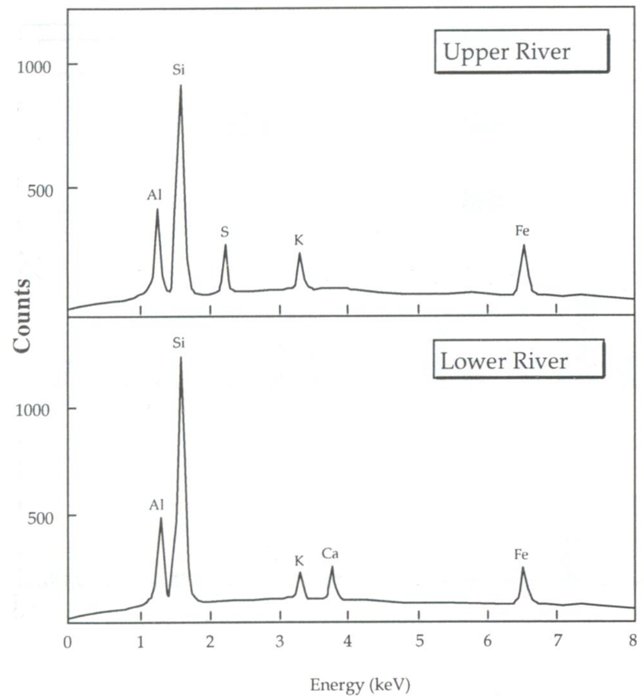

Fig. 4. EDS spectra of the whole sediment from the upper (Nerva station) and lower (San Juan station) course of the river.

In general, the relative proportions of illite increase gradually seaward in opposite to kaolinite. They are mainly clastic dioctahedral micas, with Kubler index values (0.24° $\Delta 2\theta$ in average) within the typical range of illite crystallinity from the Iberian Pyrite Belt (Galán et al. 1991). Sediments from Candón tributary contain illite with a crystallinity index greater than 0.45° $\Delta 2\theta$. Chlorite has been only found as accessory mineral (< 5 %) in the upper course of the Tinto river, in spite of this phyllosilicate is a component relatively abundant of the Paleozoic rocks exposed in the drainage basin.

Clay minerals are usually coated with an iron oxide film that makes difficult the examination of surface textures by SEM. Nevertheless, aggregates of flaky grains with an irregular outline can be distiguished often showing microscopic fissures. A combined SEM-EDS study has allow us to prove that the content of major chemical elements of suspended sediments is consistent with their mineral composition (Fig. 4).

Standard treatments performed on clays collected from the Candón tributary show some interesting diffractometric results (Fig. 5): 1) the basal 001 X-ray reflection of micas remains unaffected in all cases; 2) kaolinite does not expand completely by solvation with DMSO; 3) smectites are characterized by a broad basal reflection, which disappears upon treatment with acidic water from the Tinto river after one hour; and 4) the latter treatment produces neutralisation of acidic water and precipitation of gypsum from clay solution, which can be naturally found as authigenic mineral in the flood plain of lower river.

Discussion and conclusions

Suspended matter in rivers consists generally of a mixture of amorphous and crystalline phases whose composition depends mainly on the source rocks and weather conditions (e.g. Chamley 1989). In the study case, suspended sediments show a simple and monotonous clay mineral assemblage composed of illite+kaolinite±chlorite, with little or no significant variation in the relative abundance of phyllosilicates. By contrast, they display a wide variation in their non-clay mineral composition from the upstream, where Fe-rich minerals such as hematite, jarosite, pyrite are present in conspicuous amounts, to fluvial estuary where quartz, feldspars and carbonates are the dominant non-clay species.

The relative proportions of different mineral phases is closely related to grain-size distribution. Thus, quartz, feldspars, jarosite, hematite and carbonates increase in frequency with the increasing of grain-size particle sediments whereas phyllosilicates are more abundant in the finest fractions. The relative low content of phyllosilicates observed at the San Juan sampling station could be explained by clay flocculation, due to salinity change when the river reach the upper estuary, which leads to a depositional acceleration of clay particles (Konta 1991).

In any case, distribution of clay and accompanying minerals along the river course is in good agreement with composition of the rocks and soils drained and submitted to erosion by the water flow. Thus, well-crystallized micas and chlorites have their source area in the low-grade

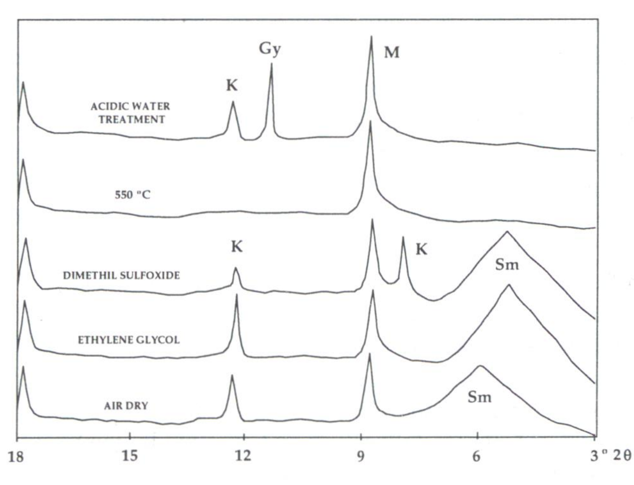

Fig. 5. XRD patterns of oriented samples from Candón stream after different treatements. Note the disappearance of smectites and formation of gypsum after attack with acidic water (pH= 2.4) from the Tinto river.

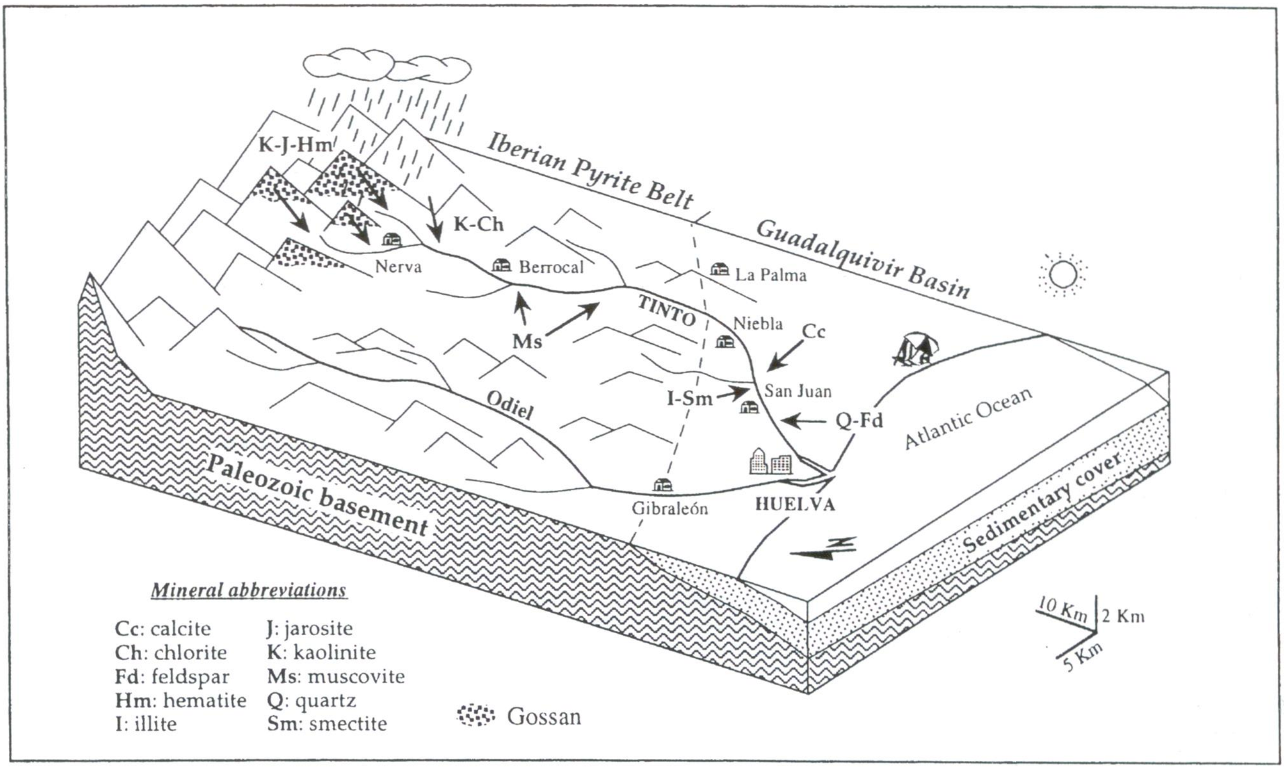

Fig. 6. Simplified block diagram showing the drainage basin and provenance of mineral particles suspended in the Tinto river.

metamorphic rocks of the Paleozoic basement that contain the large pyritic deposits (Fernández-Caliani & Galán 1991). The gossan and zones of secondary enrichment of the orebodies provide the sources of hematite and jarosite, whereas kaolinite is a common weathering product of the acid volcanoclastic rocks that constitutes the host of the sulphide masses (Poyato et al. 1981). Likewise, the poorly crystallized and amorphous components of suspended sediments derive from the residual soils resulting of the weathering processes. In the lower course of the river, quartz, feldspars and carbonates, as well as smectite-rich clays collected at the Candón stream, are clearly supplied by sedimentary materials belonging to the Guadalquivir Basin (Galán & González 1993).

Relating to provenance and distribution pattern of mineral assemblages, figure 6 shows schematically the picture described above. Therefore, mineral composition of the suspended matter in the Tinto river is strongly controlled by the source-area lithology and soil types regionally exposed in the drainage basin. There is no evidence for neoformed clay minerals, and consequently mineral assemblages largely reflect the inherited detrital character of the suspended sediments. The detrital clay minerals are similar to those present in the bottom sediments of the neighbouring Odiel river (Requena et al. 1991).

Futhermore, it is interesting to note some effects of the acid mine-drainage on clay minerals, which could have paleoenvironment implications. Although illite and kaolinite are transported over long distances by current, they do not show significant mineralogical changes due to their high chemical stability. Only textural evidences of abrasion and mechanical disintegration during transport have been recognized. In constrast, chemical weathering processes have produced the disappearance of chlorite as a stable mineral phase at the mid-river, since this phyllosilicate possess a high corrosion index in neutral aqueous environments (Konta 1984). The general lack of smectites in clay suspensions of the lower river and formation of authigenic gypsum by the reaction of calcite and acid sulphate water also suggest that mineralogical transformation occurred, as we have experimentally demonstrated from clay acid treatment on a laboratory scale. Thus, when smectite-rich sediments carried in suspension by tributaries reach the Tinto river, smectites become unstable under new chemico-physical water conditions and they begin to undergone mineralogical transformation.

In conclusion, clay minerals and associated non-clay species distribution has allowed us to determine the provenance of suspended sediments, to understand the transport pathways and disposal pattern, and finally to recognize some mineralogical tranformations induced by the acid mine-drainage.

Acknowledgement: This work has been supported by the Applied Mineralogy Research Group PAI-4031 of the Government of Andalucía (Spain).

References

Borovec Z., 1994: Distribution of toxic metals in stream sediments. *Acta Univ. Carolinae Geol.* **38**, 91–103.

Borovec Z., 1996: Evaluation of the concentrations of trace elements in stream sediments by factor and cluster analysis and the sequential extraction procedure. *Sci. Total Envir.* **177**, 237–250.

Cabrera F., Conde B. & Flores V., 1992: Heavy metals in the surface sediments of the tidal river Tinto (SW Spain). *Fresenius Envir. Bull.* **1**, 400–405.

Chamley H., 1989: Clay Sedimentology. *Springer-Verlag*, Berlin, 623 pp.

Eisma D., 1993: Suspended Matter in the Aquatic Environment. *Springer-Verlag*, Berlin, 315 pp.

Fernández-Caliani J.C. & Galán E., 1991: Las pizarras de la Faja Pirítica Ibérica: Geología, mineralogía y aplicaciones industriales. *Estudios Geol.* **47**, 295–303.

Fernández-Caliani J.C., Requena A. & Galán E., 1996: Clay mineralogy and heavy metal content of suspended sediments in an extremely polluted environment: the Tinto river. *Preliminary report. Spanish-Italian Meeting on Clay Mineral*, Granada, Spain.

Galán E., Fernández-Caliani J.C. & Mesa J.M., 1991: Metamorphic conditions of metapelites in the Iberian Pyrite Belt as determined by crystal chemistry parameters of phyllosilicates. *Proc. 7th Euroclay Conf. Dresden*, 391–397.

Galán E. & González I., 1993: Contribución de la mineralogía de arcillas a la interpretación de la evolución paleogeográfica del sector occidental de la Cuenca del Guadalquivir. *Estudios Geol.* **49**, 261–275.

García-Vargas M., Ruiz-Abrio M.T. & Guerrero M.A., 1980: Determinación de metales pesados por espectroscopía de absorción atómica en la cuenca del río Tinto. *Técn. Invest. Trat. Med. Amb.* **2**, 12–24.

Konta J., 1984: A new way to express the relative stability of silicates during weathering in aqueous environment. *9th Conf. Clay Min. & Petrol.* Prague, 11–22.

Konta J., 1985: Crystalline minerals and chemical maturity of suspended solids of some major world rivers. *Miner. Petrogr. Acta*, **29**, 121–133.

Konta J., 1991: Phyllosilicates in rivers: Result of weathering, erosion, transportation and deposition. In: Galán E. & Ortega-Huertas M., (Eds.) *Conferencias XI Reunión Soc. Esp. Arcillas,* pp. 23–44.

Martín Pozas J.M., 1968: El análisis mineralógico cuantitativo de filosilicatos de la arcilla por difracción de rayos-X. *Thesis Univ.* Granada.

Nelson C.H. & Lamothe P.J., 1993: Heavy metal anomalies in the Tinto and Odiel river and estuary system, Spain. *Estuaries*, **16**, 496–511.

Poyato J., Pérez-Rodríguez J.L., Strauss G.K., Lopera E. & González-García F., 1981: Caolinizaciones asociadas a los yacimientos de sulfuros metálicos del suroeste de España. *Bol. Soc. Esp. Min.* **2**, 263–275.

Requena A., Clauss F.L. & Fernández-Caliani J.C., 1991: Mineralogía y aspectos geoquímicos de los sedimentos actuales del río Odiel. *Cuad. Lab. Xeol. Laxe*, **16**, 135–144.

Schermerhorn L.J.G., 1971: An outline stratigraphy of the Iberian Pyrite Belt. *Bol. Geol. Min.* **82**, 239–268.

Schultz L.G., 1964: Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale. *U.S. Geol. Surv. Prof. Paper* 391–C, 39 pp.

Strauss G.K. & Madel J., 1974: Geology of massive sulphide deposits in the Spanish-Portuguese Pyrite Belt. *Geol. Rund.* **63**, 191–211.

Viguier C., 1974: Le Neñgene de l'Andalousie Occidentale (Espagne): Histoire Geologique du Basin du Bas Guadalquivir. *Thése Univ.* Bordeaux.