Geochemical and Mineralogic features of upper Pliocene to Quaternary clayey sediments of the Lower Guadalquivir Basin

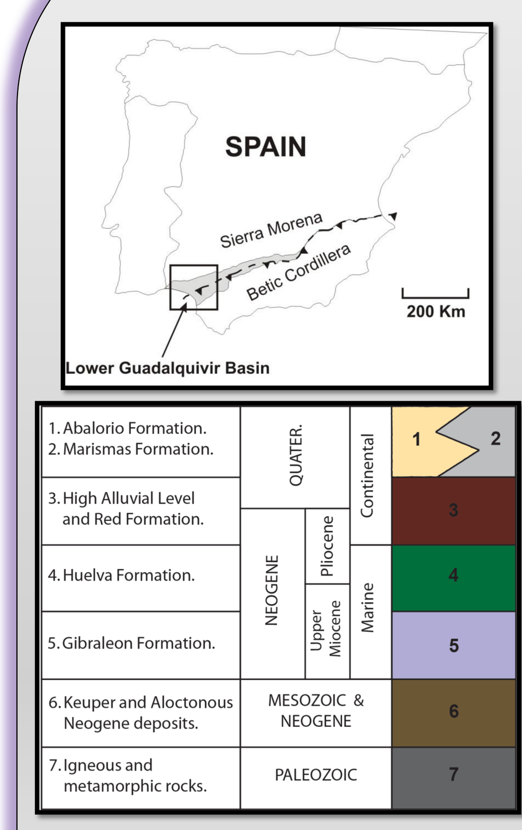
M. P. Mata (1), F. J. Valdepeñas Polo (2), J. M. Salvany (3), M. Castillo (1), E. Bellido (1), and C. Mediavilla (4),

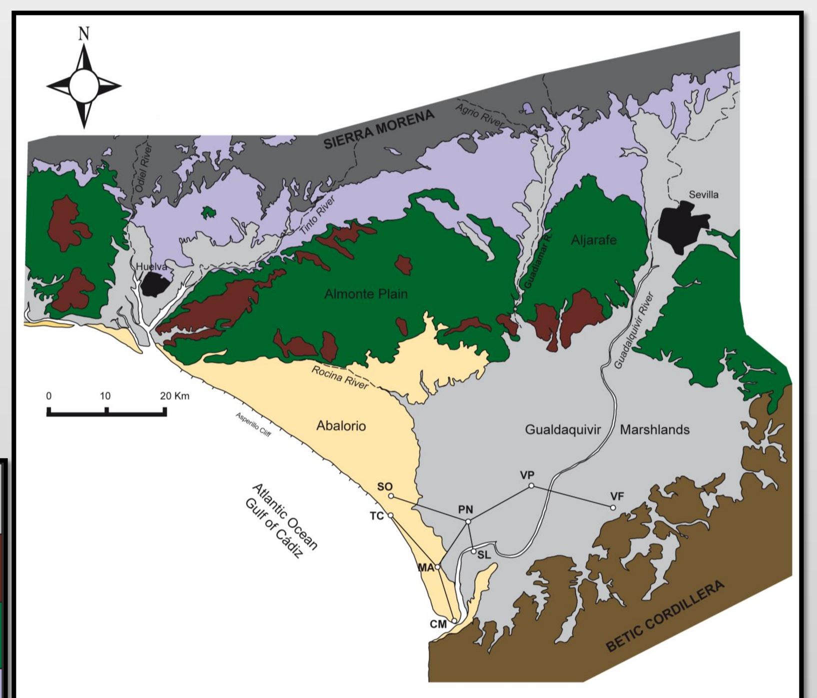
(1) Instituto Geológico y Minero de España (IGME), C/ La Calera, 1, 28760 - Tres Cantos (Spain)
(2) Universidad complutense de Madrid (UCM), C/ José Antonio Novais, 2, Ciudad Universitaria – Madrid (Spain)
(3) Departament Enginyeria del Terreny, Universitat Politècnica de Catalunya, C/ Gran Capità s/n, 08034 - Barcelona (Spain)
(4) Instituto Geológico y Minero de España (IGME), Unidad de Sevilla, Plaza de España, Torre Norte, 41013 - Sevilla (Spain)

V Regional Comitee on Atlantic Neogene Stratigraphy CONGRESS HUELVA - 2013 24-26 SEPTEMBER

Instituto Geológico y Minero de España

INTRODUCTION.





Location of studied boreholes (modified of Salvany et al. 2011) SO Santa Olalla; VP: Veta la Palma, 1 & 2, SL: SanLucar; VF: Villafranco (Poblado Escobar); CM: Cuartel de Malandar; TC: Torre Carbonero; MA: Corral de la Marta

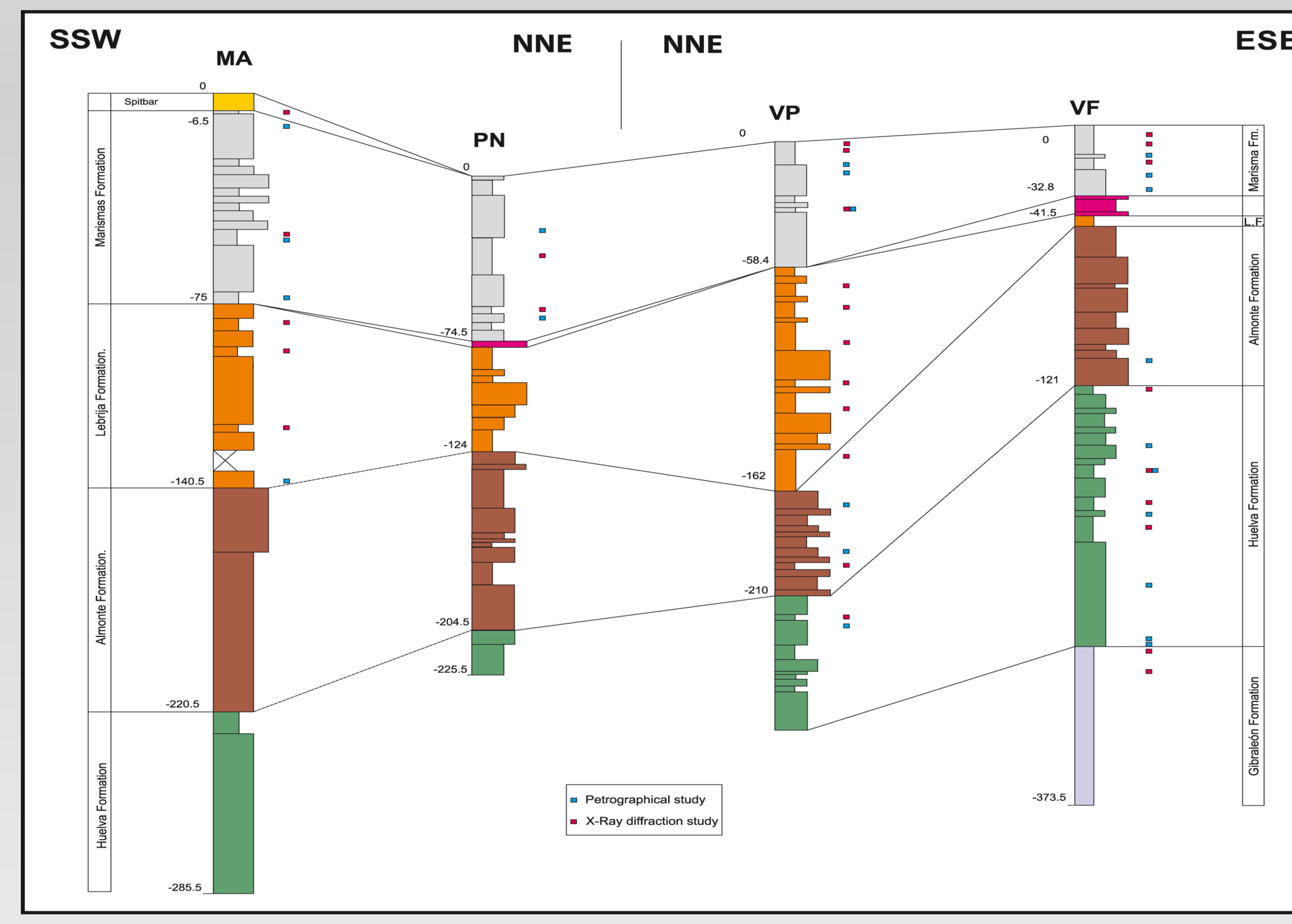
The Guadalquivir Basin (GB) in southern Spain is an ENE-WSW elongated foreland basin developed during the Neogene and Quaternary between the external units of the Betic Cordillera and the Iberian Massif. It is located at a strategic position for studying the role of tectonic and climatic processes in the functioning of the connection between the Mediterranean Sea and the Atlantic Ocean, which has played an important role on the Earth´s climate since the late Neogene. Geochemical and mineralogical data are very scarce (Pozo et al, 2011), so new data are necessary to clearly explain and constrain new environmental data.

This is a preliminary work in the framework of the Guadaltyc project that deals with the tectonic and climatic evolution of GB. The aim of this study is to define the general geochemical features of the upper Neogene units of the Lower GB and to look for the best proxies to study the environmental changes along the sequence and changes on source areas.

MATHERIALS AND METHODS.

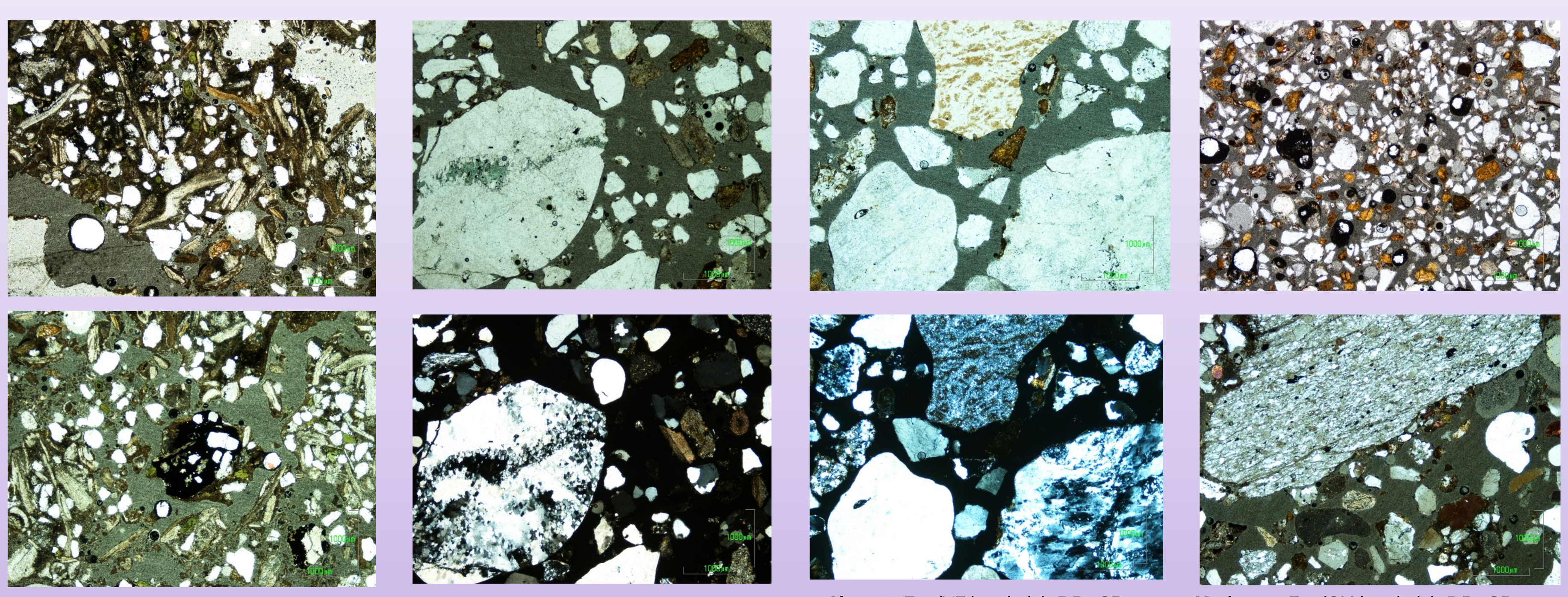
In this study 60 fine-grained samples, Pliocene to Holocene in age, corresponding to 10 boreholes of the lower Guadalquivir basin have been analyzed at the IGME laboratory by means of XRF analysis (major and traces). Bulk and <2 micron mineralogy as been determined by X-Ray diffraction. In addition, a petrographical study on 70 coarser-grained samples and a statistical analysis integrating all data have also been made in order to compare and discriminate the compositional characteristics of different units.

Composition of oxides and trace elements over the 53 samples analyzed was determined by analysis FRX + atomic absorption (sodium), data management software used was Protrace. For statistical analysis of the composition of the 53 samples analyzed was used STATGRAPHICS Centurion XVI.I. software.



Correlation of some boreholes with the location of studied samples MA (Corral de la Marta; PN: Palacio de las Nuevas; VP: Veta la Palma; VF: Villafranco (Salvany, et al. (2011)

PETROGRAPHY



Huelva Fm (VF borehole): Left: P.P. quartz, glauconite, metamorphic R.F. Right: PP CP,

Almonte Fm (VF borehole): P.P.- CP. Quartz, metamorphic Rock Fragments

Marismas Fm (CM borehole): P.P.- CP. metamorphic rock Fragments, quartz, brownish-orange grains (altered grains?)

GEOCHEMISTRY

Table on the right shows maximun, minimun, and average σ values for all the samples grouped in three of the units of the studied boreholes. As shown, average values for the different units are very close, with no significant differences between fine-grained sediments of Marismas, Lebrija and Huelva Formations. Only Br values for Marismas Fm can be considered higher and these high values can be possibly related to the presence of organic matter.

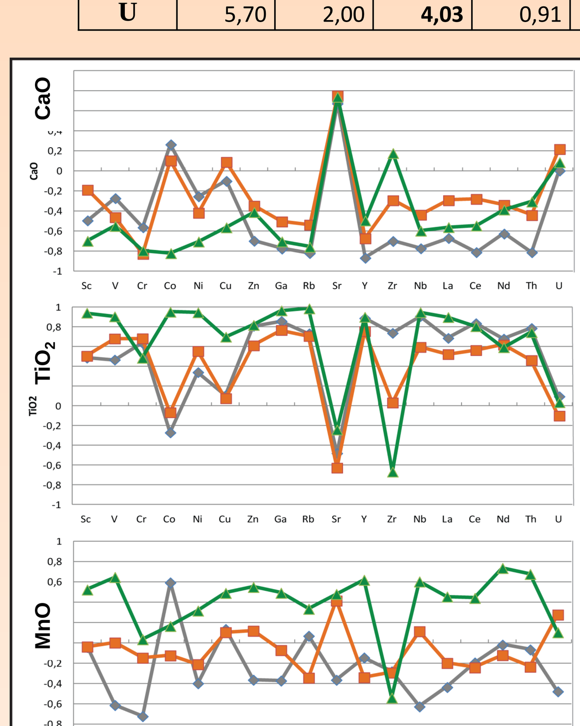
	MARISMAS FORMATION				LEBRIJA FORMATION				HUELVA FORMATION			
	Max.	*Min.*	*Average*	*σ*	*Max.*	*Min.*	*Average*	*σ*	*Max.*	*Min.*	*Average*	*σ*
SiO_2	61,930	34,100	**42,214**	6,421	69,650	38,250	**48,382**	7,301	51,500	39,500	**43,807**	3,686
Al_2O_3	16,860	8,450	**11,472**	1,765	15,800	8,660	**12,545**	1,874	13,610	6,420	9,673	2,326
Fe_2O_3	5,711	3,538	**4,552**	0,605	8,552	3,462	**5,330**	1,199	5,675	2,459	3,715	0,935
CaO	19,735	0,735	**15,703**	4,387	20,937	0,615	**11,624**	4,836	20,260	11,633	17,340	2,880
TiO_2	0,962	0,391	**0,569**	0,109	0,826	0,498	**0,645**	0,072	0,659	0,400	**0,514**	0,083
MnO	0,090	0,030	**0,058**	0,015	0,119	0,032	**0,062**	0,023	0,055	0,027	**0,040**	0,008
K_2O	3,094	1,613	**2,255**	0,437	3,156	1,514	**2,425**	0,405	2,845	1,628	**2,153**	0,358
MgO	3,628	1,795	**2,614**	0,502	3,014	1,485	**2,572**	0,369	3,108	2,592	**2,870**	0,204
P_2O_5	0,200	0,040	**0,123**	0,046	0,225	0,046	**0,127**	0,047	0,122	0,078	**0,102**	0,015
Na_2O	2,503	0,226	**1,078**	0,687	1,056	0,280	**0,579**	0,205	0,832	0,479	**0,675**	0,125

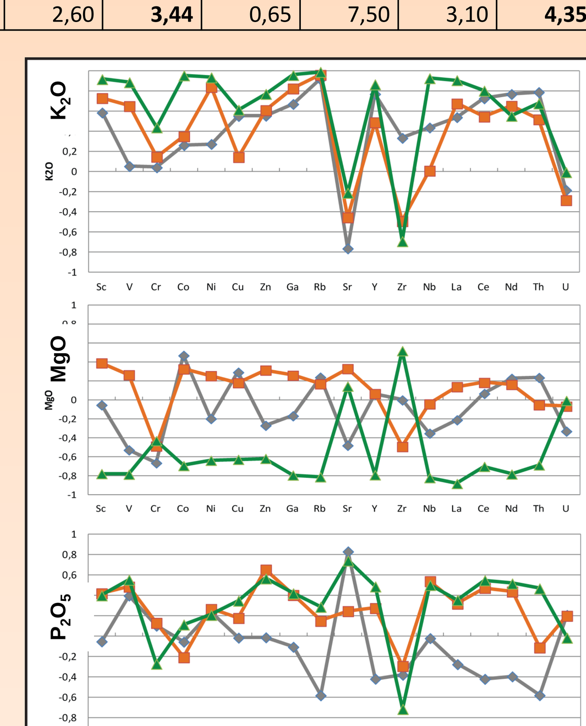
	MARISMAS FORMATION				LEBRIJA FORMATION				HUELVA FORMATION			
	Max.	*Min.*	*Average*	*σ*	*Max.*	*Min.*	*Average*	*σ*	*Max.*	*Min.*	*Average*	*σ*
Sc	18,90	9,20	**14,33**	2,56	18,70	10,10	**15,48**	2,49	18,40	6,60	**12,26**	3,97
V	144,30	80,40	**114,69**	18,11	142,00	82,60	**115,72**	17,65	122,60	59,20	**92,04**	22,40
Cr	128,30	80,10	**98,98**	12,81	123,60	78,40	**105,38**	11,42	103,90	74,90	**88,34**	10,33
Co	14,90	7,80	**11,97**	1,93	19,30	8,70	**13,32**	3,31	19,50	4,60	**11,55**	4,17
Ni	65,10	49,90	**56,43**	3,80	72,10	46,90	**58,75**	7,42	66,90	41,20	**52,07**	8,60
Cu	32,90	16,80	**25,50**	4,54	60,30	17,20	**26,21**	10,20	60,30	13,80	**25,54**	12,84
Zn	100,10	55,10	**71,08**	9,15	104,90	48,90	**76,15**	14,49	74,50	37,40	**55,27**	10,70
Ga	21,40	11,20	**14,89**	2,38	21,20	9,70	**16,25**	2,92	17,30	7,60	**12,39**	3,24
As	49,20	2,00	**9,47**	9,38	18,20	1,30	**7,65**	4,50	9,70	2,50	**5,78**	2,27
Br	79,40	1,20	**22,60**	23,75	23,30	0,80	**6,04**	5,51	20,30	4,10	**8,76**	5,52
Rb	139,50	70,40	**95,13**	19,45	130,50	62,70	**102,51**	17,31	115,30	62,00	**85,46**	16,30
Sr	650,60	107,20	**361,72**	151,91	333,50	90,50	**243,98**	67,90	394,60	259,70	**329,57**	44,56
Y	36,60	17,40	**21,80**	3,98	31,50	2,80	**23,37**	5,89	23,90	16,80	**20,91**	2,16
Zr	223,30	92,30	**137,24**	31,49	251,00	113,50	**164,26**	34,61	187,10	142,50	**160,30**	15,04
Nb	18,60	8,60	**12,44**	2,02	24,10	10,90	**14,51**	2,83	13,90	8,40	**11,21**	1,80
Mo	2,00	0,20	**0,97**	0,43	1,60	0,10	**0,96**	0,40	1,30	0,50	**0,97**	0,26
Sn	8,30	3,80	**6,07**	1,11	8,30	3,40	**6,22**	1,24	6,90	3,00	**5,79**	1,13
Cs	12,10	1,20	**7,70**	3,33	12,10	3,20	**8,74**	2,28	11,00	3,30	**7,06**	2,42
Ba	492,20	195,20	**309,22**	66,93	387,50	203,20	**329,99**	47,47	387,50	230,60	**283,26**	43,63
La	54,60	29,00	**37,44**	5,57	52,40	27,50	**41,32**	6,18	43,30	28,00	**35,43**	4,67
Ce	100,90	52,50	**67,85**	9,31	91,70	56,90	**74,46**	9,27	79,60	43,20	**64,52**	11,14
Nd	44,60	22,90	**30,86**	5,15	41,80	22,60	**32,85**	4,68	39,70	22,40	**29,11**	5,02
W	10,70	1,80	**6,65**	2,28	10,40	2,10	**5,97**	2,16	9,10	3,80	**5,55**	1,60
Th	12,90	5,40	**8,34**	1,64	11,30	8,20	**9,60**	0,94	9,20	6,40	**8,01**	0,82
U	5,70	2,00	**4,03**	0,91	4,50	2,60	**3,44**	0,65	7,50	3,10	**4,35**	1,41

Below: correlation values of major oxides and traces for Marismas, Lebrija and Huelva Formations.

- **Ca-Sr** high-positive and **Sr-Si** high-negative values are consistent with variations in bioclastic contents and/or carbonate vs siliciclasti abundance in the samples.
- **Ti-K-Fe-Al** *vs* **Sr** indicates also fine grained detrital components vs bioclastic content in the samples.
- **La-Ce-Nd –Al_2O_3** indicates also that REE elements are related to clay minerals.
- **Zr-Si** high positive values can be explained as a sorting process.

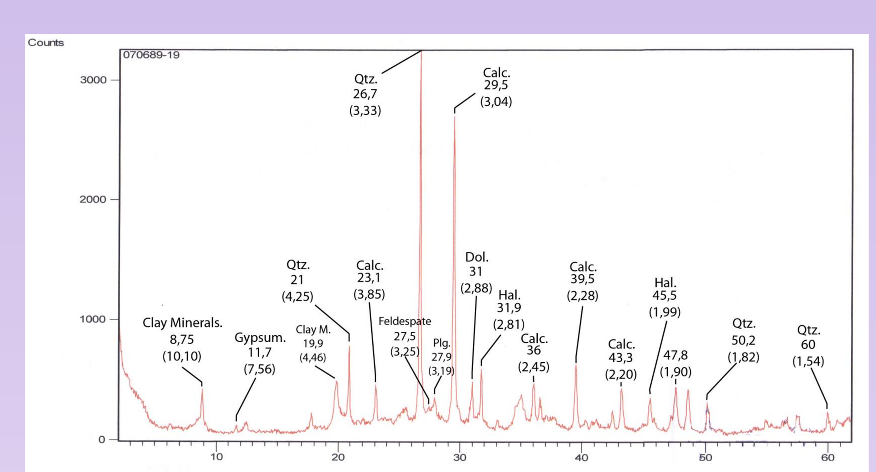
•Different values have been found in Huelva Fm regarding Lebrija and Huelva formations, for Cu-Co-Ni-Zn metals *vs* major oxides and MgO-trace metals, that can be interpreted as presence of other metal carriers (oxides or sulphides not detected by XRD) and, for MgO, differences in the content and composition of clay minerals / carbonates (both Mg-carbonated bearing minerals).



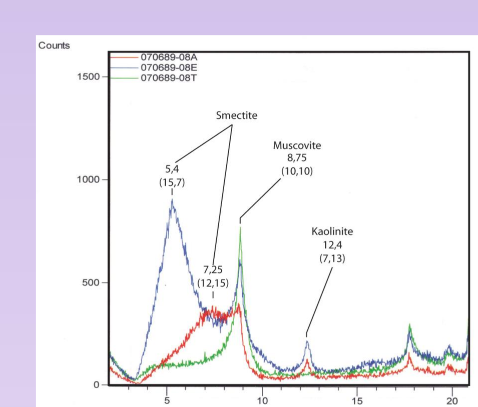


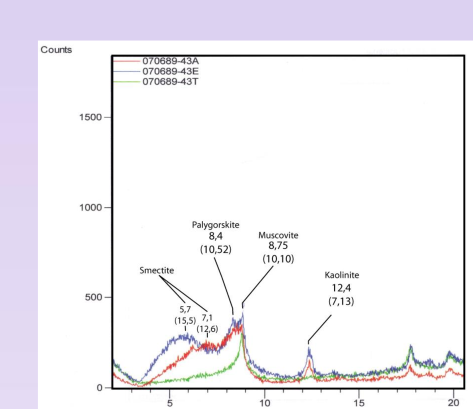
MINERALOGY AND CLAY MINERALOGY

Results of **bulk mineralogy** of 60 samples show that quartz, calcite, K-feldspars are the main minerals, dolomite, albite are present as minor minerals and gypsum and halite are sporadic showing no significative differences between samples from different boreholes and units.



Representative XRay Diffractogram of the studied samples . Quartz and calcite are major minerals in most of the studied samples. Dolomite, halite and gypsum occur as secondary minerals.





Clay Minerals (Air dried): red; ET: blue; TT: green)

Clay mineralogy is made of abundant smectite, interstrafied illite/smectite, illite, kaolinite and sporadic palygorskite and chlorite. Significant differences have been found in the smectite crystallinity and illite-smectite interlayering along different cores mainly in SL, VP y VF in Huelva Formation that can be related to environmental changes in source area.

In addition to the clay minerals as determined by XRD, glauconite has been identified on coarse grained samples as grains and pellets. Textural features and optical properties on coarser grains may indicate that some of the clay mineralogy of Marismas Fm can be related to the alteration of previous Fe-Mg rich silicates

This study gives a general view of main compositional features of the upper units of the Low-Guadalquivir basin. Main compositional variations seems to be related to sorting, and siliclastic vs bioclastic components, being the main siliclastic components very close in nature.

Nevertheless, these preliminary results show that clay minerals seems to be a promising proxy of environmental and source areas changes to be used on this area.

REFERENCES.

➢Salvany, J.M., Larrasoaña, J.C., Mediavilla, C., Rebollo, A. (2011) ***Chronology and tectono-sedimentary evolution of the Upper Pliocene to Quaternary deposits of the lower Gudalquivir foreland basin, SW Spain***. Sedimentary Geology 241 22-39

➢Pozo, M., Ruiz, F., Carretero, M.I., Vidal, R. J., Cáceres, L.M., Abad, M. y González-Regalado, M.L. (2010) ***Mineralogical assemblages, geochemistry and fossil associations of Pleistocene-Holocene complex siliciclastic deposits from the Southwestern Doñana National Park (SW Spain): A paleoenvironmental approach.*** Sedimentary Geology 225, 1-18.

This abstract is a contribution to Guadaltyc project: CGL- 2012-30875