



Anomaly threshold estimation and data normalization using EDA statistics: application to lithochemical exploration in Lower Cretaceous Zn–Pb carbonate-hosted deposits, Northern Spain

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Abstract—A lithochemical survey of Lower Cretaceous sediments (1293 samples) in the Basque–Cantabrian basin (northern Spain) was carried out in order to estimate the mean contents of major oxides and Ba, Co, Cu, Ni, Pb, Rb, S, Sr, V, Zn and Zr in different lithological subsets and to identify anomalies related with Zn–Pb carbonate-hosted mineralization.

After a detailed evaluation of different anomaly recognition methods, using both real and synthetic data, the cut-off values used in the Exploratory Data Analysis (EDA) were selected as thresholds. A prior classification of the rocks (based on chemical, mineralogical and petrographical data) guarantees appropriate homogeneous (with respect to major oxides) rock-groups during the evaluation of the data. A data standardization method was developed and applied to the samples collected from the Carranza sector ($n = 330$). Zinc and Pb values for each sample were normalized to the particular threshold and interquartile range of their corresponding rock-type. These normalized values were plotted in geochemical maps.

The results reveal the presence of Zn (up to 0.6%) and Pb (max. 1380 ppm) anomalies concentrated in carbonate facies, mainly in limestones, dolostones and dolomitic limestones. Magnesium-rich carbonates host the most significant anomalies. In the Carranza area, the great majority of outliers occur around known Zn–Pb mineral occurrences and are concentrated at the edge of the carbonate platform. In some cases fault control of the anomalies is indicated. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

As a general rule, the large data sets managed in geochemical exploration comprise background data, anomalies and spurious values—analytical, sampling and/or manipulation errors—(Zhou, 1985). Identification of these errors and determination of geochemical characteristics of background populations are necessary and unavoidable steps for the adequate isolation of anomalies associated with ore mineralizations, whose recognition becomes the principal task of geochemical exploration.

In lithochemical surveys, the inherent heterogeneous character of the sampling media complicates anomaly selection techniques and forces the use of a prior classification of the data set in order to handle rock-groups with normal or lognormal frequency distributions. Taking into account mineralogical and petrographical data, a chemical classification for sedimentary rocks based on normative mineralogy calculations and on certain major oxide ratios has been applied (Yusta, 1993).

In this study, several anomaly detection procedures were reviewed in order to decide the most appropriate technique for the exploration of Zn–Pb carbonate-hosted deposits from northern Spain. Simple methods were tested that use geochemical information in a univariate way. Data extracted from a lithochemical survey in Lower Cretaceous sedimentary rocks from the Bilbao Anticline, Northern Spain (Fig. 1) were used for the evaluation of these methods. In most cases, the entire data set ($n = 1293$ samples) was used, but in selected cases there is discussion of the behaviour of a smaller population ($n = 330$) from a particular area (the Carranza valley, NW Vizcaya sector). In addition to this real case, synthetic data (not discussed here), which contained known outliers and whose distributions were predetermined and generated with a computer, were used for the same purpose.

DESCRIPTION OF THE SURVEY AREA

The studied area, previously explored by Herrero (1989), is located in the middle of the Bilbao Anticline, an Alpine–Pyrenean structure located in the central part of the Basque–Cantabrian Basin,

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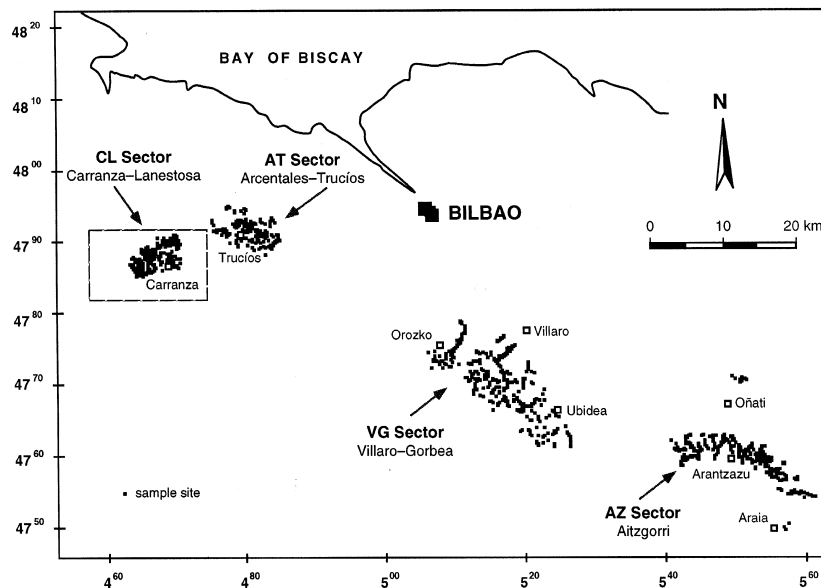
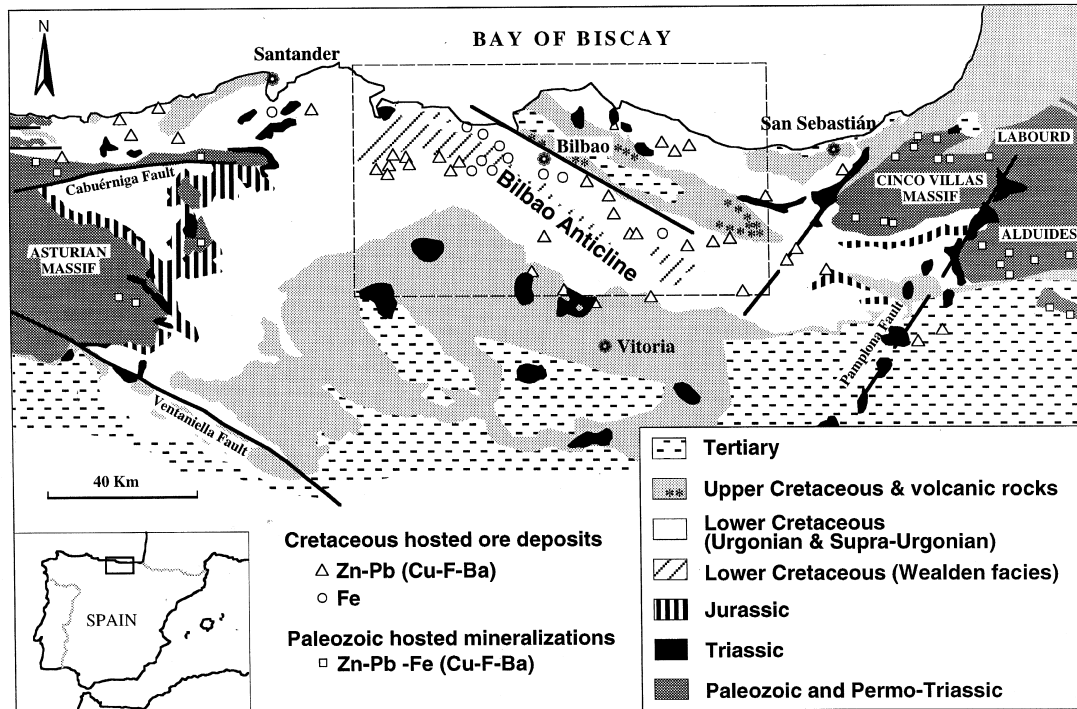


Fig. 1. Simplified geological map of the Basque-Cantabrian region (northern Spain) showing the location of the main Zn-Pb and Fe ore deposits and occurrences. The outlined area shows the Bilbao Anticline, where the regional lithogeochemical studies for Zn-Pb have been performed. The clusters of small black squares in the lower figure show the sample sites.

Northern Spain (Fig. 1). Some of the geochemical data used in this investigation were extracted from a broader study (Yusta, 1993) that covers the entire extent of the Bilbao Anticline.

The Basque-Cantabrian Basin (Rat, 1959, 1988), which comprises Mesozoic to Middle Eocene sediments and local volcanic rocks, is surrounded by

several Palaeozoic massifs (Asturian, Cinco Villas and Sierra de la Demanda). The largest exposures are of Mesozoic rocks, dominantly of Cretaceous age, although Jurassic sediments, at the eastern and western boundaries, and scattered diapiric Triassic outcrops are also present. The thick Lower Cretaceous series are of particular interest since

they are the host rocks for a great number of Zn–Pb–(F–Ba) and Fe occurrences and some productive ore deposits (Velasco *et al.*, 1994).

In the Bilbao Anticline the Lower Cretaceous has been subdivided into 3 major “complexes”: the continental to transitional clastic “Wealden” facies (Late Jurassic–Barremian), the mainly marine “Urgonian” complex (Aptian–Albian), and the siliciclastic fluvial to turbiditic “Supra–Urgonian” complex (Late Albian–Lower Cenomanian). In this study, we have concentrated on the first two complexes because the ore deposits are hosted by “Urgonian” rocks and the lower units have been considered as a possible metalliferous source.

In the western region of the basin (Cantabrian graben), the “Wealden” is composed of reddish sequences—up to 1000 m thick (Pujalte, 1981)—of alternating clays and sandstones (Vega de Pas Formation), and it represents weathered lands and depressed areas with alluvial plains and swamps. In turn, in the Bilbao graben a dark sequence of the same age (Villaro Formation) of at least 2000 m of shale and sandstones indicates brackish estuarine and lacustrine environments (García-Garmilla, 1987).

The “Urgonian” complex (García-Mondéjar, 1990a,b; Fernández-Mendiola, 1986; Pascal, 1985) represents a rapid accumulation of more than 4000 m of carbonate and siliciclastic terrigenous sediments, in a differentially subsident basin under the influence of a warm and wet climate. Tectonic pulses in an epicratonic basin bordering a thin continental crust, during the rifting of the Bay of Biscay (opening of the north Atlantic), has resulted in a cyclic eustatic rise of sea level where carbonate ramps were emplaced between continental environments and relatively deep marine intraplatform troughs.

Within the “Urgonian” complex, 4 main depositional sequences, generated by a characteristic cyclic sedimentation, have been established (García-Mondéjar, 1990a). Each sedimentary sequence is made up of a lower terrigenous unit and an upper fine grained terrigenous and/or marine carbonate unit. Each cycle suggests a long transgressive episode followed by a regressive one in which tops are erosional surfaces, sometimes with paleokarst features and more or less extensive dolomitization.

In the Carranza sector ($\approx 40 \text{ km}^2$), located in the western part of the Bilbao Anticline, the “Urgonian” complex (Fig. 2, Table 1) constitutes a sediment pile 500 m thick, lying between the “Wealden” Vega de Pas Formation (CLw unit) and the “Supra–Urgonian” Valmaseda Formation (CL9 unit). The first “Urgonian” terrigenous cycle (Ereza Formation, CL2 unit) is scarcely represented in the sampled area. The Ramales Limestones Formation (CL8 unit) represents the platform carbonate facies of cycles 2 and 3 and is flanked by deeper water,

thin-bedded, more or less impure limestones of platform margin origin (unit CL4). Carbonate talus and basin deposits of marl and calcareous shales are typical facies in the Soba Formation (CL7 unit). Siliciclastic talus lenticular sandstone units (CL6) are intercalated between CL7 marls or are at the top of CL4 limestones. Dolostones and dolomitic limestones (CL81) are related to paleoemersions of platform (CL8) and platform margin carbonates (CL4), or with local hydrothermal alteration of carbonates, contemporaneous with ore deposition.

The tectonic arrangement of the sedimentary sequences in the sector of Carranza displays a gently anticlinal disposition. Also worth noting is the N120–N130° oriented alpine fracture system, because of its role in the late dolomitization and/or mineralization processes.

The economic interest of the cited sector is demonstrated by a great number of mineral occurrences (more than 20) recognised therein (Fig. 2), some of which were exploited until the early 1970s. The majority of these Zn–Pb (and F, Ba and Fe) occurrences are hosted by carbonate rocks of the “Urgonian” complex and are broadly classified as Mississippi Valley-type (MVT) deposits (Table 1) (Herrero, 1989; Velasco *et al.*, 1994).

SAMPLES AND ANALYTICAL TECHNIQUES

Representative sets of sedimentary rocks were collected ($n = 1293$) in an area covering the entire length of the Bilbao Anticline (Fig. 1), mainly from surface outcrops and in some cases from old mine galleries and drill cores, and achieving a sampling density of ≈ 4 per km^2 . For surface rocks, every outcrop found was sampled; and in the case of drill core sampling or in locations near ore occurrences, mineralized samples were rejected. All the “Wealden” and “Urgonian” lithostratigraphic units and different rock types represented therein were sampled, selecting rocks with no visual evidence of alteration or mineralization. The whole rock sample ($\approx 1 \text{ kg}$ weight) was crushed into chips of approximately 2 cm, split after visual inspection in order to avoid pieces of rock with oxidation or ore minerals not discarded previously in the field, and grounded in a WC disc mill to less than 240 mesh.

The samples were chemically analysed for major oxides (SiO_2 , Al_2O_3 , FeO_{tot} , MnO , MgO , CaO , Na_2O , K_2O , TiO_2 and P_2O_5) and for 11 trace elements (Ba, Co, Cu, Ni, Pb, Rb, S, Sr, V, Zn and Zr) on powder discs and fused glass discs by wavelength dispersive X-ray Fluorescence (WD–XRF) at the Laboratorio de Mineralogía de la Universidad del País Vasco (Spain) following the methodology described by Yusta (1993) and Yusta *et al.* (1994a; Yusta *et al.*, 1994b).

Major element contents were determined on 30.5 mm diameter fused glass disks, which in detail are made of 0.8000 g of rock powder (previously dried overnight in an oven at 105°C) mixed with 4.7000 g

of a Li tetra-metaborate flux (Spectromelt A12, Merck ref. 11802). We also added 2 or 3 drops of a LiBr solution (50% wt) in ultra pure water as non-wetting agent. The mixture was ignited with oscil-

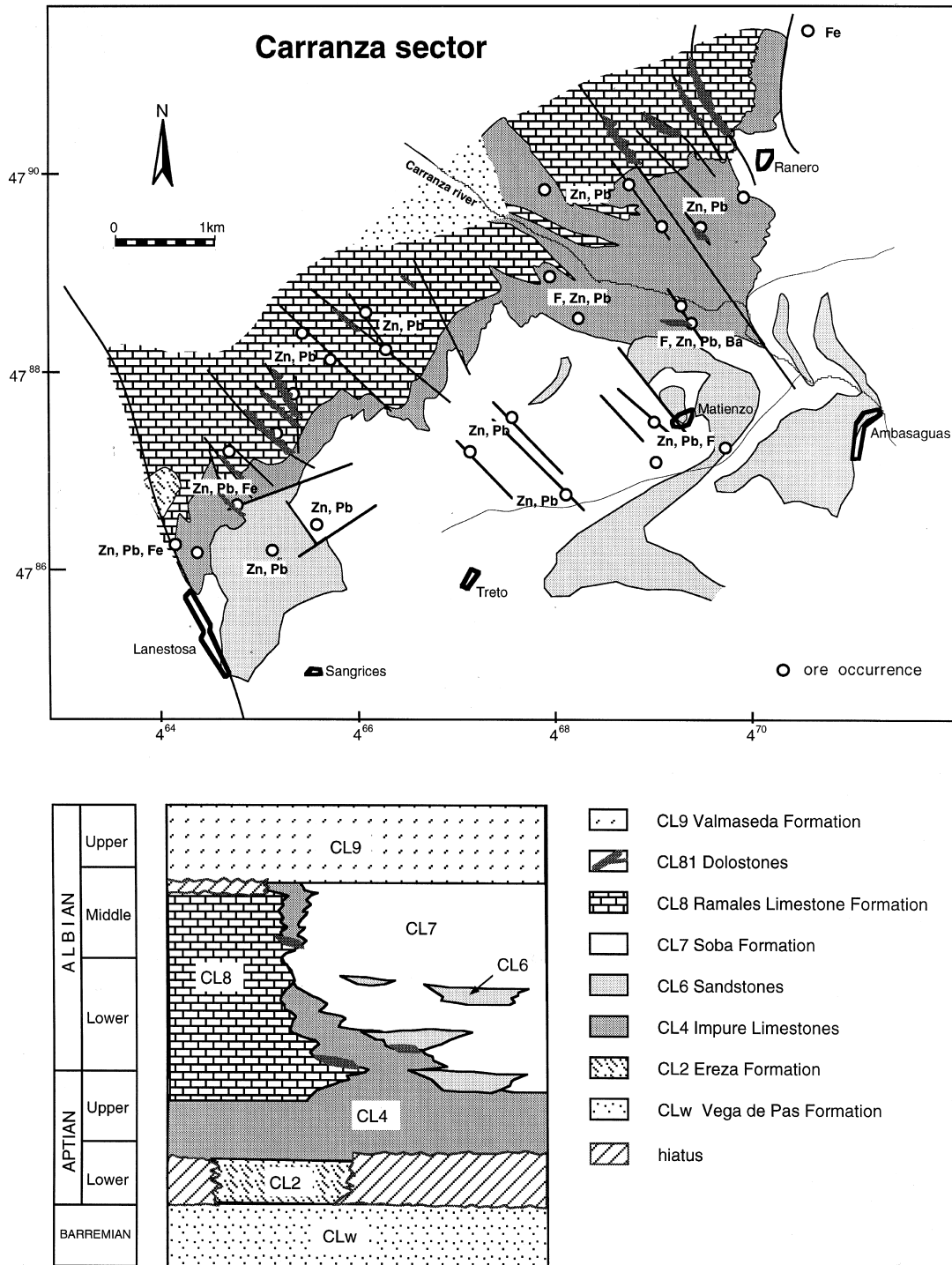


Fig. 2. Geological map and lithostratigraphic scheme of the Lower Cretaceous in the Carranza area with location of ore occurrences (see Table 1 for description of units and lithologies therein).

Table 1. Main characteristics of the lithostratigraphic units recognized in the Carranza sector, with indication of the ore occurrences and their type

Unit	Formation	Age	Lithology	Environment	Ore occurrences	Type of mineralization
CL9	Valmaseda Fm	M. Albian–L. Cenom.	Sandstone, shale	Siliciclastic platform		
CL81	Dolomitizations	Albian	Dolostone and dolomitic limestone	Vein and diagenetic replacements	Zn, Pb	Vein and stratabound
CL8	Ramales Fm.	L. Aptian–M. Albian	Rudistid and coralline limestones	Carbonate platform	Zn, Pb, (Fe)	Vein and stratabound
CL7	Soba Fm.	L. Albian–M. Albian	Marly limestones, marls, and carbonate shale	Talus base, basin	Zn, Pb, F, (Ba)	Veins
CL6		Bedoulian–Clansayesian	Arenaceous limestones, calcareous sandstones and sandstones	Channeled terrigenous in talus and basin	Zn, Pb	Channel replacement
CL4		M. Aptian–M. Albian	Limestones finely stratified, arenaceous limestones, spiculites	Border of platform, talus	Zn, (Pb, F, Ba)	Stratabound
CL2	Ereza Fm.	L. Aptian, Bedoulian	Shale, sandstones eventually with carbonate cement	Siliciclastic platform		
CLw	Vega de Pas Fm.	Barremian	Sandstones, shales	Stuarine complex with deltaic invasions		

lation in a Pt crucible on a Philips PERL'X2 automatic bead machine for 5 min, and poured into Pt–Rh dishes.

Trace element determinations, were made on 40 mm diameter pressed powder pellets following the method of Zyl (1982) with few modifications. A 4.5000 g portion of rock powder was well mixed with 1.8000 g of an organic binder—90% EMU 120 FD (BASF) and 10% Ceridust VP3910 (Hoechst)—and pressed in an Herzog HTP 4 hydraulic press (30 ton), using an Al cup as support. The pellets obtained following this method are not dusty and compact enough to prevent the contamination of the spectrometer sample chamber. Both standards and samples were stored in a desiccator.

Element determinations were performed with a Philips PW1480 sequential X-ray spectrometer equipped with a Sc–Mo side-window tube and under a vacuum path. The crystals used were LiF 200, LiF 220, Ge, PE and a multilayer PX1. Calibration of each analyte was obtained by regression analysis of a set of 58 international rock standards. Corrections factors were applied for line overlaps and matrix effects. The Philips's Alphas-on line software (Philips, 1988), based on the α -coefficients of de Jongh (1973) and the Compton scatter radiation from the Mo target as an internal ratio

(Rose *et al.*, 1986) were used to correct major and trace element, respectively. More details on instrument, analytical conditions and standards are described in Yusta *et al.* (1994b).

Detection limits (dl) estimated for Zn, Pb, Cu, Ni, Sr and Zr are close to 1 ppm, but higher for Ba, Co, V and Rb (5–20 ppm). Nevertheless, the minimum quantitative detectable limits (Jenkins *et al.*, 1981), estimated as a function of the rock-type, give more realistic figures between 1 and 5 ppm for Zn and Pb, and < 30 ppm for Ba, Co, V and Rb.

Trace element contents below dl (also “qualified” data *sensus* Sanford *et al.*, 1993) were substituted by a collection of extrapolated values that were computed by means of the robust probability plotting method (Helsel and Cohn, 1988; Helsel, 1990). In this procedure, the normal scores (n scores) of all data set (including the qualified data) are estimated. This is done in order to obtain a set of slightly different n scores that can be used later to calculate different concentration values for dls. Then, a linear regression of log of concentration on n scores is fitted, using exclusively values above dl. Non-lognormal distributions (i.e. in cases where concentration ranges are too broad or multimodal populations occur) may result in poor regression fits. In those cases, we fixed a ceiling value that ensures the linear fit for the regression. Finally, the

obtained regression parameters are applied to extrapolate a set of new values for data <dl, assuming that these values follow the left ending of a lognormal distribution. The proportion of non detectable values for Zn and Pb is of 1.5% and 14% respectively.

In selected cases, petrographical studies with both transmitted and reflected light, and XRD technique have been used to assess the classification of data and assist anomaly evaluation.

CLASSIFICATION OF THE DATA SET

When the entire data set represents multiple population, as generally occurs in litho geochemistry, it is necessary, prior to the application of statistical techniques, to undertake a classification and subdivision of the data as a function of auxiliary data (Garrett, 1989). Some authors prefer classification by geological units (Zhou, 1985; Stanley and Sinclair, 1987), but then the size and lithology of the units must be checked for homogeneity. On the

other hand, Sinding-Larsen (1975) and Selinus (1983) used multivariate approaches to group geochemical data.

In the sampled area, the geological units contain different rock types (Table 1), so lithologic criteria, instead of the unit based criteria, was chosen for classification and anomaly threshold estimation. An in depth knowledge of the mineralogy, petrography and chemistry of the Cretaceous Basque-Cantabrian rocks permits a classification based on the calculation of normative mineralogy. The chemical content of the principal oxides (SiO_2 , Al_2O_3 , FeO_{tot} , MgO , CaO and K_2O) is used, taking into account that the major mineralogy of these rocks is composed of calcite and quartz, with subordinate dolomite, muscovite, illite (in minor proportion chlorite, kaolinite and smectites). Plagioclase and K-feldspar, zircon, rutile, tourmaline, titanite, Mn- and Fe-oxides and pyrite occur as subordinated minerals, mostly in terrigenous sediments. This classification generates homogeneous subsets, in a geological sense (Rock, 1988), by the following procedure (Fig. 3a, b):

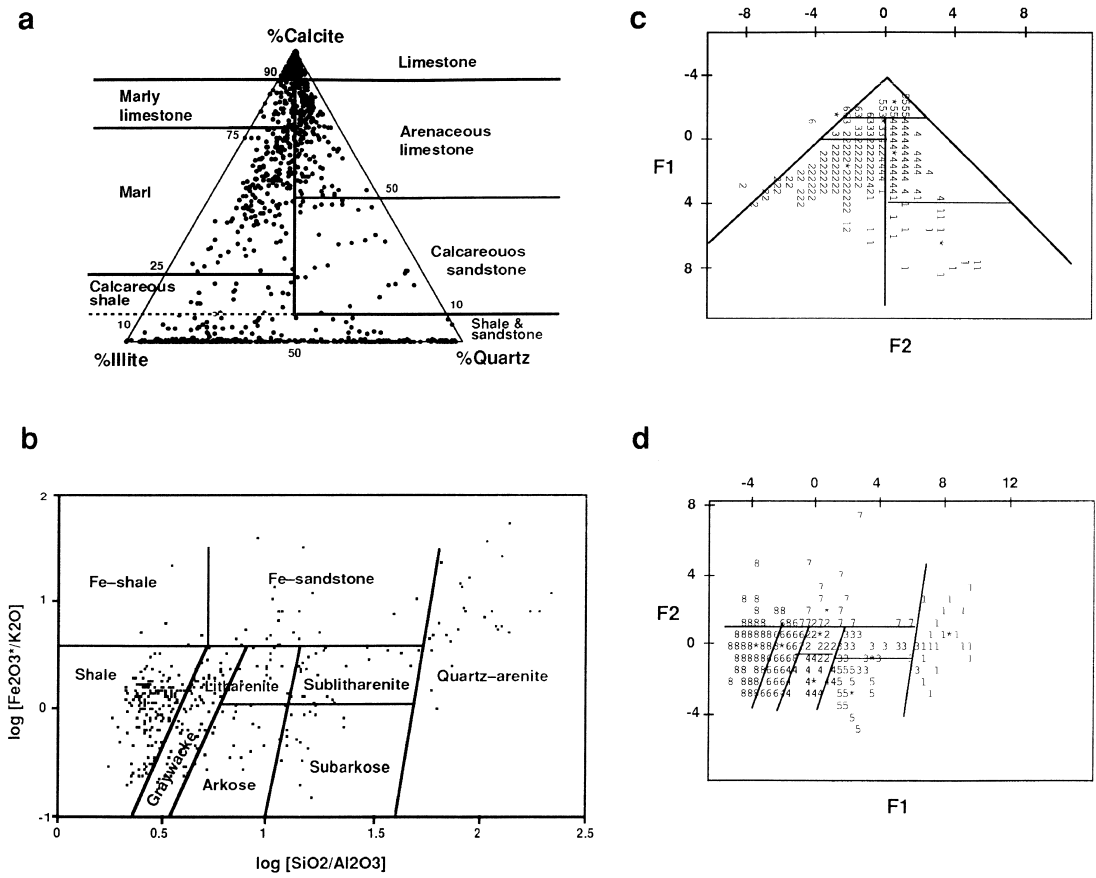


Fig. 3. (a) Triangular plot for carbonate rocks and (b) Herron based classification (1988) for terrigenous rocks of the Bilbao Anticline (n = 1265, dolostones excluded). For the same rocks, discriminant plots of the canonical discriminant functions F1 and F2 (see Table 2 for details on discriminant functions and rock group codes).

1. Separate limestones, marly limestones, marls, arenaceous limestones and calcareous sandstones from non-carbonate sandstones and shales (including calcareous shales) as a function of the normative content of calcite, illite and quartz;
2. Name as dolostones and dolomitic limestones those carbonate samples where the ratio (% wt) $\text{MgO}/\text{CaO} \geq 0.38$ in the former case, and $0.03 \leq \text{MgO}/\text{CaO} \leq 0.38$ in the latter case (Thomas, 1989); and finally;
3. classify the shales and non-carbonate sandstones following the chemical classification of Herron (1988), in which logarithmic scores of the $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios are used to categorize these rocks into the petrographical groups of Pettijohn *et al.* (1987).

In order to check the validity of this chemical classification, a linear discriminant analysis (LDA) was carried out. The complete data set was split into two different subsets: the training set, composed of well characterized samples (172 carbonate and 141 terrigenous rocks) whose petrographical and/or field observations agreed with the assigned groups by the above described procedure; and the validation set, composed of the rest of the sampled rocks (696 carbonate and 256 terrigenous rocks). The training set was used to construct the discriminant functions, which then were applied to the validation set. The discriminant module available in the SPSS statistical package (Norusis, 1992) and a strategy that maximizes the Mahalanobis distance between the two closest groups was used in this work.

In consistence with the chemical classification (steps 1 and 3), LDA on carbonate and terrigenous rocks was carried out. Unstandardized discriminant function coefficients and other statistics for these two groups are given in Table 2. Several discriminant analyses were performed using either all the major oxides or only some of them. Finally, the use of the same oxides and logs of oxide ratios as utilized in the chemical classification was decided because the inclusion of the rest of the major oxides did not substantially improve the overall percentage of correctly classified samples.

For carbonate rock types, the percentage of correctly classified cases is generally greater than 85% for both the training and validation sets, with dolomitic limestones being the category with the worst success (50% for the validation set, Table 2). Some of the dolomitic limestone samples show stronger chemical affinity with limestones or dolostones than with their own group and, therefore, it would be more correct to identify them as limestones or dolostones. Nevertheless, we decide to maintain them as a different group because of the presence of dolomite in the samples, and because of the role that dolomitization usually plays in the carbonate-hosted mineralizations. In the validation set, the

classification of calcareous sandstones and arenaceous limestones yields worse results, probably related to their position close to the class borders. As is shown in Fig. 3c, boundaries between sample groups closely resemble those in the ternary plot of Fig. 3a, which displays the location of all the sampled rocks using normative minerals. The inclusion of dolostones in the analysis somehow distorts this scheme, but gives similar success percentages.

LDA performed on terrigenous sediments shows similar success on identifying group membership (training set: 93.6%, validation set: 92.2%), when compared with the results obtained for carbonate rocks. Approximately 20% of the *a priori* assigned arkoses, were assigned to other sandstone types and, therefore, misclassified. Generally, these can be attributed to cases located close to the borders between groups, where the compositional ambiguity between different categories is larger. Ferruginous sandstones display abnormally low success percentages in the training set (54.5%, Table 2), some of them showing a greater affinity for litharenites. Studying these samples in detail shows that their large $\text{Fe}_2\text{O}_3/\text{K}_2\text{O}$ scores are a consequence of the very low K_2O values (less than 0.25% wt). In a similar way as for carbonate rocks, scatterplot of canonical discriminant functions for all terrigenous samples displays a high similarity with the described chemical classification (Fig. 3b, d).

For comparison purposes, Herron (1988) found an overall agreement with petrographic assessments of 85% for terrigenous sands and 97% for shales, in his chemical classification of terrigenous sediments. According to these observations, and although a perfect map between petrographic and geochemical classification is quite difficult to achieve, the observed high agreement between coded field observations, petrographical studies and chemical classification supports the use of this procedure as a viable tool when large datasets are involved and petrographical or mineralogical studies can not be done for all samples. Moreover, the use of specified abundances and/or ratios between major oxides in the process of classification allows us to automate the procedure by means of a custom computer program.

In general, the oxides and the major oxide ratios used in the classification process show an approximately normal/lognormal behaviour in the above identified rock groups. As an example, we present the normal probability plots for limestone, marl, dolostone, shale and quartz arenites (Fig. 4).

The Kolmogorov–Smirnov statistical test was also undertaken for each rock group and element, and the results ($K-S$ value and its significance) are shown in the same graphs. This non-parametric test is used to determine whether or not given data come from a particular distribution by comparing

Table 2. Statistics and results of discriminant analysis (confusion matrices) on carbonate and terrigenous rocks from the Bilbao Anticline (n = 1265, dolostones excluded). For both the training and the validation sets, rows of the confusion matrices represent counts and percentages of grouped cases correctly classified into the pre-defined groups by LDA

CARBONATE ROCKS

Training set (n=172)	
	F1 F2
Eigenvalues	5.67 2.41
% of variance explained	55.88 23.82
Cumulative variance	55.88 79.70
Canonical correlation	0.92 0.84
Chi-square	390.85 186.25
Unstand. Can. DF Coef.	
	F1 F2
CaO	-0.0376 0.1451
SiO ₂	0.1211 0.1497
Al ₂ O ₃	-0.0332 -0.5268
Constant	-0.5198 -6.9608

Training set (n=172)	DA Classification						
	n	1	2	3	4	5	6
1 Calcareous sandstones	(10)	9	—	—	1	—	—
2 Marls	(43)	—	40	1	2	—	—
3 Marly limestones	(15)	—	—	15	—	—	—
4 Arenaceous limestones	(38)	1	2	2	33	—	—
5 Limestones	(61)	—	—	1	1	59	—
6 Dolomitic limestones	(5)	—	—	—	—	—	5

Overall recognition: 93.60%

Validation set (n=696)	DA Classification						
	n	1	2	3	4	5	6
(18)	12	3	—	3	—	—	—
(136)	10	120	—	6	—	—	—
(33)	1	2	30	—	—	—	—
(128)	3	5	6	114	—	—	—
(375)	—	—	12	27	336	—	—
(6)	—	—	1	—	2	3	—

Overall recognition: 83.36%

TERRIGENOUS ROCKS

Training set (n=141)	
	F1 F2
Eigenvalues	13.89 1.08
% of variance explained	92.77 7.23
Cumulative variance	92.77 100.0
Canonical correlation	0.96 0.72
Chi-square	99.05
Unstand. Can. DF Coef.	
	F1 F2
log(Fe ₂ O ₃ /K ₂ O)	-0.3262 3.704
log(SiO ₂ /Al ₂ O ₃)	8.1532 -1.7346
Constant	-7.3481 0.6239

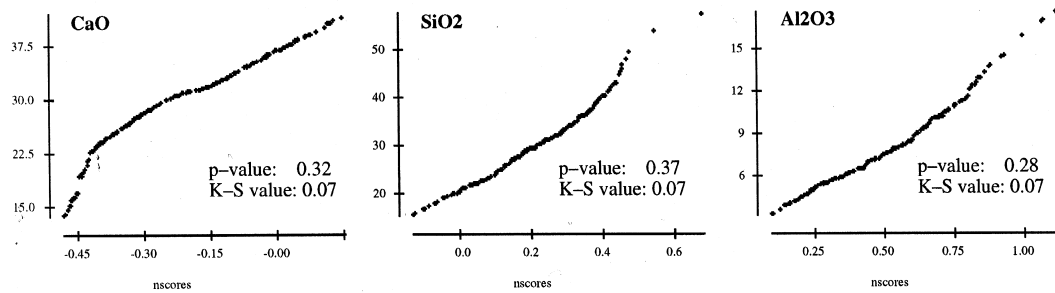
Training set (n=141)	DA Classification								
	n	1	2	3	4	5	6	7	8
1 Quartz arenites	(11)	11	—	—	—	—	—	—	—
2 Litharenites	(15)	—	13	1	—	1	—	—	—
3 Sublitharenites	(23)	—	—	23	—	—	—	—	—
4 Arkoses	(5)	—	—	1	4	—	—	—	—
5 Subarkoses	(9)	—	—	—	—	9	—	—	—
6 Graywackes	(24)	—	—	—	—	—	24	—	—
7 Fe-sandstones	(11)	1	3	—	—	1	6	—	—
8 Shales	(43)	—	—	—	1	—	—	42	98%

Overall recognition: 93.62%

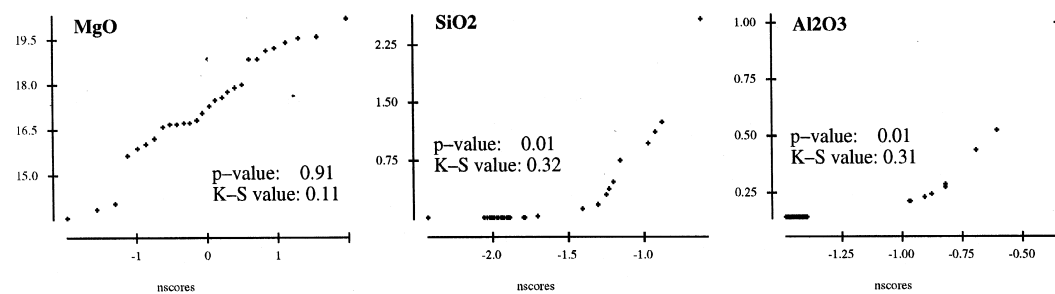
Validation set (n=256)	DA Classification								
	n	1	2	3	4	5	6	7	8
(20)	19	—	—	1	—	—	—	—	—
(7)	—	7	—	—	—	—	—	—	—
(5)	—	—	—	5	—	—	—	—	—
(16)	—	2	—	—	12	2	—	—	—
(9)	—	—	—	1	1	7	—	—	—
(37)	—	1	—	—	—	36	—	—	—
(10)	1	—	—	—	—	—	9	—	—
(152)	—	—	—	—	—	10	1	141	92.8%

Overall recognition: 92.19%

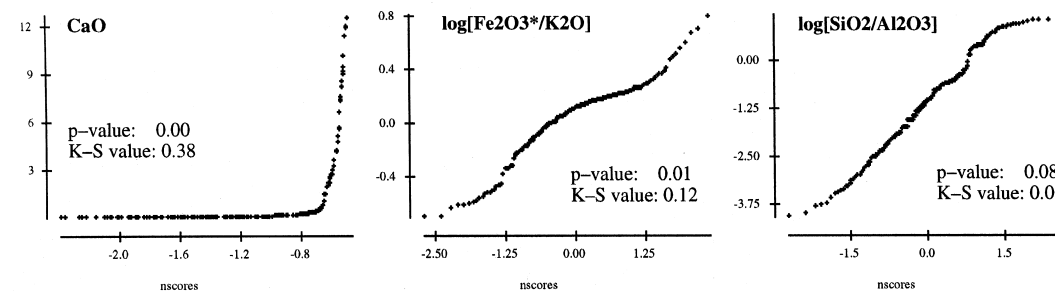
Marls (n=176)



Dolostones (n=28)



Shales (n=195)



Quartz arenites (n=31)

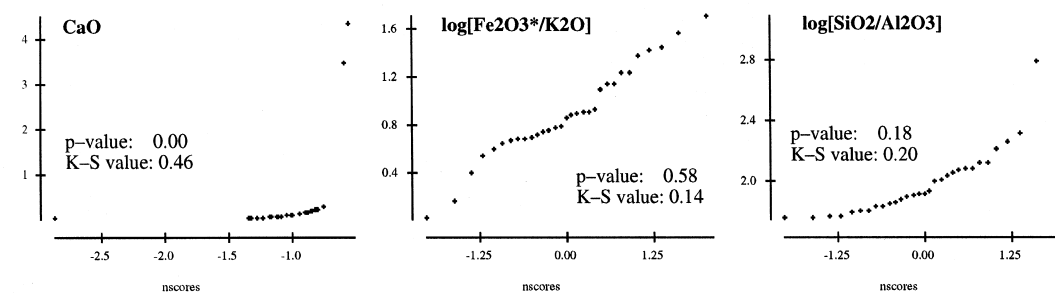


Fig. 4. Normal probability plots for selected elements for some representative rock types of the Bilbao Anticline. Vertical axes: Major oxide contents in % wt or ratios between oxides. Results for the Kolmogorov–Smirnov test are shown in the same graphs. n scores are the normal scores calculated for each population.

the empirical distribution of the ordered data set to a specified theoretical distribution. This K–S test is designed to perform the comparison of a sample with any normal distribution. With regard to the populations that depart from normal patterns, it is observed that they generally show probabilities

> 0.01 for the estimated K–S value when a simple transformation to their natural logarithms is done. Nevertheless, in cases like SiO₂ and Al₂O₃ for limestones, the normality is not achieved after log transformation. When analysed in detail, normal probability plots of these elements for limestones in-

Table 3. Statistical parameters of Zn and Pb (ppm) in rocks from the Bilbao Anticline

Rock	n	Zn					Pb				
		Q2	IQR	Q3	f_u	F_u	Q2	IQR	Q3	f_u	F_u
Quartz arenites	31	18	62	69	162	255	11	29	35	79	122
Litharenites	22	26	32	47	95	143	12	10	19	34	49
Sublitharenites	28	17	21	28	59	90	9	8	13	24	36
Arkoses	21	13	25	33	69	106	16	17	26	51	76
Subarkoses	18	12	23	30	63	97	13	10	16	32	47
Graywackes	61	25	50	64	138	212	20	16	29	52	76
Fe-sandstones	21	33	70	85	190	295	14	21	30	61	92
Calcareous sandstones	28	40	68	82	183	285	12	11	18	34	51
Shales	193	67	70	106	211	316	26	15	34	57	79
Marls	179	38	25	51	89	126	14	7	18	29	39
Marly limestones	48	23	19	36	64	92	8	4	10	16	21
Arenaceous limestones	166	18	14	28	50	71	7	6	11	20	29
Limestones	436	11	10	18	33	48	4	3	6	11	15
Dolomitic limestones	11	16	27	34	75	115	2	7	8	19	29
Dolostones	28	13	12	20	38	56	3	5	7	14	21

Q_2 = median; IQR = interquartile range; Q_3 = upper quartile; f_u = positive upper inner fence; F_u = positive upper outer fence, n = number of samples.

dicating the presence of subgroups of samples, shown as several straight line segments that separate the data into discrete populations. These sub populations are interpreted to be the result of the presence of a large number of limestones with different proportions of arenaceous or argillaceous components in the entire population of limestones (n = 436). In short, limestones would deserve an adequate separation into different groups to discuss them separately, but in a geological classification sense, they constitute a particular rock type and this is the way they were considered here. However, it should be pointed out that in all rock classification schemes, the divisions between different rock types are sometimes artificially placed in a compositionally continuous space (Rock, 1988), so the differences between rock types may not be very clear.

ANOMALY RECOGNITION METHODS

In recent years, the diversity of anomaly recognition approaches described in scientific publications has forced geochemists to investigate various methods to suit to their data. Consequently, it seems wise to evaluate several methods with “previously known” data sets and afterwards decide which is the most adequate. In addition, software and hardware equipment availability and the time consumed in data analysis may be taken into account. Generally, the “blind” use of statistical and geochemical packages may result in incorrect interpretations of data, so it is quite reasonable and advisable to train geochemists in evaluating various anomaly recognition methods (Aucott, 1987).

Sharing this point of view we have evaluated several anomaly selection methods, studying mainly those which consider anomalies “element by element”. Taking into account the metal content differences shown by the sampled rock-types (Table 3), whatever the anomaly selection method used it must be performed on homogeneous data, after undertaking the classification procedure as we have discussed above.

In this work, the following methods were used to select the anomaly thresholds:

1. the normal probability plot graphical method (Howarth, 1984; Garrett, 1988; Chork and Salminen, 1993; Macdonald and Boner, 1993; Cheng *et al.*, 1994). In this method, the normal scores of the data set for each element are plotted against concentration, showing a linear trend when data perfectly fit the normal distributions. Curved patterns indicate skewed distributions, whereas several straight line segments display the presence of groups of samples from different populations in the data set.
2. EDA statistics (Tukey, 1977; Velleman and Hoaglin, 1981; Hoaglin *et al.*, 1986; Wurzer, 1988), where “outliers” are defined as those values that lie beyond the so called inner and outer “fences” (f and F), defined by the following equations:
 - Inner fences: $f_1 = Q_1 - k \cdot IQR$; $f_u = Q_3 + k \cdot IQR$, with $k = 1.5$
or simpler $f_1 = 2.5 Q_1 - 1.5 Q_3$; $f_u = 2.5 Q_3 - 1.5 Q_1$
 - Outer fences: $F_1 = Q_1 - k \cdot IQR$; $F_u = Q_3 + k \cdot IQR$, with $k = 3$

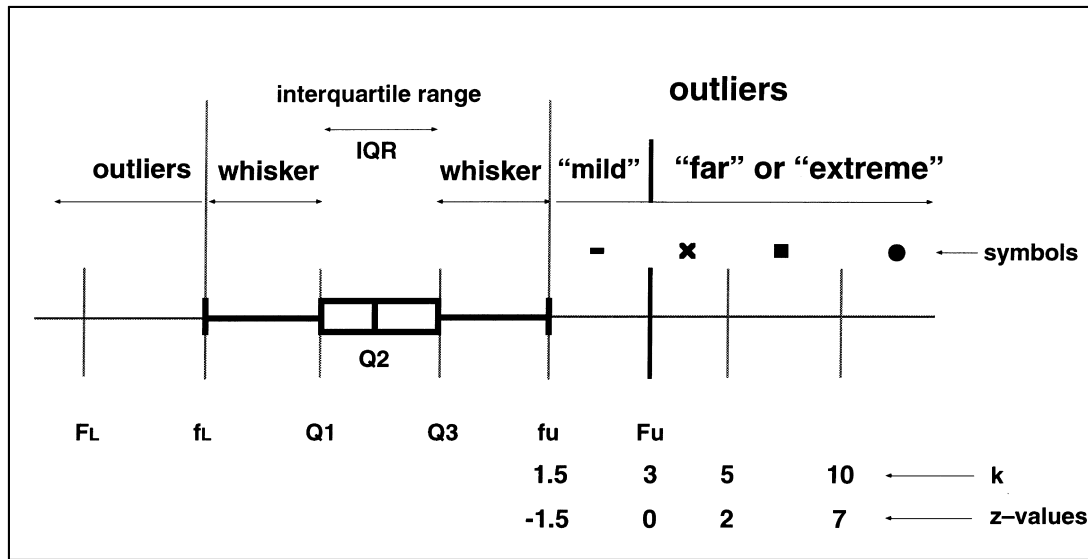


Fig. 5. Boxplot of an idealized population standardized to the anomaly threshold F_u and the spread measure IQR, showing the EDA symbols used for geochemical mapping. The numbers indicate the z values—algebraically calculated—of selected location measures of the standardized data. The k parameter indicates times of IQR.

or simpler $F_1 = 4 Q_1 - 3 Q_3$; $F_u = 4 Q_3 - 3 Q_1$

where Q_1 and Q_3 are the lower and upper quartiles of the data, equal to the 25th and 75th percentiles, and the interquartile range IQR is $Q_3 - Q_1$.

Data values between inner and outer fences are referred as to *mild* outliers while values that lie outside the outer fences are *far* or *extreme* outliers (Kotz and Johnson, 1985) (Fig. 5). The value used to multiply the hinge spread (IQR) to obtain the outlier cut-off is a somewhat arbitrary value between 1 and 3, although generally the constant 3 is adopted for outer fences. In our study, we are particularly interested in positive anomalies, therefore, we make use of the equations for F_u above.

Method (2) of data analysis has become an analytical tool of increasing utilization by geochemists because of the resistant and robust character of the location (median) and dispersion (interquartile range) estimates used in EDA statistics, in contrast to the common but non-robust data mean and standard deviation. Some references where EDA techniques are implemented in some part of the data analysis are: Garrett (1988), Kürzl (1988), Rock (1988), Chork and Mazzucchelli (1989) and Cook and Fletcher (1993).

The adequacy of these anomaly selection procedures with real data has been tested with the distribution of Zn in the rock groups classified in the previous section. The data used comprise all the

values obtained in the survey performed in the entire Bilbao Anticline (Fig. 1).

For the great majority of rock groups, the thresholds determined by both methods give approximately similar results, although several threshold levels are indicated in the normal probability plot method in limestones, marly limestones and quartz arenites, instead of obtaining a single cut-off as in the EDA procedure. It should be pointed out that because of the several possible thresholds delineated in Fig. 6a (horizontal lines), the lowest threshold is difficult to determine, becoming an arbitrary decision. Therefore, in these cases we decided to choose the threshold above the lower linear part of the distribution (which coincides with the background population), or at other times placed the threshold where a significant change of slope took place. However, the selection of cut-off values in curved patterns also poses a difficult task (Fig. 6c), and in consequence it could be aided by EDA thresholds.

Another problem may arise when dealing with populations dominated by a large number of anomalous samples. In our example, the majority of dolostones appear associated with Zn–Pb mineralization, even though we identify some dolostones with low base metal contents not related with ore occurrences. For dolostones, Zn and Pb anomaly thresholds were determined on the basis of a barren subpopulation and contrasting them with external values derived from the literature.

Although using methods (1) and (2) the estimated thresholds were similar for the majority of the sampled rock types, some discrepancies were found

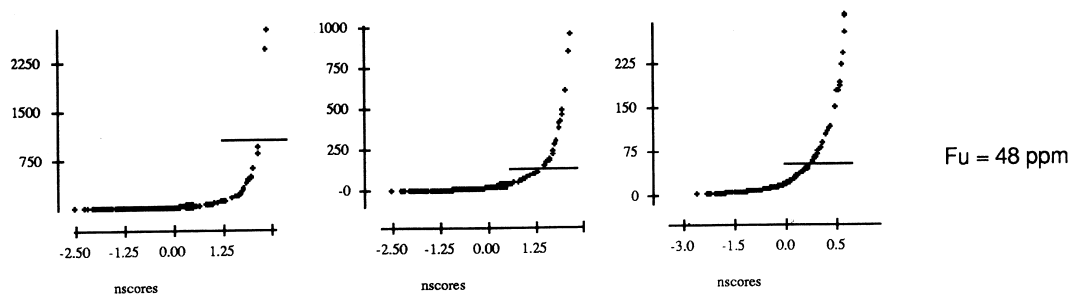
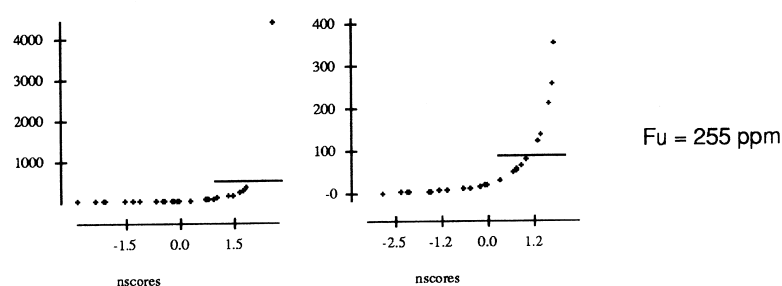
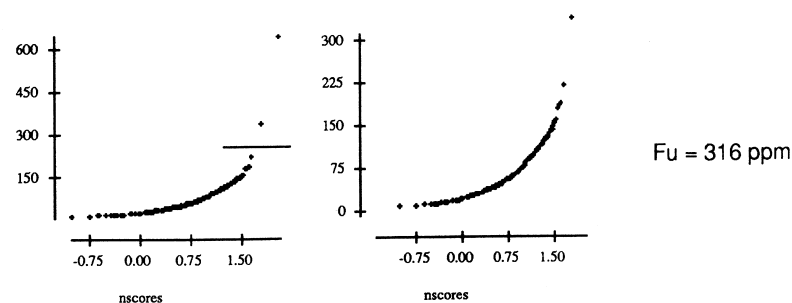
a. Zn in Limestones (n=436)**b. Zn in Quartz arenites (n=31)****c. Zn in Shales (n=195)**

Fig. 6. Normal probability plots for Zn in (a) limestones, (b) quartz arenites, and (c) shales from the Bilbao Anticline (northern Spain). Sequential plots for each rock type illustrate the process followed to select a background subpopulation (horizontal lines). Each series of plots displays the same population after resizing to observe the patterns in lower concentration ranges. Data for EDA thresholds for each population are also indicated. N scores are the normal scores.

in the cut-off level for quartz arenites (Fig. 6b) arkoses and graywackes (not shown), that recommended the use of both methods in conjunction.

The results of the EDA procedure applied to the investigation for the 15 established lithologies from the Bilbao Anticline, in the case of Zn and Pb, are presented in Table 3. Anomaly thresholds vary as a function of the rock type, the extreme (F_u) values for Zn being 48 ppm in limestones and 316 ppm in shales, and those for Pb being 15 ppm in limestones and 122 ppm in quartz arenites. Quartz arenites are a particular case where the sampled population is biased towards anomalous samples and the anomaly threshold is raised to 255 ppm Zn and 122 ppm Pb. In this latter case, the normal probability

plot approach gives lower cut-off values (100 and 50, respectively), and in consequence advises us on the necessity of using more than one single method for threshold selection.

As a result of the method comparison study, we conclude that good results were obtained by means of a combination of the EDA and normal probability plot approaches in the univariate space. We preferentially use the EDA's "rule of thumb" for anomaly threshold estimation because (i) it gives, in a simple way, cut-off values which can be used as reference when we use other methods in combination and (ii) standardization equations can be applied by the use of "robust" location parameters, as we will discuss in the next section.

METHOD OF STANDARDIZATION OF GEOCHEMICAL DATA

When geochemists deal with data sets of a multiple character, say (i) including different variables—major and trace elements—; (ii) lithochemical data or; (iii) integrating data for different sample media, and aim to represent all of them at the same time in a distribution map to infer new information about data, a suitable standardization method is required. The term standardization is used in the sense of any transformation that makes several different populations or variables comparable, avoiding the scale, rock and sampling media effects.

A classical method of standardization is as follows:

$$z_i = \left[\frac{x_i - \text{mean}}{s} \right], \quad (1)$$

where mean represents the arithmetic mean of data, and s the standard deviation. This method is not very useful in the context of geochemical exploration, because these parametric statistical estimators

are heavily influenced by the presence of outliers. For that reason, and in consistence with the anomaly selection method adopted—based on EDA—the choice of standardization methods which involve the use of the resistant EDA parameters is preferred. In this paper, we propose the utilization of the robust equivalent for the classical method as follows:

$$z_i = \left[\frac{x_i - Q_2}{\text{spread}} \right], \quad (2)$$

where Q_2 represents the median.

The measure of variability (spread) in the previous equation can be expressed as (i) the robust equivalent of the parametric s , that is $0.7413 \times \text{IQR}$; (ii) the halved distance between upper and lower hinges (which approximates $0.5 \times \text{IQR}$), usually utilized in EDA (Tukey, 1977); or (iii) IQR, as it is computed in this work. This standardization method is a good alternative for making populations comparable to each other when populations contaminated with anomalies are expected.

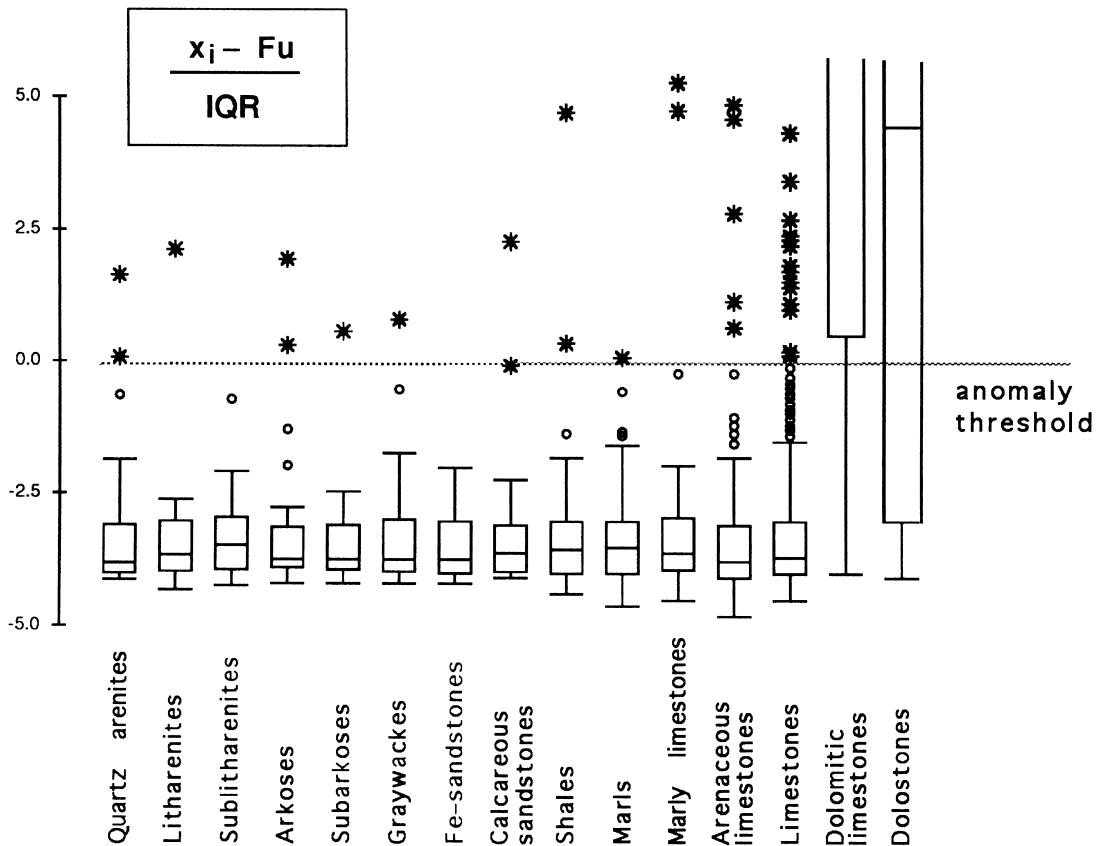


Fig. 7. Boxplot comparison of Zn standardized data (n = 1293) from different rock types of the Bilbao Anticline, after applying the indicated equation. Small circles = “mild” outliers, asterisks = “far” outliers. The plots in this figure do not represent all the range of standardized values, and as a consequence, some anomalies lie beyond the scale shown. Boxplot for Mg-rich rocks look peculiar because they were normalized to external values.

Alternative equations can be used as a function of the purpose of the study. For example, we may use the anomaly threshold in EDA, F_u , instead of the median. In these cases it is necessary to decide whether the central distribution (median) of data or its anomalous character (F_u) focuses our discussion. In this study we are particularly interested in the presence of anomalies, and for that reason, in the geochemical maps of the next section, the following standardization equation is used:

$$z_i = \left[\frac{x_i - F_u}{IQR} \right]. \quad (3)$$

Fig. 7 presents the boxplots for Zn in the sampled rock types after transformation to EDA parameters. Equations (2) and (3) permit an appropriate standardization of values because, excluding the outlying values, the range of variation of normalized Zn contents is approximately the same for all the rock types.

The proposed method allows the representation of data from different sampling media in the same plot in order to, for example, compare anomalies in rocks and soils, or identify alteration processes that

may affect different rocks in diverse manners. In addition, we can use the EDA-plotting symbols (Tukey and Tukey, 1981) for highlighting diverse ranges of standardized values on the geochemical maps. The cut-off values used to create the class intervals can be determined beforehand as a function of anomaly contrast, or other criteria. The combination of EDA-plotting symbols with the boxplot provides a basis for objective and automated class selection for geochemical mapping purposes (Kürzl, 1988; O'Connor and Reimann, 1993).

In the geochemical maps prepared for this study (Figs 8–10), the plotting symbols have been assigned according to the class intervals defined in the boxplot of Fig. 5. Besides the conventional anomaly thresholds of EDA (f_u and F_u), other class intervals have been defined arbitrarily, simply to assess different levels in the anomalous population. New class intervals adopted for z -values are set for convenience at 2 and 7 times the standardized population, facilitating automatic point selection in graphs and tables. Algebraically, it is shown that those figures correspond with k -values that exceed 5 times the interquartile range in the former case and 10 times in the latter.

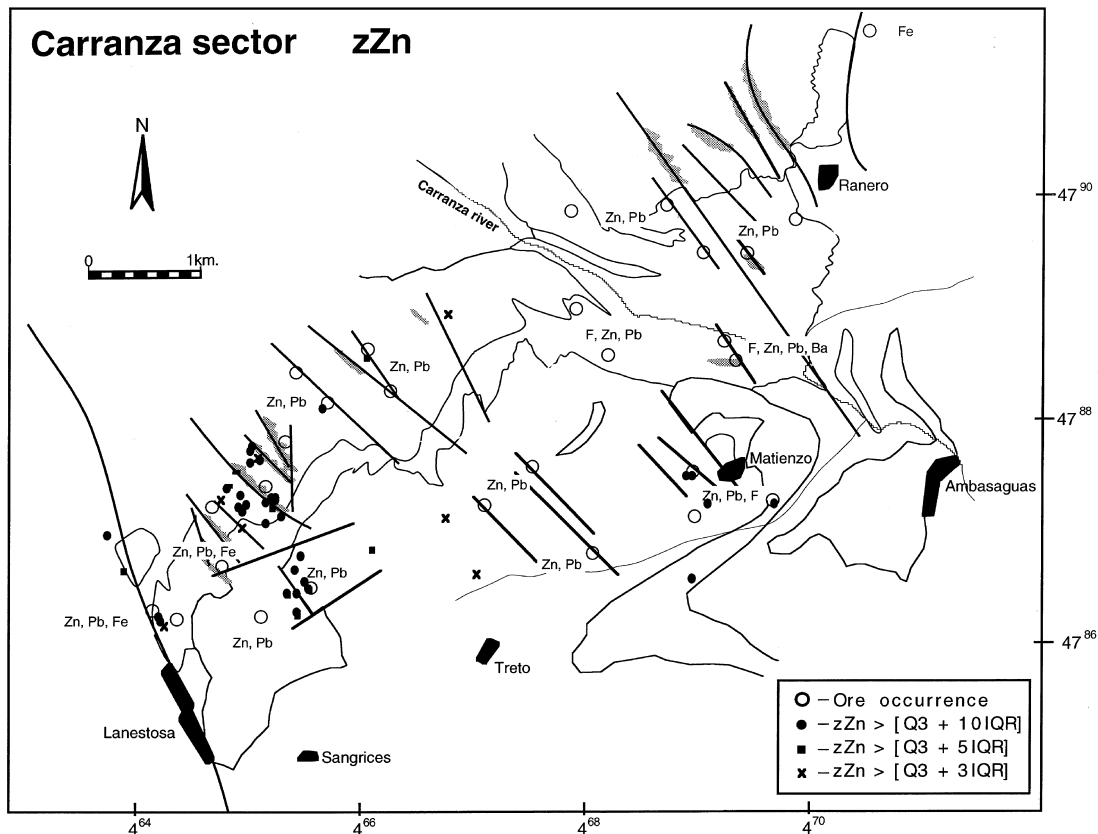


Fig. 8. Geochemical map of Zn standardized data in rocks from the Carranza sector, showing ore occurrences and outliers.

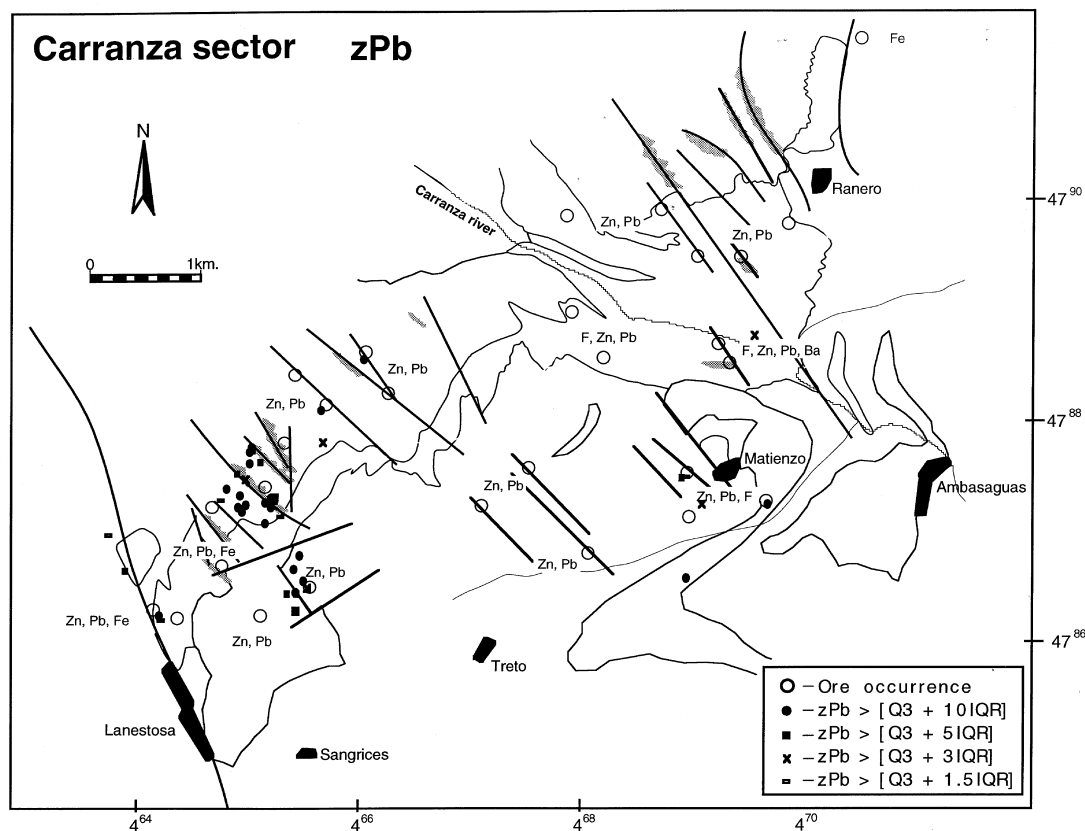


Fig. 9. Geochemical map of Pb standardized data in rocks from the Carranza sector, showing ore occurrences and outliers.

LITHOGEOCHEMICAL EXPLORATION IN THE CARRANZA SECTOR

The metallogenetic studies carried out in the Bilbao Anticline (Herrero, 1989; Velasco *et al.*, 1994) reveal the presence of ore occurrences in the 4 sectors sampled (Fig. 1). Uneconomic Zn–Pb and F deposits and Fe and Ba mineralizations of less importance have been identified in the Carranza, Arcentales and Aitzgorri sectors, whereas the Villaro sector may be regarded as a “barren” area for Zn–Pb. In this section we present the results of the study of the Carranza sector, which has been selected because of the presence of known Zn–Pb occurrences and associated dolomitization.

The determination of anomaly threshold parameters for Zn and Pb with EDA techniques in different rock types (Table 3) permits us to filter out the non-anomalous samples. In the analyzed rocks from the Carranza sector ($n = 330$), 49 samples stand out as Zn anomalous and 38 as Pb anomalous with z values beyond the positive outer fence F_u (Table 4 and 5). Some of these samples ($n = 32$) show anomalies both in Zn and Pb. The evaluation of the “mild” outliers (17 samples with Zn or Pb z -scores between -1.5 and 0) revealed the

following: (i) 6 of them had been already considered as Zn “far” outliers; (ii) two other samples (one marl and one quartz arenite) were worth being included as anomalies because of their geologic characteristics and also because they were selected by normal probability plots; and finally (iii) the remaining 9 samples were rejected because in a latter petrographic inspection, they did not show any differences from the background population.

The Zn and Pb anomalies are concentrated in magnesian carbonates. Whereas non-mineralized dolostones of the Bilbao Anticline have median values of 13 ppm Zn and 3 ppm Pb, the majority of Mg-rich samples of Carranza sector exceed the outer fence of 56 ppm Zn and 21 ppm Pb, with values up to 0.6% Zn and 1380 ppm Pb. Dolostones and dolomitic limestones (CL81 unit) represent diagenetic and epigenetic replacements of platform carbonates. Only a few samples, belonging to vein systems, result in barren Zn–Pb and have been considered as the background population.

About 11% of limestones and impure limestones (marly or arenaceous) are anomalous, with respect to their Zn– F_u outer fence; however, for the more argillaceous sediments (marls mainly) only 5% of their samples are classified as far outliers.

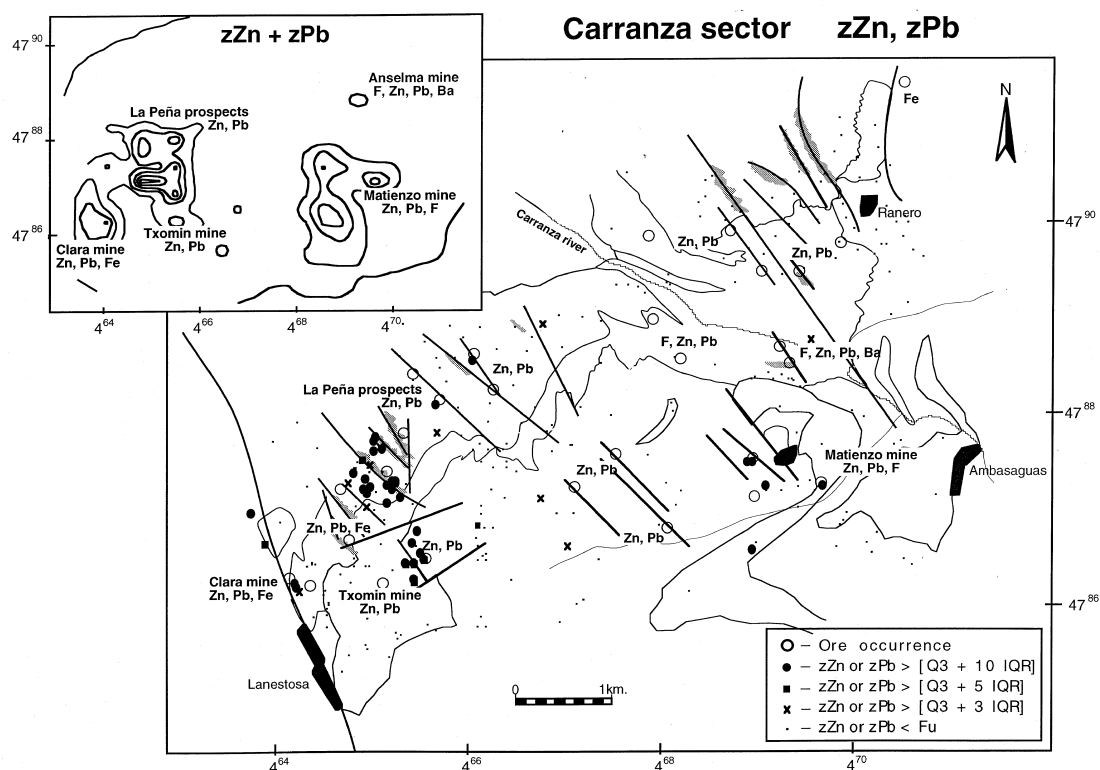


Fig. 10. $z\text{Zn}$ and $z\text{Pb}$ geochemical map based on standardized data from the Carranza sector. Upper inset shows a contour map for the combined term ($z\text{Zn} + z\text{Pb}$), with names of the major ore occurrences.

Regarding the lithostratigraphic and palaeogeographic arrangement of sediments in the Carranza sector (Figs 8 and 9, Table 5), all the sampled units were highly anomalous. Obviously, the dolomitic CL81 unit accounts for the highest percentage of anomalies, i.e. 65% of samples are far outliers for Zn and 52% for Pb. The other geological units

hold up a minimum of 9% of samples with Zn anomalies and 8% of samples with Pb anomalies. In spite of a first discarding of samples with macroscopic vestiges of mineralization, we have detected values up to 620 ppm Zn and 45 ppm Pb in the carbonate talus CL4 unit. The more argillaceous, more or less calcareous, Soba Fm. (unit CL7) displays up

Table 4. Contingency table of Zn and Pb anomalies in the rock types of the Carranza sector

	n	Zn anomalies					Pb anomalies				
		[1]	[2]	[3]	[4]	total	[1]	[2]	[3]	[4]	total
Quartz arenites	(23)	1	-	1	-	2	1	-	1	-	2
Litharenites	(2)	-	1	-	-	1	-	1	-	-	1
Sublitharenites	(7)	-	-	1	-	1	-	-	1	-	1
Subarkoses	(2)	-	-	-	1	1	-	-	1	-	1
Fe-sandstones	(1)										
Calcareous sandstones	(15)	-	1	-	-	1	-	2	-	-	2
Shales	(2)										
Marls	(37)	1	2	-	-	3	-	1	-	-	1
Marly limestones	(16)	-	2	-	-	2	-	2	-	-	2
Arenaceous limestones	(49)	1	4	2	-	7	1	3	-	-	4
Limestones	(145)	5	11	1	2	19	6	7	2	1	16
Dolomitic limestones	(7)	-	-	1	4	5	-	1	1	3	5
Dolostones	(24)	1	7	6	2	16	-	6	5	-	11
Total	(330)	9	28	12	9	58	8	23	11	4	46

n = number of samples analyzed.

Columns [1] to [4] show the number of anomalous samples for the standardizing ranges $[-1.5, 0)$, $[0, 2)$, $[2, 7)$ and $[7, \infty)$, therefore [2], [3] and [4] contain "far" outliers; whereas [1] "mild" outliers.

Table 5. Counts of anomalies in Zn and Pb for the lithostratigraphic units of the Carranza sector. See Table 4 legend for column headings

	n	Zn anomalies				total	Pb anomalies				total
		[1]	[2]	[3]	[4]		[1]	[2]	[3]	[4]	
CL2	(1)	–	–	–	–	–	–	–	–	–	–
CL4	(57)	1	6	1	–	8	1	4	–	–	5
CL6	(46)	–	2	1	1	4	–	3	1	–	4
CL7	(91)	2	5	3	–	10	1	5	1	–	7
CL8	(104)	5	8	–	2	15	6	4	3	1	14
CL81	(31)	1	7	7	6	21	–	7	6	3	16
Total	(330)	9	28	12	9	58	8	23	11	4	46

to 1200 ppm Zn and 250 ppm Pb. Some samples of the edge of the Albian carbonate platform (Calizas de Ramales Fm., CL8 unit) show anomalous Zn contents of up to 2500 ppm and 480 ppm Pb.

In some instances, high Zn values in sandstones of CL6 arenaceous sediments (with up to 0.15% Zn and up to 367 ppm Pb) are consistent with optical microscopic observations, indicating the presence of some sphalerite microcrystals concentrated in stylolitic surfaces. This sandstone unit represents channel filling over eroded talus and basinal sediments.

These results can be visualized in geochemical maps, such as those depicted in Figs 8–10, for the z values of Zn and Pb, and the combined term $z\text{Zn} + z\text{Pb}$ respectively. The maps clearly outline the location of anomalies with respect to ore occurrence sites and geologic emplacement of lithostratigraphic units. Nearly all anomalies lie in places where known old mines and ore occurrences appear. In some examples there is a fault control of the anomaly distribution. Such alpine-reactivated N120° normal faults represent pathways for ore forming fluids, with diagenetic and or epigenetic replacement of carbonates. The Zn and Pb standardized values (and their representation in geochemical contour maps, see upper inset in Fig. 10), emphasize the concentration of anomalies in mineralized areas, such as Matienzo and La Peña-Txomin mines, where carbonate hosted Zn–Pb ore deposits have been described (Herrero and Velasco, 1988, 1989).

CONCLUSIONS

Lithogeochemical data from the Bilbao Anticline were classified into 15 rock groups mainly on the basis of chemistry and taking into account the mineralogical and petrographical data in order to obtain appropriate homogeneous (with respect to principal oxides) rock-groups during the evaluation of the data.

After the evaluation of theoretical and real data, the use of Exploratory Data Analysis (EDA) in combination with normal probability plots were determined as the best indicators of the outliers and anomaly thresholds. EDA statistics provide useful

procedures for the recognition of anomalies in univariate geochemical space for populations subjected to an *a priori* classification. In this study, the anomaly threshold for each element and rock type was determined by means of these approaches. For lithogeochemical mapping purposes we propose a normalization method that uses EDA parameters and gives particular attention to the anomalous character of the element contents of the samples. The result of the normalization method is the integrated representation of multiple population and multielement data in geochemical maps.

The statistics and data analysis techniques discussed in this paper have been successfully applied to a lithogeochemical survey in the western part of the Vizcaya region (Carranza sector) in order to interpret the Zn and Pb distributions on the basis of known Zn–Pb Mississippi-Valley type deposits.

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