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A detailed stream sediment Geochemical survey in the Canoves St. Pere de Vilamajor area (Montseny massif. NE Spain)

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RESUMEN

Se ha realizado una prospección geoquímica táctica de sedimentos aluviales en el área de Cánoves-St. Pere de Vilamajor (Macizo del Montseny, Barcelona), como consecuencia de una exploración geoquímica estratégica de sedimentos aluviales previa, en la que se localizó un área anómala en Pb, Zn, Cu, As, Cd, Ni, y Co. El área estudiada tiene 35 km^2 y está constituida por materiales sedimentarios y volcánicos del Paleozoico, metamorfizados en mayor o menor grado e intruidos por el granito de Vallfornés, y materiales detríticos terciarios. Las muestras, recogidas con una densidad de 7 por Km^2, fueron analizadas mediante espectrofotometría de absorción atómica para el Pb, Zn, Cu, Ni, Co, As, Cd y Ag, con análisis adicionales para el Sn y W con fluorescencia de rayos X. La interpretación estadística de los resultados mediante técnicas univariables y multivariables permitió localizar y delimitar los sectores más anómalos. Posteriores reconocimientos geológicos de detalle permitieron descubrir un nuevo tipo de mineralización estratiforme relacionado con los niveles volcano-sedimentarios del Ordovícico superior hasta el momento desconocido en las Cadenas Costero Catalanas, así como sus removilizaciones debido al emplazamiento del granito de Vallfornés, que originaron mineralizaciones de tipo skarn y filonianas.

Palabras clave: Prospección geoquímica táctica. Muestreo de sedimentos aluviales. Areas anómalas. Minéralización estratiforme.

ABSTRACT

A detailed stream sediment geochemical survey has been undertaken in the Cànoves-St. Pere de Vilamajor area (Montseny Massif, Barcelona province) as a consequence of a previous reconnaisance stream sediment geochemical survey which located an area of anomalous Pb, Zn, Cu, As, Cd, Ni and Co. The area under study is 35 km^2 and consists of Palaeozoic and Tertiary sedimentary. Samples collected at a density of seven per square kilometer were analysed by atomic absorption spectrophotometry for Pb, Zn, Cu, Ni, Co, As, Cd and Ag with some additional analyses of results by univariate and multivariate techniques lead to isolation and limitation of the anomalous areas. Subsequent investigation discovered a new occurrence of stratiform mineralisation of Upper Ordovician age.

Key words: Detailed survey. Stream sediment sampling. Anomalous area. Stratiform mineralisation.

INTRODUCTION

A regional stream sediment survey was carried out in 1982 in the Montseny Massif by the Departament de Prospecció Geològica i Geofísica of the University of Barcelona in collaboration with the Servei Geològic de Catalunya. One conclusion of these studies, using single element analyses, was the location of an area, 60 km^2 in size, on the south-western margin of the Massif, containing anomalous values of Pb, Zn and Cu. In addition, multivariate analysis illustrated the distribution of the anomalies and showed them to be concentrated in the area between La Garriga and St. Pere de Vilamajor (Font, 1983). Within this area, the Cànoves-St. Pere de Vilamajor sector has the highest concentration of anomalies with some samples containing over 1.500 ppm Pb and 2.000 ppm Zn. These high values and the high density of anomalies are the reason for the present study which consisted of a detailed stream sediment survey covering an area of 35 km^2. Previously recognised mineralisation was related to quartz and barite veins with associated galena and chalcopyrite (Mata, 1981).

The following methods were employed during the survey:

1. Reconnaissance of previously recognised areas of mineralisation and mining with geological mapping at 1:10.000 scale (Carmona and Baro, 1983).
2. A detailed stream sediment survey.
3. Reconnaissance of anomalous areas discovered in the previous stream sediment survey.

This resulted in the identification of a new zone of mineralisation. Subsequent geological studies enabled this new stratiform mineralisation to be placed within the context of the surrounding Palaeozoic strata.

DESCRIPTION OF THE STUDY AREA

The study area is situated 50 km from Barcelona (fig. 1) in the Southwestern part of the Montseny Massif. This is an antiform of Palaeozoic sediments and volcanics, with a northeastern axial trend. It is cored by an intrusion of granodioritic to granitic-monzonitic composition and lies adjacent to the Tertiary tectonic graben of Vallés. The Palaeozoic lithologies of the area can be divided into four units (Alcalde, 1984):

1. A «Lower» Unit, of Cambro-Ordovician age lying to the north equivalent to the Jujols Formation in the Pyrenées. This unit is composed of a detrital series of banded schists, which in places have small intercalated sandstone layers.
2. A «Lower-Middle» Unit, of Upper Ordovician age, including Caradoc sericite schists, black shales and tuffaceous sandstones, and Ashgillian carbonate, skarn and andesite rocks.
3. A «Upper-Middle» Unit the lower part of which consists of Silurian black shales and cherts overlain by limestones and highly fossiliferous carbonate schists of possible Devonian (Emsian - Eiffelian) age.
4. An «Upper» Unit, of Carboniferous age resting unconformably on the previous unit, and consisting of cherts and siliceous shales overlain, also uncorfomably, by a thick sequence of shales, greywackes and conglomerates.

All these units, but particularly those of Cambrian and Upper Ordovician age, have been affected by regional low-to very low-grade metamorphic event. The subsequent intrusion of the Vallfornés granite body induced contact metamorphism of medium grade (Alcal-

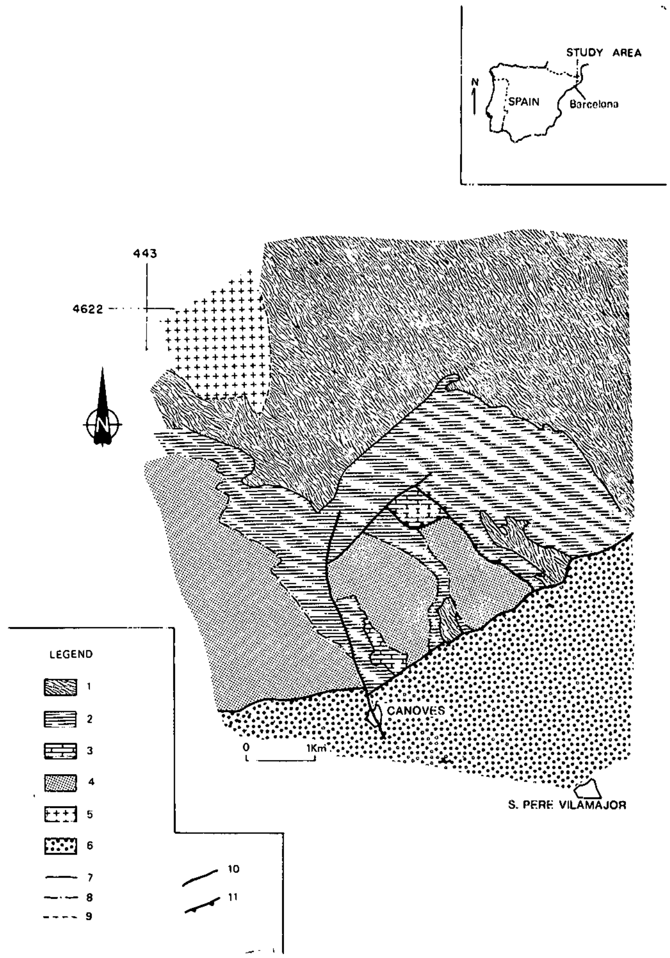

Figure 1.- Simplified geological map of the Cànoves -St. Pere de Vilamajor area (modified after Carmona and Baro, 1983). Legend: 1. Lower unit: banded schists; 2. Middle -Lower unit: black shales, tuffaceous sandstones, andesites and carbonate rocks; 3. Middle - Upper unit: black shales and carbonate rocks; 4. Upper unit: lidite, limestones, sliceous shales, greywackes and conglomerates; 5. Vallfornés granite; 6. Miocene conglomerates and lutites; 7. Concordant contact; 8. Unconformity; 9. Intrusive conctact; 10. Fault; 11. Overthurust.

Figura 1.- Mapa geológico simplificado del área de Cànoves - St. Pere de Vilamajor (modificado de Carmona y Baro, 1983). Leyenda: 1. Unidad inferior: esquistos bandeados; 2. Unidad intermedia inferior: pizarras negras, areniscas tobáceas, andesitas y rocas carbonáticas; 3. Unidad intermedia superior: pizarras negras y rocas carbonáticas; 4. Unidad superior: liditas, calizas, pizarras silíceas, grauvacas y conglomerados; 5. Granodiorita de Vallfornés: 6. Lutitas y conglomerados del Mioceno; 7. Contacto concordante; 8. Contacto discordante; 9. Contacto intrusivo; 10. Falla; 11. Cabalgamiento.

de, 1984 and Alcalde and Viladevall, 1984) which is surimposed on the older cleavages and metamorphic assemblages. Three main polyphase deformations of Hercynian age have also been recognised, each generating a cleavage or schistosity. Further phases are indicated by the local development of kink-bands (Viladevall, 1975).

SAMPLING, ANALYTICAL TECHNIQUES AND DATA PROCESSING

One hundred seventeen samples were collected in the study area during the regional survey (Font 1983). In addition, 121 new stream sediments were taken during the detailed geochemical survey, mainly at the headwaters of rapidly flowing streams and for completing the previous sampling grid to generate greater homogeneity in the study area. Fine sediments has been collected where possible and organic material avoided. The samples were dried and then dried-sieved in the laboratory with the minus 180 μ (80 mesh) material retained. All samples were then analysed by atomic absorption for Pb, Zn, Cu, Ni, Co, Cd, As and Ag using a Perkin-Elmer unit. Some additional X-ray fluorescence analyses were undertaken to determine Sn and W contents. These particular elements were chosen because they most clearly illustrate the anomalies brought to light by the previous regional survey (Font, 1983 and Font *et al.,* 1984).

TABLE 1.- Main statistical parameters of the elements analysed.

TABLA 1.- Principales parámetros estadísticos de los elementos analizados.

Elements	X	S	Min.	Max.
Pb (ppm)	255.25	200.15	14.00	1550.00
Zn	709.14	541.11	10.00	2350.00
Cu	47.68	31.39	4.00	243.00
Ni	40.73	24.57	0.00	214.00
Co	22.89	10.02	2.00	75.00
Cd	6.18	5.20	0.10	36.00
Ag	1.00	0.60	0.10	4.00
As	24.33	18.58	0.0	192.00

X = mean; S = Standar deviation; Min. = Minimum value;

Max. = Maximum value.

Statistical analysis to identify anomalous populations was acomplished using multivariate and univariate analysis techniques based on work carried out by Lepeltier (1969). The background and threshold values used are those determined by the previous study as the values calculated in the detailed survey are too high to be useful (Table 1) due to the anomalous nature of the study area. The multivariate technique chosen for this study was Principal Component Analysis. This technique attempts to explain several elemental variations simultaneously in terms of the smallest number of non —correlated groups, called components of those variables. Each component may then be related to a geological or geochemical influence, and the factor scores for all the samples, and their spatial distributions can then be calculated to provide information concerning the recognition of the relevant environmental conditions.

ANALYTICAL RESULTS

Univariate analysis

The anomalous distributions have been graphically represented by means of geochemical prospecting maps, in figures 2 to 5. The entire area studied shows anomalies in Zn with several values over 2.000 ppm (fig. 3). In addition there are higher but more dispersed Pb anomalies up to 1.500 ppm (fig. 2). The univariate analyses enabled the identification of four areas within the study sector, which are particularly anomalous (Table 2).

TABLE 2.- Location of areas of anomaly by univariate analysis.

TABLA 2.- Localización de las áreas anómalas detectadas mediante análisis univariable.

LOCATION OF ANOMALY	ANOMALOUS ELEMENTS
EL VILAR	Cu, Cd, As
SANT SALVADOR	Cu, Cd, Ni
CAN RIU	Cu, Cd, Ni, Co, As, Ag
CAN CORTES	Cu, Cd, Ag

TABLE 3.- Eigen values and proportions.

TABLA 3.- Valores propios y varianza explicada por los diferentes componentes principales.

Component Number	Eigen values	Variance	Cumulated Variance
1	3.35	41.83	41.83
2	1.33	16.62	58.45
3	0.90	11.22	69.67
4	0.78	9.70	79.36
5	0.53	6.57	85.94
6	0.47	5.89	91.93
7	0.38	4.76	96.59
8	0.27	3.41	100.00

TABLE 4.- Principal Component Analysis of the data.

TABLA 4.- Análisis de Componentes Principalès de los resultados geoquímicos.

Variables	Components							
	1	2	3	4	5	6	7	8
Pb	0.30	-0.41	0.56	0.06	-0.40	-0.30	0.32	0.26
Zn	0.40	-0.35	-0.08	-0.25	-0.13	-0.18	-0.72	-0.29
Cu	0.34	0.55	0.01	-0.18	-0.17	-0.34	0.32	-0.55
Ni	0.40	0.31	-0.43	-0.20	-0.14	-0.11	-0.04	0.70
Co	0.42	-0.08	-0.14	0.21	-0.34	0.77	0.15	-0.17
Cd	0.36	-0.37	-0.14	-0.33	0.67	0.04	0.40	-0.05
Ag	0.33	0.03	-0.12	0.84	0.30	-0.28	-0.09	-0.02
As	0.26	0.41	0.66	-0.08	0.35	0.29	-0.29	0.15

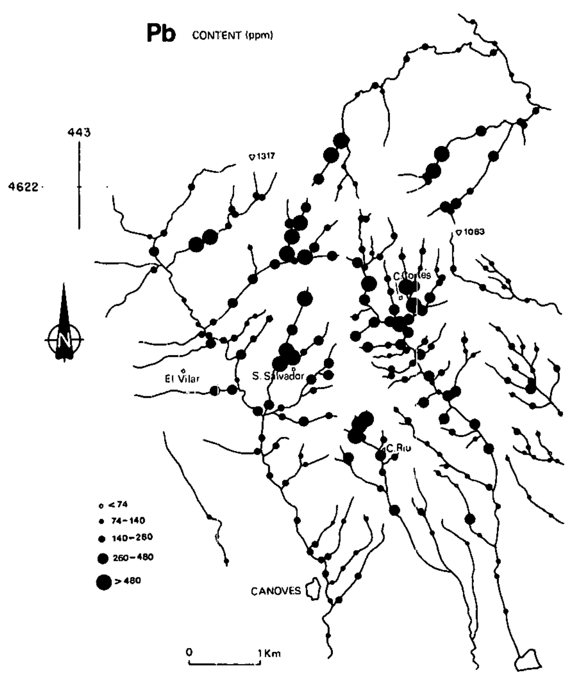

Figure 2.- Pb distribution in stream sediments of the Cànoves - Sr. Pere de Vilamajor area.

Figura 2.- Distribución de los contenidos de Zn en los sedimentos aluviales del área de Cànoves - St. Pere de Vilamajor.

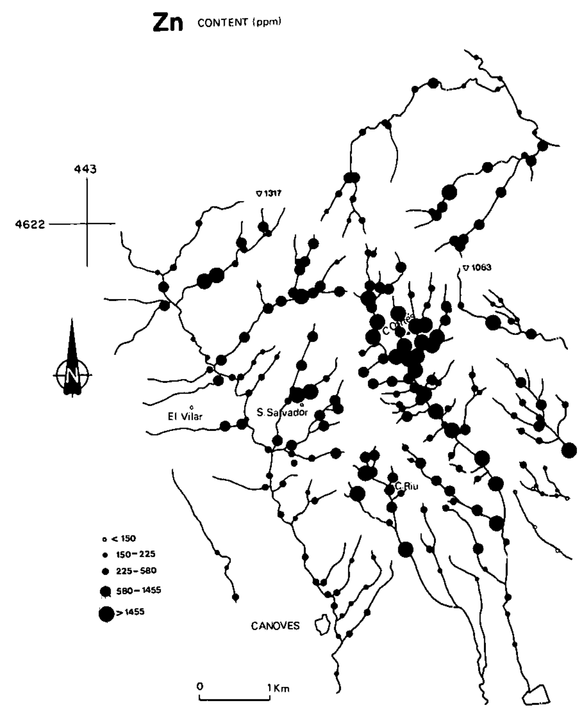

Figure 3.- Distribution in stream sediments of the Cànoves - St. Pere de Vilamajor area.

Figura 3.- Distribución de los contenidos de Zn en los sedimentos aluviales del área de Cànoves - St. Pere de Vilamajor.

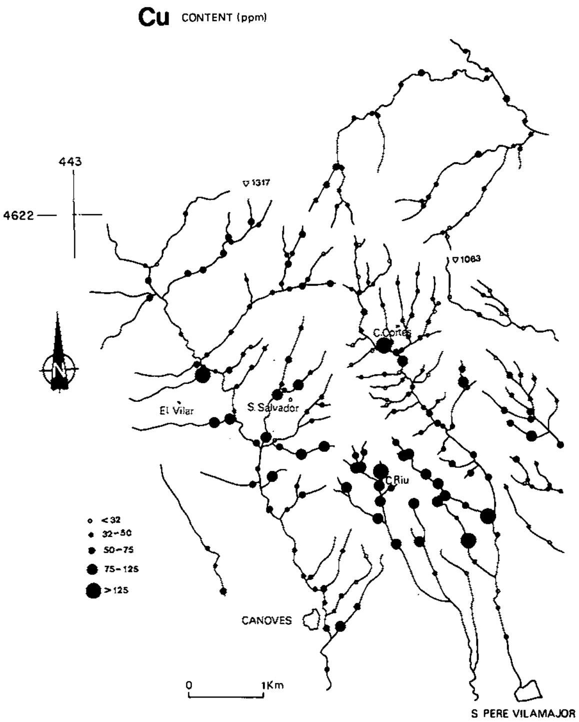

Figure 4.- Cu distribution in stream sediments of the Cànoves - St. Pere de Vilamajor area.

Figura 4.- Distribución de los contenidos de Cu en los sedimentos aluviales del área de Cànoves - St. Pere de Vilamajor.

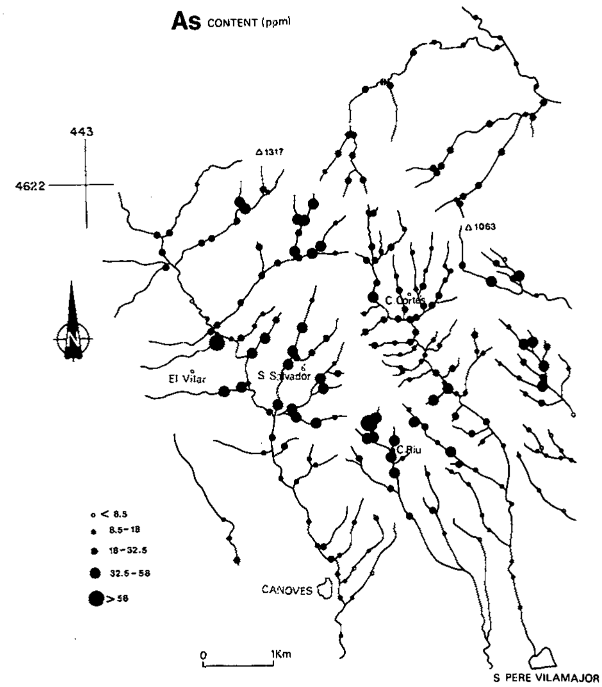

Figure 5.- As distribution in stream sediments of the Cànoves - St. Pere de Vilamajor area.

Figura 5.- Distribución de los contenidos de As en los ediemntos aluviales del área de Cànoves - St. Pere de Vilamajor.

Other anomalous zones are characterised by significant Cu and As values. These elements display the same behavioural relationships shown by the distribution maps (figs. 4 and 5) which illustrate their verlapping anomalous distributions. It is important to note the high Sn and W contents of some samples, several of which have over 450 ppm and in one case, over 3.000 ppm Sn.

Multivariate analysis

Multivariate analysis shows the existence of only two significant components from the eight initially produced (Table 3). These new components account for most of the data variability (about 60%) and have eigen values above unity. Table 4 shows the factor loadings of these components, and several important features:

a) Component 1, which is an indicator of mineralisation, shows a positive relationship between Co, Zn, Ni, Cd, Cu, Ag and Pb, with component loadings greater than 0.3.

b) Component 2 is of greater interest, as it enables discrimination between anomalies with different causes and shows two metal associations which account for 16.2% of the data variability. These are the Cu-As-Ni association (positive loadings of 0.55, 0.41 and 0.31 respectively) and the Pb-Zn-Cd association (negative loadings of 0.41, 0.35 and 0.37 respectively).

c) Component 3 has not been represented in map form as it is of lesser significance but indicates a Pb-As association with positive component loadings and a Ni component with negative loading of 0.43.

d) Component 4 appears as a single component, Ag, with a component loading of 0.84.

The spatial distribution of the factor scores for Component 1 are represented in figure 6. The highest positive factor scores, although somewhat dispersed, clearly define distinct areas: El Vilar, St. Salvador de Terrades, Can Riu and Can Cortés. These coincide with anomalous areas shown by the univariate analysis. It is con-

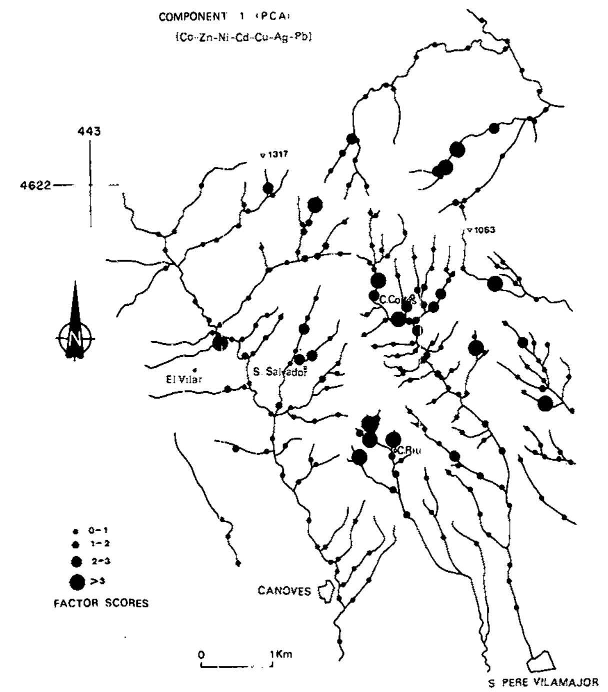

Figure 6.- Distribution of scores on component 1.

Figura 6.- Distribución de las «cargas componenciales» del componente 1.

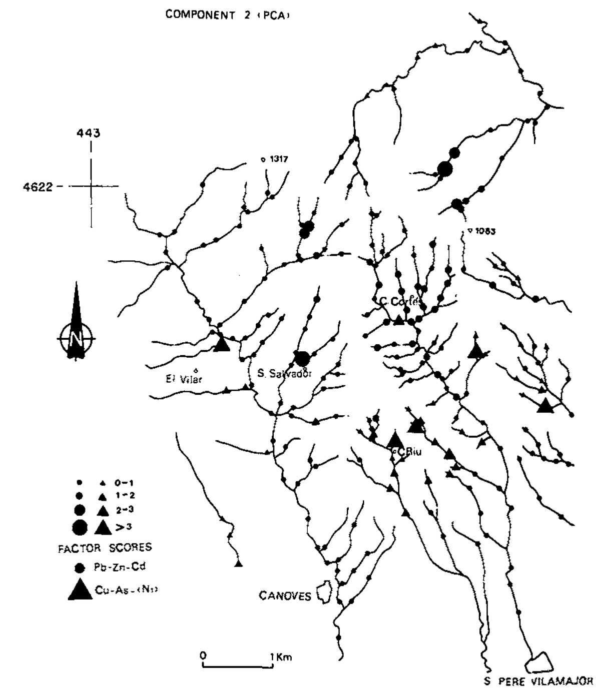

Figure 7.- Distribution of scores on component 2.

Figura 7.- Distribución de las «cargas componenciales» del componente 2.

cluded that the factor scores have been affected by the high contents of all the analysed elements. The spatial distribution for Component 2 factor scores is shown in figure 7 and can be used to define a zonation between the Pb, Zn, Cd metal association restricted to the central and northern parts of the study area, and the Cu-As-Ni association occurring in a belt to the south of the previous zone (fig. 8). The principal areas of anomaly for Component 2 coincide with those of Component 1, and can be divided into several areas (Table 5).

TABLE 5.- Location of areas of anomaly by multivariate analysis.

TABLA 5.- Localización de las áreas anómalas detectadas mediante análisis multivariable.

LOCATION OF ANOMALY	ANOMALOUS ELEMENTS
EL VILAR	Cu - As - Ni.
SANT SALVADOR DE TERRADES	Pb - Zn - Cd.
CAN RIU	Cu - As - Ni.
CAN RIU (AT STREAM HEADWATERS)	Pb - Zn - Cd.
CAN CORTES	Pb - Zn - Cd.

SUBSEQUENT GEOLOGICAL SURVEY AND DISCUSSION

The detailed sediment geochemical survey enabled the isolation and delineation of the anomalous sectors found in the previous regional campaign. A follow-up study was then carried out to examine oxidised zones in the drainage area of the anomalous samples. This lead to the location of a new zone of stratiform mineralisation related to the «Lower-Middle» Unit o fUpper Ordovician age in the Can Cortés, Can Riu, El Vilar and Sant Salvador areas, and identified a new mineralised vein network extensively distributed throughout the area (see figure 7).

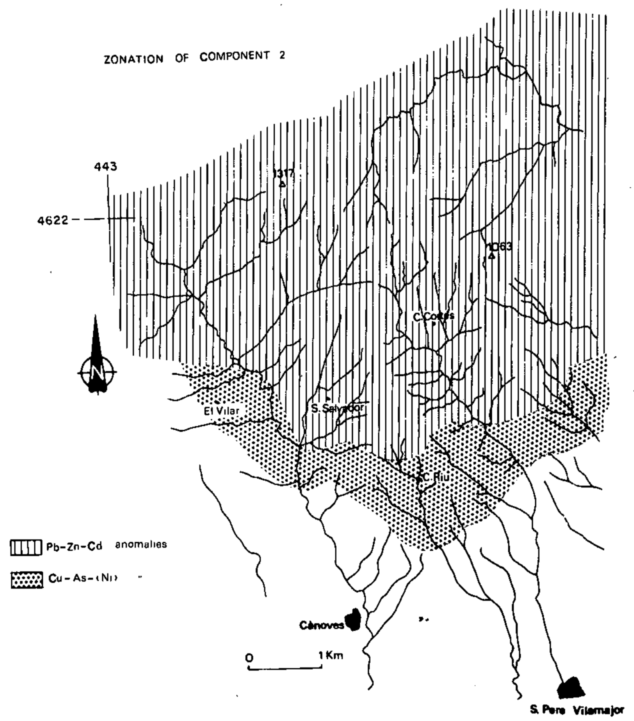

Figure 8.- Zonation betwen the two metal associations of component 2.

Figura 8.- Zonación de las dos asociaciones metálicas deducidas del componente 2.

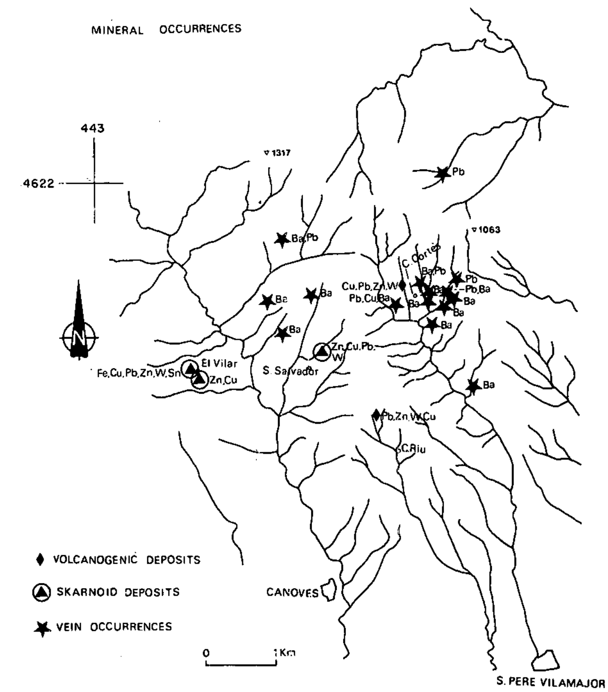

Figure 9.- Mineral occurrences in Cànoves - St. Pere de Vilamajor area.

Figura 9.- Principales mineralizaciones e indicios mineros del área de Cànoves - St. Pere de Vilamajor.

These are summarised below:

1. Disseminated suphides occurring within the Caradoc tuffaceous sandstones. These outcrop in the Can Riu and Can Cortés areas and consists of pyrite, pyrrhotite, galena, sphalerite, chalcopyrite and scheelite and seem to be related to interbedding with black shales.

2. Skarnoid deposits (sensus Zharikov, 1970) related to Upper Ordovician carbonates. These occur in the El Vilar and Sant Salvador areas, there are lenticular bodies consisting of pyrite, pyrrhotite, galena, sphalerite, chalcopyrite and scheelite.

3. Vein deposits composed of barite with galena and occasional chalcopyrite.

The dissymmetry between the two metal associations of Component 2 can be explained by their different sources: the Pb-Zn-Cd anomalies are caused by stratiform mineraliation rich in sphalerite and galena, whereas, the Cu-As-Ni anomalies are related to black shales in the Upper Ordovician «Lower-Middle» Unit. These shales are located in a east-west belt crossing the whole study area. Spectroscopic analysis has indicated that they are rich in Cu, As, Ni, V, Cr and Mo (Alcalde, 1984).

The high metal contents, especially Zn, in the streams sediments could be attributed to the orientation of the mineralised layers parallel to the streams wich would produce wide meteorization surfaces and high leaching rates with a consequent higher metal content.

The highest Sn levels were found in the samples collected in areas with skarn-related mineralisations. These deposits consist of epidote, grossularite-andradite and other silicates, which according to several authors (Dadak and Novak, 1965; McIver and Mihalik, 1975; Mulligan and Jambor, 1967) may have high Sn contents included within their lattice structure. There are also high Sn values in the stream samples collected from the Can Cortés area related to tuffaceous sandstones.

CONCLUSIONS

It has been possible by means of statistical multielement analysis of geochemical data and a subsequent follow-up survey to isolate and limit the anomalous areas found in a previous regional geochemical survey. Statistical screening of different elements for different sources has enabled the identificaton and subsequent discovery of a new set of statiform and vein deposits. The elemental distribution patterns shown by the univariate analysis, and the additonal use of Principal Component Analysis, has led to a notable simplification of the data, as it was possible to identify the metal associations of the dominant features. The most significant results of this study can be summarised as follows:

A) Identification of a Pb-Zn-Cd metal association related to Upper Ordovician volcano-sedimentary and skarn deposits, composed of pyrite, pyrrhotite, chalcopyrite, galena, sphalerite and scheelite.

B) Identification of a Cu-As-Ni association related to the Upper Ordovician black shales of the «Lower-Middle» Unit.

C) Identification of a zonation between these two associations, with the Pb-Zn-Cd anomalies related to sericitic shales and tuffaceous sandstones in the northern and central part of the area, and the Cu-As-Ni anomalies related to the black shales and carbonate rocks in the southern part.

D) Additional causes of geochemical anomalies were established as originating from vein mineralisation containing barite, galena and chalcopyrite.

E) High levels of W were identified as being related to the presence of scheelite in volcano-sedimentary and skarn deposits.

F) The anomalous Sn levels in the skarn deposits are thought to be related to the presence of epidote and garnet. The increased Sn levels in the volcano-sedimentary deposits are at present unidentified but are thought to reflect the occurrence of cassiterite (Viladevall, et al., 1984).

Finally, it is concluded that the area studied may be of great metallogenetic interest and could have considerable economic potential particularly for Cu, Sn and W.

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