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Drainage basin controls on geochemical heterogeneity of modern stream sediments in the Guadalhorce basin (Spain)

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Abstract Geochemical data on modern stream sediments in the Guadalhorce basin (Province of Malaga, Spain) were used to explore the role of parent lithology and drainage basin size as well as grain-size differentiation. Sand-sized sediments (189 samples) with median grain sizes ranging from 2 to 0.125 mm were collected at 136 locations along different river segments. These segments represent streams of various order draining areas with different rock types. For the individual sampling site the area of influence, i.e. the sample catchment, was defined. The catchments were classified on the basis of quantitative parameters: catchment size and the areal proportions of parent rock sources. Geochemical data were described in terms of the relative abundances of major elements (SiO_2, TiO_2, Fe_2O_3, Al_2O_3, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5) in a bulk sample measured with X-ray fluorescence spectroscopy after pre-treatment of the samples, including loss on ignition (LOI) determination. The compositional data were used as the input for end-member modelling which allowed an objective unravelling of the distinct sediment populations.

Key words catchments; chemical composition; classification; end-member modelling; Guadalhorce basin; stream sediments

INTRODUCTION

Chemical composition of stream sediments within a single river basin usually shows a high degree of spatial variations. These variations reflect several factors, such as: (a) provenance; (b) fluvial transport and deposition; (c) post-depositional processes (Kroonenberg, 1992; Johnsson, 1993). There is a long history of research that uses stream sediments as the principle sampling medium to characterize the geology of catchments, to isolate areas with atypical geochemistry and to relate these anomalies either to natural sources or to man's environmental activities (Rose *et al.*, 1979; Förstner, 1989). For better interpretation of sediment geochemical survey results the quantitative consideration of all the factors which influence the spatial variability of sediment is required (Bonham-Carter *et al.*, 1987). This study was undertaken to investigate the relative importance of such factors as basin lithology, basin size and grain-size differentiation in determining sediment geochemistry in a heterolithic river basin. The study area is the Guadalhorce basin, located in the south of the Iberian peninsula (Province of Malaga, Spain). Recent alluvial sands of different granulometry were used as the main sampling medium. Relative abundances of 11 macroelements (analysed with XRFS) in bulk samples were regarded as geochemical signals from drainage area and fluvial processes and treated as multivariate geochemical measurements. The sources as well as spatial patterns of geochemical variability were detected and described using end-member modelling. The modelling results were integrated with the bedrock geology and basin-size data to observe the relationship between source area and composition of the sediments.

STUDY AREA AND SOURCE ROCKS

The Guadalhorce River is a Mediterranean fluvial system of the 6th order. Its drainage basin covers approximately 2600 km^2 and is located in the western part of the Betic Cordilleras, a mountain chain belonging to the actively uplifting Alpine-Mediterranean Fold Belt. The Betic Cordilleras is traditionally subdivided into the Internal zone, most closely to the coast, and the External zone (Weijermars, 1991). The Guadalhorce basin intersects both the structural units of the Betic orogen (Fig.1). The upper Guadalhorce basin (891 km^2) and the catchment area of its right tributary, the Turon River (224 km^2), are situated in the Subbeticum, which is the allochtonous subdivision of the External zone. It is composed by non-metamorphic carbonate rocks of essentially Mesozoic and Tertiary age (limestones and marls partly gypsiferous). The lower Guadalhorce basin is located in the Betic zone where the bedrock is represented mainly by Triassic and older low-grade metamorphic and metasedimentary rocks (phyllite, crystalline schist and shale), Lower Liassic dolomites and limestones, as well as plutonic (ultramafic) masses. The average differences in major element concentrations can be grouped into five broad units (Table 1) according to the lithologies occurring in the Guadalhorce basin.

SAMPLING AND CATCHMENT ANALYSIS

During the low-water period a total 186 sediment samples with median grain size ranging from 2 to 0.125 mm were collected from active channels and the lower flood plain in the

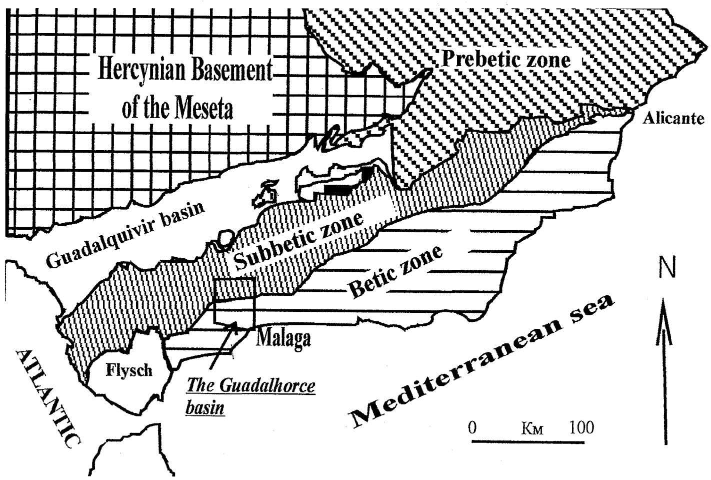

Fig. 1 Sketch map of the major tectonic provinces of the Betic Cordilleras (after Weijermars, 1991) showing geographical location of the Guadalhorce basin.

Table 1 Lithogeochemical types of rock sources in the Guadalhorce basin.

Lithogeochemical units	Typical macroelements	Rocks in the Guadalhorce basin	% total area
Calcareous units	Ca (Mg)	Limestones, dolomites, argillaceous limestones, marbles, limestones and dolomites	13.4
Calcareous and argillaceous	Ca, Al (Mg)	Marls and clays of flysch formations argillaceous limestones	17.8
Gypsiferous and marly	Ca, S, Al, Na, K	Transitional and shallow water facies (Triassic), dominated by speckled clays in association with evaporites and dolomites	12.1
Arenaceous siliciclastic	Si, K, Na	Sands, conglomerates, sandstones dominating in terrigenous clastic formations. Quaternary alluvial, colluvial and alluvial fan deposits.	32.9
Schistose	Al, Fe, Ti	Gneiss, phyllite, crystalline schist and shale	20.8
Ultramafic	Mg, Fe, (Ti, Ca)	Peridotite, pyroxenite and serpentinite	3.0

Guadalhorce basin. The sampling was performed at 136 locations. The choice of the locations was related to the scale of spatial variations in rock types and the size of the corresponding drainage areas. For each sample point the area of influence, i.e. the sample catchment, was defined and characterized in terms of its size and parent lithology. Stream order indices were used as a proxy of drainage basin size and fluvial transport distance. The indices were given according to Rzhanitsin (1960). The rock parentage was characterized using the rock groupings described in Table 1. According to the areal proportion of these units all subcatchments were assigned to three broad categories of terrain: monolithic catchments, differentiated catchments and compound heterolithic catchments. The monolithic catchments are areas composed of one type of lithology. The geochemically differentiated catchments are represented by areas with two or more parent rock types, one of which occupies more than 50% and less than 90% of the total area. Compound heterolithic catchments are terrains with several lithogeochemical units, each occupying less than 50% of the total area. Chemical analysis of the sediments representing all the studied sub-catchments was performed with a Philips PW1410 X-ray fluorescence spectrometer in the laboratory of the Department of Soil Science and Geology at Wageningen Agricultural University (The Netherlands). The analysis was carried out after the pre-treatment of the samples and loss on ignition (LOI) determination. The XRFS suit of elements used in this study included SiO_2, TiO_2, Fe_2O_3, Al_2O_3, MnO, MgO, CaO, Na_2O, K_2O and P_2O_5.

END-MEMBER MODELLING

Context

The present study was built upon the assumption that compositional variation among recent alluvial sands in relatively small river basins of mountainous regions originates mainly from the physical mixing of heterogeneous erosional material, derived from different rock sources. In this case spatial heterogeneity of sediments can be conveniently described in terms of a linear mixing model. Data sets which conform to this model can be expressed as mixtures of a limited set of end members (EMs). In natural systems the exact nature of the mixing process is often unknown. For such cases the mixing parameters are estimated by means of inverse modelling techniques. In this study we used the inversion "unmixing" algorithm proposed by Weltje (Weltje, 1994; Prins & Weltje, 1999) to estimate the number of EMs (the first modelling stage), the EM compositions and the EM proportional contributions to each observation (the second modelling stage). The choice of q, the number of linearly independent EMs in the mixing model, is a crucial step in the unmixing procedure. Different measures can be used as guidelines for the best choice of q. In this approach a minimum number of EMs which allows one to "explain" the observed compositional variations is chosen on the basis of the goodness-of-fit statistics by calculating the mean determination coefficient across the variables. After the "best" solution has been chosen, the bilinear problem of estimating of fully non-negative mixing proportion matrix and "conservative" end-member compositions is solved. The algorithm has been tested on two different types of compositional data: on petrographic data of modern beach sands (Weltje, 1994) and on the grain-size distribution data of terrigenious deep-sea sediments (Prins & Weltje, 1999). In this study the modelling is performed on geochemical data.

Interpretation of the modelled end-members in terms of their chemical composition

The results of EM modelling revealed that the compositional variations within three grain-size groups of sediments in the Guadalhorce and Turon basins are adequately described as mixing of four EMs. Silica and aluminium, the major constituents of aluminosilicates, were two dominant components in the first EM of all grain-size groups (Table 2). The concentrations of Fe, Ti, K, Na as well as of Mg were in agreement with the abundance of these elements in sedimentary rocks that are dominated by aluminosilicate minerals—feldspars, micas and clays. Therefore the first EM was interpreted as an *aluminosilicate component* of alluvial sands. The major compositional variations of the aluminosilicate EM across the grain-size spectrum are related to SiO_2 abundance, which is enhanced in the finer sand fractions. The increase of SiO_2, which apparently can be induced by the admixture of quartz, causes the "dilution" effect—the relative decrease of concentrations of other elements except Na, also suggest the minor feldspar enrichment in sediments of coarse and medium grain size and in the fine fraction.

The major chemical constituents of the second EMs for all grain-size groups of sandy sediments are CaO and the LOI. Other elements, including Mg, are not abundant. These EMs can be interpreted as the *calcareous component* of alluvial sands. The calcareous phase is obviously dominated by carbonate minerals. Across the grain-size spectrum, the calcareous EMs of the finer sediments have higher concentrations of the elements associated with aluminosilicate minerals: Si, Al, and Fe. The increase of SiO_2 up to 10% for the group of coarse and medium alluvial sands suggests that the calcareous EM includes not only a minor amount of aluminosilicate minerals, but also quartz (Table 2).

The third EM in all groups of the sediments is characterized by a very high amount of Mg, relatively high concentrations of Si and Fe, and a high LOI. These EMs were interpreted as the *magnesian component* of alluvial sands. Low Al concentrations, especially in the group of very coarse sands, indicate that the principle carriers of MgO are silicates and/or

Table 2 Modelled end-members of recent alluvial sands in the Guadalhorce and Turon basins.

Grain-size groups of alluvium	Chemical composition, %	End member 1 (aluminosilicate)	End member 2 (calcareous)	End member 3 (magnesian)	End member 4 (quartzose)
Very coarse sand (2–1 mm)	SiO_2	55.92	0.00	41.91	86.23
	TiO_2	1.09	0.28	0.24	0.13
	Al_2O_3	21.26	0.75	3.61	3.13
	Fe_2O_3	8.34	0.15	8.10	1.75
	MnO	0.33	0.33	0.33	0.33
	MgO	2.01	1.41	33.64	1.31
	CaO	0.00	48.69	0.19	4.71
	Na_2O	0.78	0.15	0.32	0.56
	K_2O	3.44	0.65	0.24	0.59
	P_2O_5	0.33	0.33	0.33	0.33
	LOI	6.49	47.26	11.08	0.91
Coarse and medium sand (1–0.250 mm)	SiO_2	62.76	10.43	44.84	86.07
	TiO_2	0.98	0.19	0.12	0.13
	Al_2O_3	17.94	2.71	5.17	1.39
	Fe_2O_3	7.04	1.75	7.95	0.81
	MnO	0.16	0.19	0.16	0.18
	MgO	1.69	0.77	30.41	1.65
	CaO	0.00	44.00	1.12	5.24
	Na_2O	0.95	0.00	0.31	0.22
	K_2O	3.39	0.64	0.39	0.00
	P_2O_5	0.17	0.17	0.17	0.17
	LOI	4.92	39.14	9.37	4.13
Fine sand (0.250–0.125 mm)	SiO_2	66.27	3.11	52.79	83.64
	TiO_2	1.00	0.14	0.35	0.22
	Al_2O_3	18.29	1.85	8.66	2.58
	Fe_2O_3	7.00	1.11	6.79	1.58
	MnO	0.20	0.20	0.20	0.20
	MgO	0.61	1.30	20.28	1.93
	CaO	0.00	48.77	0.43	3.89
	Na_2O	0.84	0.02	0.78	0.15
	K_2O	2.72	0.28	1.52	0.72
	P_2O_5	0.20	0.20	0.20	0.20
	LOI	2.86	43.01	8.00	4.89

Mg-rich carbonates. Across the grain-size spectrum of the magnesian EMs we observe the decrease of Mg for the sediments with finer granulometry. In parallel we found the decrease of Fe and the LOI and higher concentrations of elements of aluminosilicate association—Si, Al, K and Na—in the fine sediments. This trend can be explained both by instability of magnesium silicates in the supergene zone and/or the enriching of the finer EM sediments with aluminosilicate material.

The major chemical parameter of the fourth EM for all grain size groups is silica. In natural environments very high SiO_2 concentrations, coupled with very low contribution of other elements, are the main geochemical feature of sediments derived from quartzose rock sources. Since the concentrations of SiO_2 in the fourth EMs agrees well with the chemical data on average quartz arenites, the fourth EMs were interpreted as the *quartzose component* of the alluvium. The relative increase of Al and Fe may correspond to the presence of aluminosilicate minerals. The minor enrichment with Mg, Ca, and an increase of LOI in the finer EM sediments can be caused by the interference of fine calcareous material.

SPATIAL ANALYSIS OF GEOCHEMICAL SUBPOPULATION OF ALLUVIAL SEDIMENTS

Spatial changes in geochemistry of sediments are expressed as changes in relative abundances of the EMs. The analysis of the relative EM contributions to the sediments in the studied basins combined with the quantitative consideration of the corresponding source terrains (catchment lithology and size) revealed that the aluminosilicate, calcareous, and magnesian EMs have mainly detrital origin and can be attributed to the erosion of specific rock sources. The abundance of quartzose EM is dominantly controlled by the distance of fluvial transport (stream order), which is accompanied by maturation of sands and mixing of sediments with material from older alluvial sequences (Fig. 2).

The relative abundance of the aluminosilicate EM is dominantly influenced by the erosion of schistose lithology (schists, gneiss, slates, phillites, shales). The calcareous EM is matched with carbonate-rich sources such as limestones. The magnesian EM is mainly derived from ultramafic lithology. The sands produced by these rock types in monolithic catchments represent non-mixtures and form the distinct sediment subpopulations within the Guadalhorce basin. The proportion of the quartzose component in non-mixtures reflects the mineralogical composition of the eroding rocks: the lowest levels are typical for sediments in calcareous or ultramafic monolithic catchments.

In differentiated and compound catchments the sediment geochemistry responds differently to the catchment lithology depending on the catchment scale. Relatively small catchments might generate monocomponent sediments. The main controlling factor in such cases is the local supply from the nearest lithology through bank and channel erosion. In the 4th

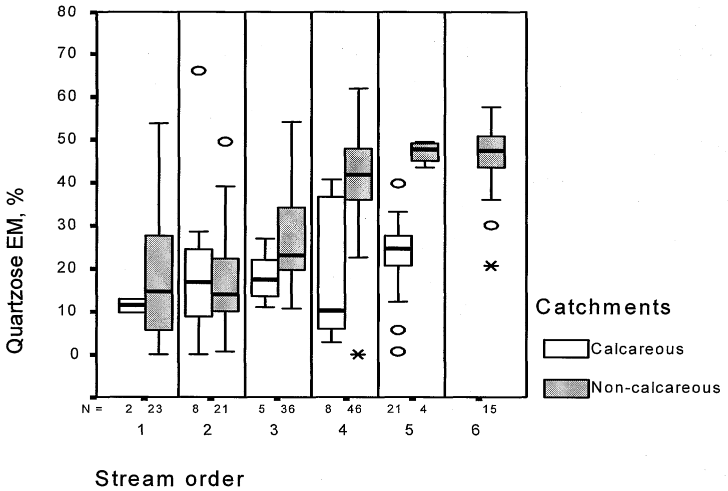

Fig. 2 Box plots of quartzose EM abundances in alluvial sands subdivided by dominant catchment lithology. Median, 75% and 25% quartiles, maximum and minimum values as well as outliers (open circles) and extremes (stars) are indicated.

order streams and larger rivers mixing and deposition processes dominate over erosion. The sands produced in such catchments show a wide spectrum of EM abundances. Major control on the sediment geochemical subpopulation appears to be rock assemblage and areas of different bedrock types and also the capacity of a given rock source to produce sand with respect to the others. To understand the relationship between the three EMs considered (aluminosilicate, magnesian and calcareous) and the proportions of the corresponding source lithologies, data from both sources and sands were analysed together. The analysis revealed that calcareous EM is poorly represented compared with the source lithology. In contrast, the aluminosilicate component is always over-represented in sediments. Schistose lithology seems to have the highest rates in generating sand. The sediments of the lower course of the Guadalhorce trunk river, intersecting the Internal zone, are largely ternary mixtures with a dominant influence of aluminosilicate EM. In the northern reaches of the Guadalhorce trunk river with sedimentary rock assemblages in the source terrains, the alluvial sands are dominantly composed of a mixture of aluminosilicate and calcareous EMs.

CONCLUSIONS

Major proportions of the geochemical variation in stream sediments (sands) in the studied basin can be explained on the basis of mixing of four EMs. The compositional resemblance of the modelled EMs to the geochemistry of some sedimentary rocks allowed interpretation of their dominant mineralogical assemblages as aluminosilicate, calcareous, magnesian and quartzose components of the alluvium. Spatial analysis matched the EMs either to the erosion of specific lithologies (aluminosilicate, calcareous, magnesian EMs) or to fluvial transport distance (quartzose EM).

Due to the strong dependence on lithological and fluvial factors the sands produced in different sub-catchment areas of the studied heterolithic basin show a wide spectrum of EM abundances. The relationships between source lithologies and sand composition found for the Guadalhorce basin confirm major inferences made in petrological studies by Palomares & Arribas (1993) and Arribas *et al.* (2000).

The EM modelling also revealed that grain-size differentiation seems to be a less important factor for geochemical heterogeneity of alluvial sands in the Guadalhorce basin: the EMs across different grain-size groups are geochemically similar. The minor variations shown by similar EMs might indicate the systematic grain-size changes in mineralogy that occur during weathering and fluvial transport, or suggest the difference in lithological parentage for the sediments of different granulometry.

The results presented above show that EM modelling can be a valuable tool both for unravelling complex patterns of variations in chemical composition of sediments and for evaluating the controls on sediment geochemistry.

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