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An assessment of the use of a cold-extraction technique in geochemical exploration in North - East Algeria

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Abstract: Under arid or semi-arid climatic conditions, mechanical weathering predominates over chemical weathering. In this study, conducted in semi-arid climatic conditions in northeastern Algeria, a cold-extraction technique was used to analyse those chemical elements weakly bonded onto minerals surface, and considered to have been released during chemical weathering. The results were compared with those of total analysis and both data sets were used to assess the effectiveness of stream sediment samples in delineating known mineralisation and bedrock types. Dispersion trains of 1000-1300 m were found to occur, essentially in ephemeral streams, whereas background values were found in water-bearing rivers. Known lead, zinc and copper-bearing veins as well as the chromite-bearing serpentinites were well delineated by both analytical techniques, however, the iron mineralisation could only be confirmed by the total analysis. In addition, new sulphide anomalies were outlined by both analytical techniques. It is suggested that the cold-extraction technique used may offer an acceptable and cheaper alternative to the total analysis for outlining serpentinites (cxCo and cxNi) and base-metal mineralisation (cxCu, cxPb and cxZn).

Key words: Geochemical survey - Stream sediments - Semi-arid climate - Total analysis - Cold-extraction analysis - Metal dispersion.

Evaluation d'une technique d'analyse chimique partielle en prospection géochimique au Nord-Est de l'Algérie

Résumé: Sous climat aride ou semi-aride, l'érosion mécanique domine sur l'altération chimique. Dans cette étude entreprise dans un climat semi-aride au NE de l'Algérie, une technique d'analyse partielle a été utilisée pour analyser les éléments chimiques faiblement liés à la surface des minéraux et considérés comme résultant de l'altération chimique. Ces résultats sont comparés avec ceux de l'analyse chimique totale et les deux types de données sont utilisés pour examiner le succès relatif d'échantillons d'alluvions quant à la détection de la minéralisation connue et les types de bedrock. Des anomalies ayant 1000-1300 m de longueur ont été notées essentiellement dans des ruisseaux, tandis que des valeurs du background ont été notées dans les rivières. Les veines minéralisées en Pb, Zn et Cu ainsi que les serpentinites ont été bien décrites par les deux types d'analyse, mais la minéralisation ferrifère a été seulement détectée par la méthode d'analyse totale. En outre, de nouvelles anomalies de sulfures ont été décrites par les deux méthodes d'analyse. Il est suggéré que la technique de dosage partiel utilisée peut réduire les coûts d'analyse en comparaison avec la technique d'analyse totale pour la détection des serpentinites (cxCo et cxNi) et les minéralisations à métaux de base (cxCu, cxPb et cxZn).

Mots clés: Prospection géochimique - « sédiments de ruisseaux» - Climat semi-aride - Analyse chimique totale - Analyse chimique partielle - Dispersion des métaux.

I - INTRODUCTION

The release of ore metals and associated elements by natural solutions during weathering, results in their hydromorphic transfer in stream sediments and soils. These elements are redeposited in a variety of reaction sites including iron and manganese oxides, oxides of aluminium and silica, organic matter, carbonates and secondary oxides (Chao, 1984). However, the lack of atmospheric precipitation in semi-arid and arid zones results in poor chemical weathering with the mechanical weathering predominating. In addition, prospecting under semi-arid or arid climatic conditions is subject to additional problems which may be summarised as follows (Zeegers *et al.*, 1985; Bugrov, 1988): dilution by eolian material (quartz and carbonates); lack of well developed soil profiles; dominance of evaporation over precipitation often leading to the «artificial» accumulation of certain elements; duricrust; and the nature of the watercourses and the sharp variations in their power during periods of rainfall, often leading to the development of mechanical barriers where minerals of a high specific gravity can accumulate leading to false anomalies.

It is well known that partial extraction techniques may increase the geochemical contrast between background and anomalous samples and thus enhance the dispersion, i.e. the distance downstream of the deposit at which the mineralisation may be detected, (e.g. Chao, 1984; Martin *et al.*, 1984; Cardoso Fonseca and Martin, 1986; Church *et al.*, 1987; Bolle *et al.*, 1988). However, almost all studies of this type have been conducted in temperate and glaciated parts of the world. A reason for this is the intense chemical reactivity of these environments which make these techniques very suitable. A review of the literature showed that the use of partial extraction techniques have had very limited application in semi-arid and arid terrains. An investigation by Bugrov (1974) in the Eastern Desert of Egypt came to an important result in that he found that cold extractable copper gives higher contrast values and longer dispersion trains relative to total analysis. In this study, a cold-extraction analytical method was used in order to analyse those chemical elements, released during chemical weathering, found in labile form and weakly bonded onto the coatings of minerals such as those adsorbed onto clay minerals, Fe-Mn-oxides and organic matter. The analytical method used is non-selective (Chao, 1984) as it is not concerned with specific «reaction sites». Relative to the total analysis, cold-extraction results have been shown to enhance the dispersion train of some elements and to give higher anomaly-background contrast values (Rose *et al.*, 1979).

The results presented in this paper are taken from a regional stream sediment survey in the Collo area (N.E. Algeria). A comparison between the data sets obtained from total analysis and cold-extraction analysis of more than 280 stream sediment samples is presented.

II - GEOLOGICAL BACKGROUND AND MINERALISATION

The Collo area lies in north-east Algeria, on the 6th eastern meridian. It is characterised by a rugged topography with the altitude ranging from sea level up to 1137 m. Vegetation cover is thick, consisting mainly of bush. The drainage system is well developed and dominated by ephemeral stream with only a few flowing rivers existing. The climate consists of wet winters and dry and hot summers with a mean annual temperature of 18°C and an average annual rainfall of 1000 mm, but the incidence of precipitation is very irregular and evaporation is important.

Details about the geology may be found in Roubault (1934) and Bouillin (1977). The area prospected is underlain, from younger to older units, by the Kabyly basement complex, the sedimentary series (Kabyle Oligo-Miocene and Numidian units), a post-nappe formation consisting of a sedimentary series, and igneous rocks intruding almost all these formations (Fig. 1). The Kabyly basement (Fig. 1) consists of a strongly serpentinised plagioclase-lherzolite associated with a highly deformed sillimanite-cordierite gneiss (Bouillin, 1977; Bouillin and Kornprobst, 1974). The serpentinite mineralogy consists of bronzite, diallage, plagioclase, olivine and, chromite with accessory magnetite. The south and south-west of the study area is occupied by the Oligo-Miocene unit (KOM) made up mainly of a detrital formation derived from the Kabyly basement. The KOM has the Numidian as a discordant cover made up also of detrital material. The sedimentary post-nappe formation consists of a sandstone transgressive onto the marls, the sandstone material being derived from the Numidian unit and flysches. Apart from the Numidian formation, all these units are intruded by the granitic intrusion consisting of the Bougaroun Cape granite (CBG), and micro-granites and microgranodiorites. The CBG has S-type and peraluminous characteristics (Penven and Sabaté, 1980). Mineralogically it is composed of quartz, orthoclase, plagioclase, biotite, cordierite, muscovite, apatite, zircon, monazite and tourmaline. The microgranites and microgranodiorites are located in the east and the north-east of the study area.

Chromite, iron oxide, arsenopyrite and base-metal sulphides are the known mineralisation in the Collo area (Fig. 1).

- The iron mineralisation (Ain Sedma, Chabet El Mordj and Ezzam deposits) consists of massive ore, hosted almost exclusively in veins of silica-rich rhyolite (80% $SiO2$). The ore consists of magnetite and limonite with quartz as the gangue (Bolfa, 1948).

- The chromite mineralisation consists of pods reaching up to 10 m in length and 5 m in height. The ore consists of picrochromite (44-57% $Cr2O3$) while Cr-diopside forms the gangue (Leblanc and Temagoult, 1989).

- The sulphide mineralisation consists of veins of either Pb, Zn and Cu sulphides or arsenopyrite. The arsenopyrite mineralisation, associated with bismuthinite, occurs at Djebel El Ghorba, and is hosted by a granophyre. Its chemical composition is as follows: As: 0.05%, Bi: 0.02%, Pb: 0.10%, Zn: 0.05% and Cu: 0.12%. The main characteristics of the veins are a north-south direction, 85° dip, a width of 1-2 m and a length of approximately 10 m. The Pb-Zn-Cu mineralisation is contained in two rock types: granophyre at Djebel El Ghorba and carbonate rocks at the eastern side of Djebel El Mezaber.

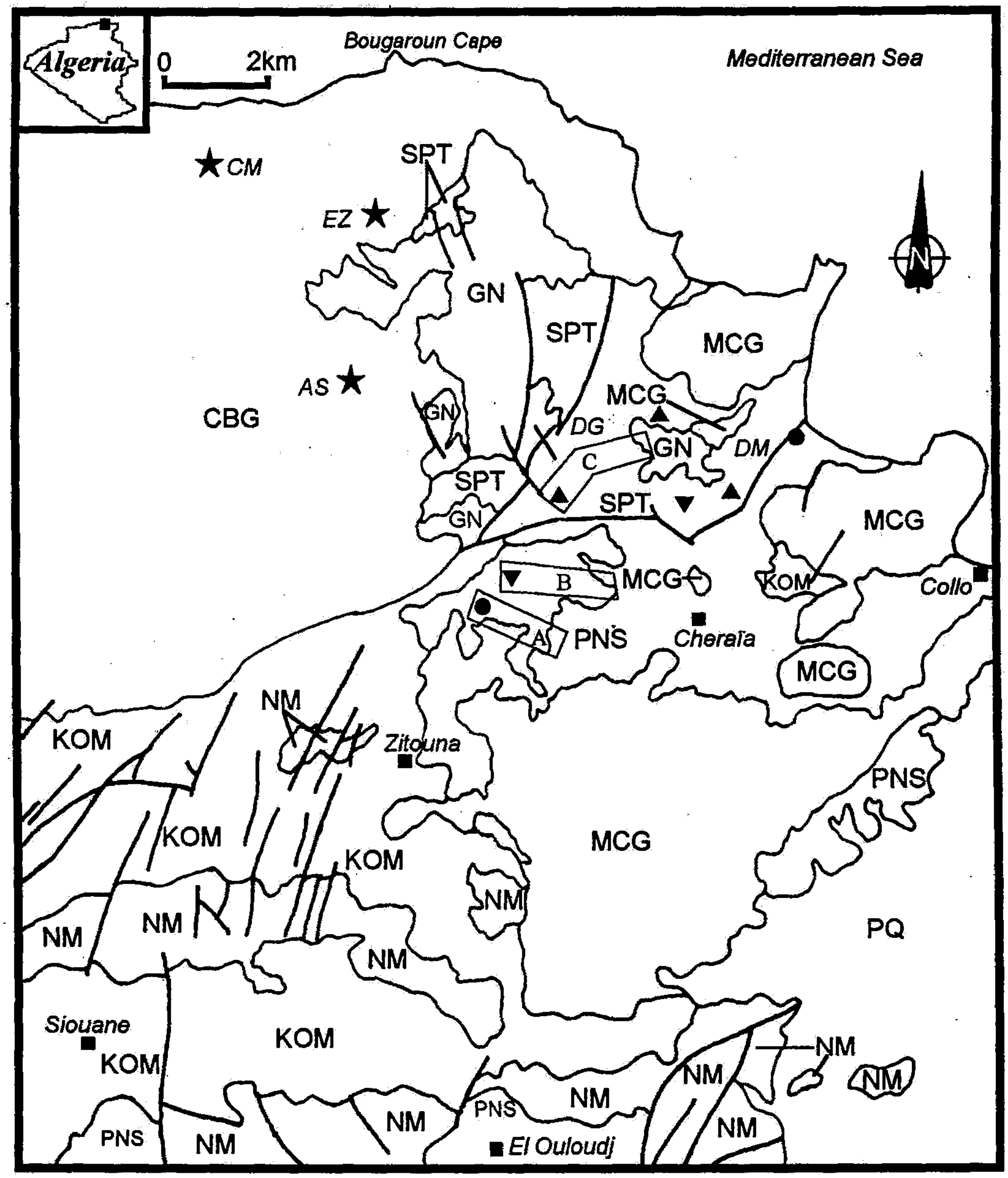

Fig. 1 - Geological sketch map of the Collo area *(from younger to older stratigraphic units)*
Esquisse géologique de la région de Collo

PQ: Plio - Quaternary formation ***(formation plio-quaternaire).*** **MCG:** microgranites and microgranodiorites ***(microgranites et microgranodiorites).*** **CBG:** Bougaroun Cape granite ***(granite de Cap Bougaroun).*** **PNS:** post-nappe sedimentary unit «marls and sandstones» ***(unité sédimentaire post - nappe "marne et grès").*** **KOM:** Kabyle Oligo - Miocene unit ***(unité de l'Oligo - Miocène Kabyle).*** **NM:** Numidian unit ***(unité numidienne).*** **SPT:** serpentinites ***(serpentinites).*** **GN:** gneiss ***(gneiss).*** After Bouillin (1977) ***(d'après Bouillin, 1977).*** **(★):** Fe mineralisation ***(minéralisation ferrifère);*** **(▲):** Cr mineralisation ***(minéralisation chromifère);*** **(▼):** Pb-Zn-Cu sulphide veins ***(veines à sulfures de Pb - Zn - Cu);*** **(●):** As-Bi veins ***(veines à As - Bi);*** **CM:** Chabet El Mordj; **EZ:** Ezzam; **AS:** Ain Sedma; **DG:** Djebel El Ghorba; **DM:** Djebel El Mezaber.

Table 1. Summary of < 150 μm stream sediment geochemistry of cold-extractable and total Fe,Co, Cr, Ni, Pb, Zn and Cu
Résultats de l'analyse chimique totale et après mise à froid de la fraction granulométrique < 150 μm pour Fe, Co, Cr, Ni, Pb, Zn, et Cu

	Range	Mean	Median	SD	CV	Th
Fe (%)	1.55-13.31	4.82	4.43	2.26	0.47	5.6
cxFe (ppm)	65-8050	1377	963	1240.05	0.90	3767
RTFe (%)	0.13-18.97	3.09	2.23	2.79	0.90	-
co (ppm)	<3-212	25	16	33.81	1.36	44
cxCo (ppm)	<3-34	5	4	5.77	1.28	15
RTCo (%)	0-85.71	18.55	18.75	16.88	0.91	-
Cu (ppm)	3-228	38	32	32.35	0.84	89
cxCu (ppm)	<3-120	15	12	12.30	0.84	33
RTCu (%)	0-88.89	42.10	40	19.4	0.46	-
Ni (ppm)	4-5055	220	33	653.78	2.97	130
cxNi (ppm)	<5-345	13	<5	42.81	3.23	15
RTNi (%)	0-61.1	3.58	10	7.75	2.08	-
Pb (ppm)	7-705	63	36	8.12	1.40	129
cxPb (ppm)	<5-300	25	11	42.68	1.67	51
RTPb (%)	0-78.85	35.52	36.11	20.88	0.60	-
Zn (ppm)	8-3177	133	80	246.21	1.85	257
cxZn (ppm)	<5-300	28	12	68.01	2.47	46
RTZn	2.37-85.13	19.45	16.85	13.83	0.71	-
Cr (ppm)	8-10207	424	125	1080.97	2.55	509
cxCr*	-	-	-	-	-	-

SD: standard deviation (***déviation standard***); **CV:** coefficient of varition «standard deviation/mean» (***coefficient de variation "déviation standard / moyenne arithmétique"***); **th:** threshold =75th percentile+ (1.5* (75th -25th percentile)) ***(seuil d'anomalie =75ème centile + (1,5 * "75ème - 25ème centile"))***; **cx:** cold-extractable metal (***métal extrait après mise à froid***); **RT**= (total metal/cold- extractable metal) x 100 ***(analyse totale/ métal extrait après mise à froid)*** x ***100***;

*: not detected *(valeur inférieure à la limite de détection)*.

extractable metal with total metal),
ii) the metal content distribution relative to stream orders,
iii) dispersion trains and geochemical contrasts,
iv) spatial distribution patterns. The summary statistics, the regional threshold and the ratio of total metal to cold-extractable metal for Fe, Co, Cr, Ni, Pb, Zn, Cu, cxFe, cxCo, cxCr, cxNi, cxPb, cxZn and cxCu (cx = cold - extractable metal) are shown in Table 1.

The normality of data was tested using the Kolmogorov-Smirnov test for normality (Conover, 1980) and it was found that all elements approached a log normal distribution at the 95% confidence level. The relationship between pairs of elements was sought using the Spearman rank correlation coefficient (sr) (Table 2) as it is suitable to non-normally distributed data and resistant to outlier values (Howarth and Sinding-Larsen, 1983).

The first type consists of 0.5-2 m wide veins containing pyrite, sphalerite, chalcopyrite and galena. The second type is contained in dolomite and limestone rocks located at the contact of the serpentinites with the post-nappe sedimentary formation in the north-east of the study area. The mineralisation consists of 2-4 m wide veins of pyrite, sphalerite, galena, marcasite and chalcopyrite having a very irregular chemical composition (SONAREM, 1974).

The area prospected has previously been subjected to a heavy mineral concentrate investigation mainly along rivers (Thiebaut, 1949). The results showed strong Cr and Fe anomalies and a few weak base-metal anomalies downstream of known mineralised sites.

III - METHODS

Details about sampling and analytical techniques used in this study may be found in Bounessah (1993) and Bounessah and Atkin (1995). A total of 288 stream sediments samples (<2 mm) were collected in ephemeral streams and water - bearing rivers. One hundred and forty one samples were taken from water-bearing rivers and 147 others from ephemeral streams. The ephemeral streams have low quantities of sediment material in their stream beds and a limited length (<2000 m). The majority of them are of first, second or third order and drain into flowing rivers which feed the Mediterranean sea. The samples were taken at a depth of 15-20 cm in the water-bearing and 10-15 cm in the ephemeral streams. Throughout the sampling procedure care has been taken to avoid sampling collapsed bank material by sampling in the centre of the streams (Rose *et al.*, 1979; Davy *et al.*, 1980).

The minus 150 microns grain fraction was selected for analysis as this fraction was found to give the best geochemical response for most chemical elements of economic interest (Bounessah, 1993). This size range consists mainly of fine-grained sand and silt, and a small proportion of clays (illite and kaolinite). The <150µm fraction was analysed for the cold-extractable metal and total metal contents for the following elements: Fe, Co, Cr, Ni, Pb, Zn and Cu. Total analysis was carried out by wavelength-dispersive X-ray fluorescence. Detection limits are: Fe: 50 ppm; Cu: 1 ppm; Ni, Pb and Zn: 2 ppm; Co and Cr: 3 ppm. Matrix variations were corrected for using a modified Compton scatter technique (Harvey and Atkin, 1982). Precision and accuracy were assessed by analysing duplicate and standard samples. The analytical precision at 10 times the detection limit is ± 10% (95% confidence level). The cold-extraction technique used in this study was modified from Siegel (1990). The sample powder was leached using 3% HCl. Pb, Zn and Cu were analysed using the Slotted Tube Atom Trap facility (STAT) (Watling, 1977). The detection limit for each element (in the sediment) is as follows: Cu: 3 ppm, Pb: 5 ppm, Zn: 1 ppm, Co: 3 ppm, Cr and Ni: 5 ppm, Fe: 6 ppm. The analysis of Cr was suspended as samples from both anomalous and background populations all showed values below the detection limit. The average analytical precision, at ten times the detection limit, was ±5% (95% confidence level).

IV - TOTAL ANALYSIS VS. COLD-EXTRACTION ANALYSIS

Assessment of the cold-extraction and total analysis results is carried out by comparing:

i) the relationship of pairs of elements (cold-

Table 2. Spearman rank correlation matrix for pairs of total and cold-extractable metals. All coefficients are significant at the 99% confidence level.
Matrice de corrélation de Spearman. Tous les coefficients ont une signification à un niveau de confiance de 99%.

Fe-cxFe	Co-cxCO	NI-cxNI	Pb-cxPB	ZN-cxZn	Cu-cxCu
0.29	0.67	0.73	0.79	0.70	0.73

The threshold was estimated from the Box-and-Whisker plot distribution (Fig. 2) i.e., threshold = 75th percentile + 1.5 * H; H being the value of the 75th percentile minus the 25th percentile (Kürzl, 1988). The threshold determined by this method is found to be resistant to inconsistencies and disturbances in the raw data and was therefore chosen (Bounessah, 1993). Anomalous values were defined as those exceeding the regional threshold value. For this study, a regional background is thought to be sufficient, however the influence of the local thresholds exist (Bounessah, 1993). 3D-surface maps were used to portray the geochemical relief patterns, based on 251 samples making up a sampling density of 1 sample km-2. A krigging gridding method based on a simple search method was used for this purpose (Davis, 1986). The algorithm utilised for the search method is of the following form:

$$Gj = \sum_{i=1}^{n} WijZi$$

where: Gj is the interpolated grid node j; n is the number of data points used to interpolate at each node, ten in this case (optimum number); Zi is the Z value at the ith data point; and Wij is the weight associated with the ith value when computing Gj.

The weighting factor Wij varies between 0.0 and 1.0 for each data point considered during grid interpolation. The sum of the all weighting factors used to calculate a grid node value is equal to 1.0. Data points given more weight are assigned weighting factors closer to 1.0, while data points given less weight are assigned weighting factors closer to 0.0.

1 - Metal content variation relative to stream orders

Data of the regional survey (251) was subdivided into 5 groups according to the stream order number and their distributionwas portrayed on Box-and-Whisker plots (Fig. 3). The number of samples falling into each group of stream orders (SO) is as follows: SO1 = 88, SO2 = 91, SO3 = 41, SO4 = 24 and SO5 = 7. The two highest orders correspond to water-bearing rivers whereas the three lowest ones are taken as ephemeral streams. The most striking feature from this analysis is that anomalous values for both total and cold-extractable metals are found in samples collected in ephemeral streams (stream orders 1 to 3 mainly). On the other hand, the box plot distribution of pairs of elements (total and cold-extractable metal) are very similar. The number of anomalous samples generally decreases from SO1 to SO3 and only a very few high values are encountered in SO4 and SO5. However, one of the controlling factors is the proximity of the mineralised sites which are mainly drained by streams of low orders. The highest values for total and cold-extractable results accounted for in the ephemeral streams are due to the following reasons:

i) proximity of the collected samples to the mineralisation;
ii) short distance of the ephemeral streams in comparison with the water-bearing rivers;

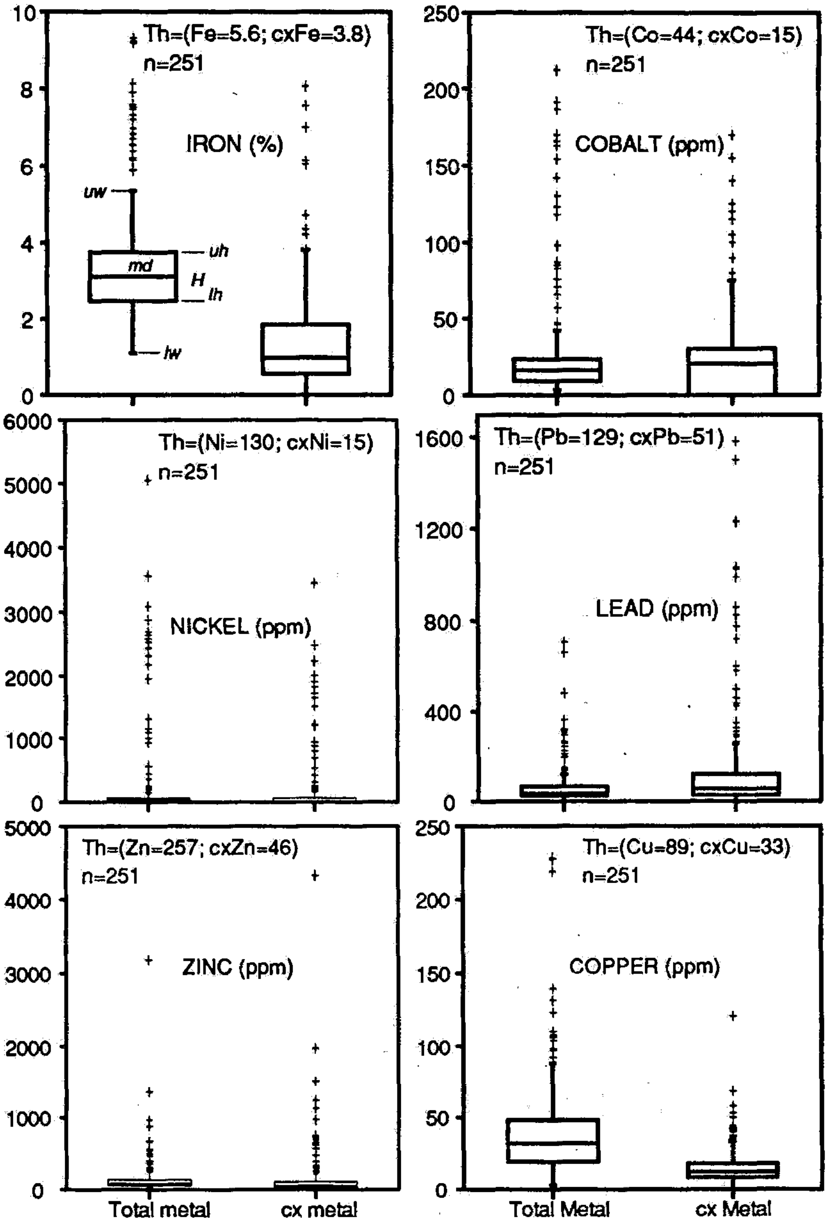

Fig. 2 - Box-and-Whisker plot distribution of total and cold-extractable Fe, Co, Ni, Pb, Zn and Cu in the minus 150µm fraction
Diagrammes Box-et-Whisker montrant la distribution des résultats obtenus par analyse totale et après mise à froid pour Fe, Co, Ni, Pb, Zn et Cu

For clarity, cxFe and cxNi results are multipied by 10, and cxCo and cxZn by 5 (***Pour des raisons de clarté, les valeurs de cxFe et cxNi ont été multipliées par 10 et cxCo et cxZn par 5***). **md** = median ***(médian)***; **uh** = upper hinge (75 th percentile)***(75ème centile)***; **lh** = lower hinge (25th percentile) ***(25ème centile)***; **H** = interquantile (uh - lh) ***(H = uh - lh)***; **uw** = upper whisker (75th + (1.5 * H)) ***(uw = (75ème + (1,5 *H))***; **lw** = lower whisker (25th - (1.5 *H)). ***(lw = (25ème - (1,5 *H))***.

The plus signs show values higher than the threshold, i.e. the upper whisker (Tukey, 1977)
le signe "plus" montre les valeurs supérieures aux seuils d'anomalie (Tukey, 1977)

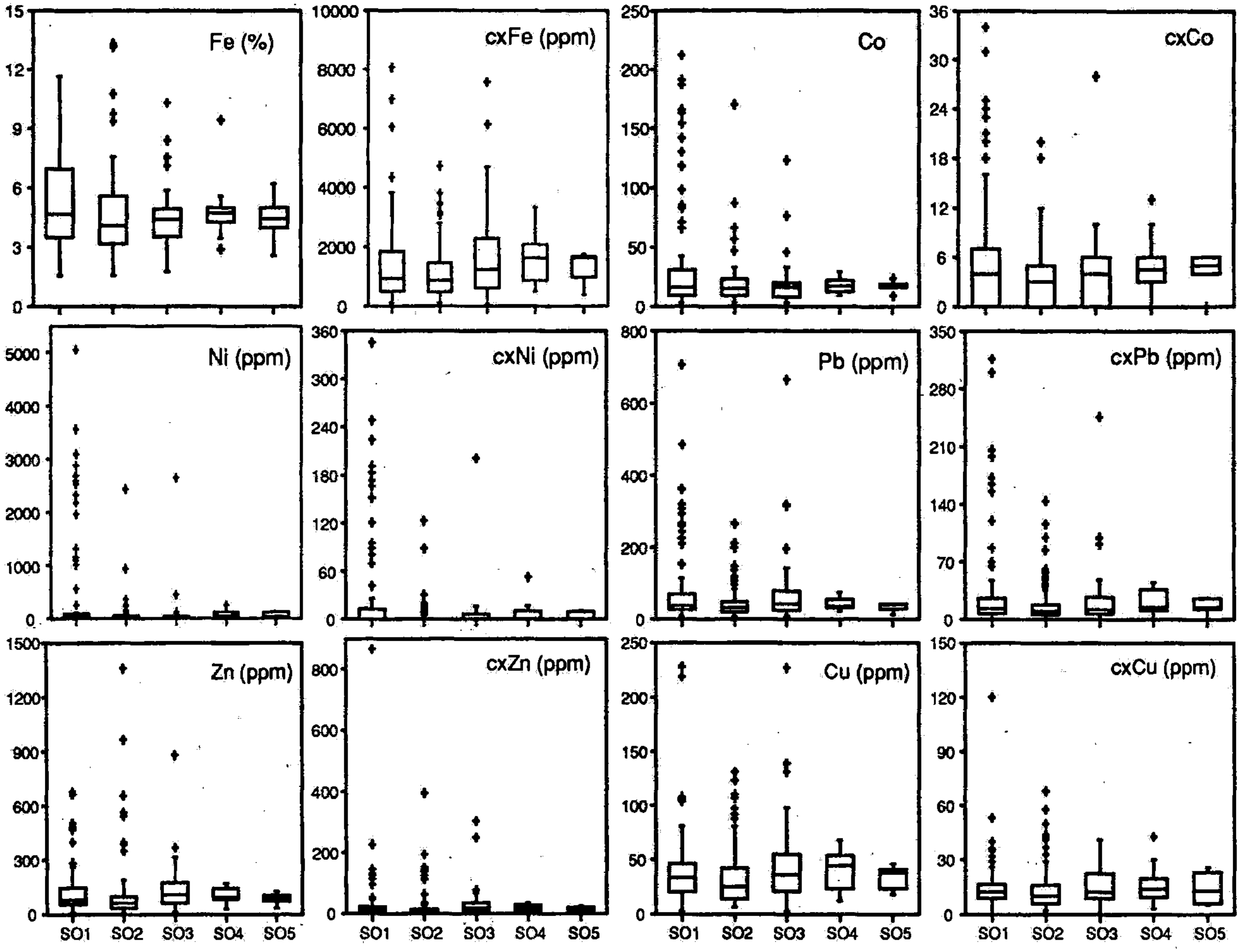

Fig. 3 - Box-and-Whisker plot distribution of total and cold-extractable metal content relative to 5 stream orders
Diagramme Box-and- Whisker montrant la distribution des résultats obtenus par analyse totale et après mise à froid dans 5 ruisseaux de différente magnitude

SO: stream order ***(magnitude du ruisseau)***
Number of samples as follows ***(Nombre d'échantillons)***: SO1 = 88; SO2 = 91; SO3 = 41; SO4 = 24; SO5 = 7

iii) dilution in the ephemeral streams is much less acute than in water-bearing rivers;
iv) enrichment in the -150μm grain fraction due to the development of iron and manganese oxides was not observed (Bounessah, 1993).

2 - Dispersion trains and geochemical contrasts

The comparison between the dispersion train length and geochemical contrasts for both analytical methods was undertaken downstream of mineralised sites. The geochemical contrast (GC) was defined as the ratio of the anomalous metal (Me_{an}) to the corresponding regional background value represented by the arithmetic mean (Me_{bg}). The GC provides a measure of the length of downstream dispersion trains, and therefore serves as a criteria to gauge the relative effectiveness of the analytical techniques utilised. For this comparative study, 37 samples were collected downstream of 3 known mineralisation sites (Fig. 1):

a) Oued Bou Snane,
b) Djebel El Ghorba,
c) Tamanart.

In each case, the three furthest samples were taken from flowing rivers (Bou Snane in case of a) and Tamanart in case of b) and c)), whereas the others were collected from ephemeral streams.

Figure 4, shows the variation of metal contents downstream of sulphide veins (a and b) and chromite pods (c). A systematic and consistent decrease in anomaly magnitude, for total and cold-extractable metal is observed in the three cases. Variation patterns for the 3 cases are similar for both analytical results. Generally, a sharp decrease in the intensity of the anomalies is noted after 400 meters. Then, the magnitude of the anomalies decreases quite gently to reach, in the water-bearing rivers, values similar to the regional background concentration levels.

An analysis of GC values downstream of the mineralised sites (Bou Snane, Djebel El Ghorba and Tamanart sites) shows that, generally the magnitude of the geochemical contrasts for the three cases is low to moderate. It is only high for the few first hundred meters but decays rapidly to reach unity in the water-bearing rivers (the last three samples). Comparison between the GC yielded by the two analytical techniques shows that values are mostly similar and differences are not very significant and both analytical methods show equal effectiveness in detecting the mineralisation and the serpentinite bedrock (case c). In the case of a) and b), dispersion trains of 1000 and 1300 m are encountered, respectively; after these distances there is a general tendency for the GC to reach unity. In case of c), much longer train dispersion is noted owing to the fact that the collected samples are underlain by the serpentinite bedrock. In this case, Co, Ni, cxCo and cxNi may be used as «pathfinders» for the mapping of the chromite-bearing serpentinites.

3 - Single-element distribution patterns

a - Iron

Iron values vary from 1.55 to 13.31% for total results (median = 4.43%) and from 65 to 8050 ppm for the cold-extraction analysis (median = 963 ppm). The highest total values are related to two features: the serpentinite bedrock in the north-east of the area and to the known iron mineralisation of Ain Sedma, Chabet El Mordj and Ezzam. These samples were taken from ephemeral streams of limited length (<1200 m) which drain into flowing rivers. These streams cut into valleys and the sediments are mixed with scree material. Correlation between cxFe and Fe is poor (sr = 0.29) and the proportion of readily extracted iron is low, not exceeding 19% (mean = 3.1%). This poor relationship is reflected by the spatial distribution of total Fe and cxFe (Figs. 5a and 5b). The iron mineralisation is poorly delineated by the cold extraction analysis, whereas samples underlain by the serpentinite

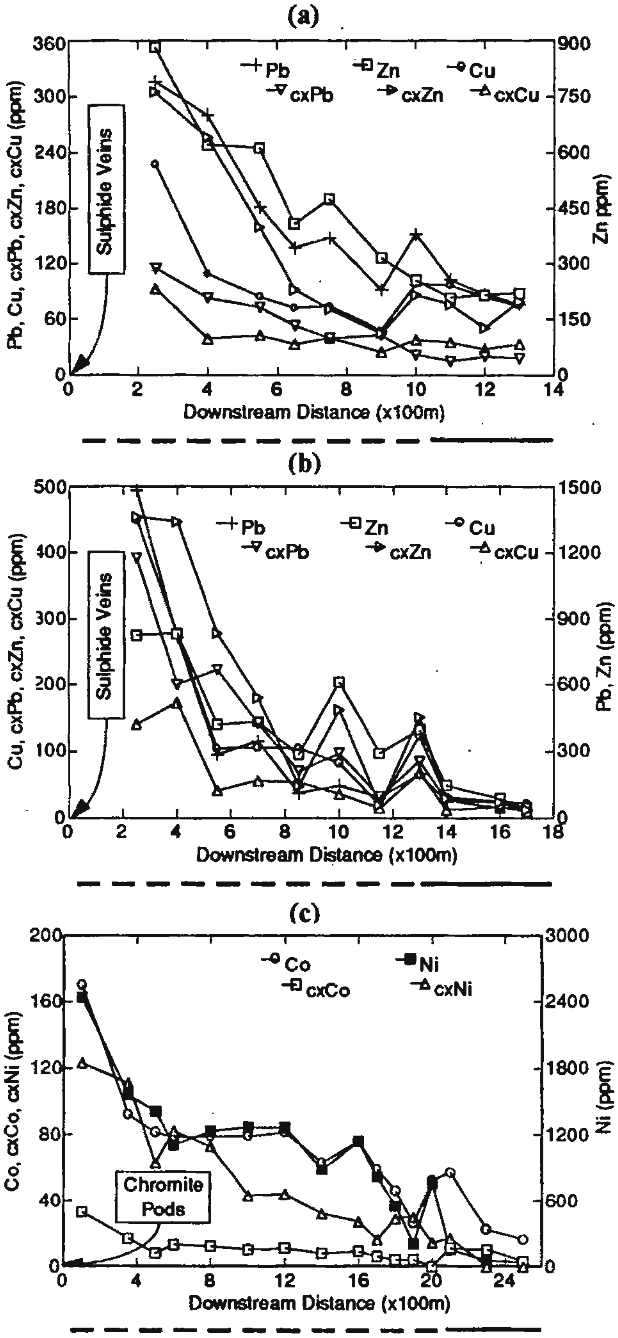

Fig. 4 - Element distribution patterns downstream of known mineralised sites

Distribution des éléments chimiques le long des sites minéralisés

(**a**) Oued Bou Snane: As-Bi-(Pb)-(Zn)-(Cu); (**b**) Djebel El Ghorba: Pb-Zn-Cu; (**c**) Tamanart: chromite. — — —: ephemeral stream ***(ruisseaux à sec)***; ————: water-bearing rivers ***(rivières)***
Bou Snane river (**a**) and Tamanart river (**b** and **c**)

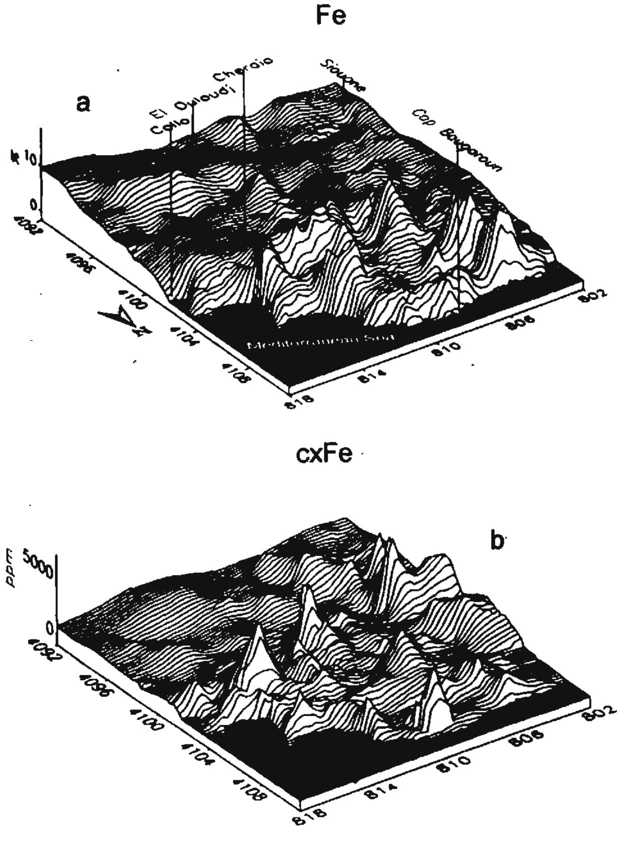

Fig. 5 - 3D - surface plots showing the geochemical relief of total and cold - extractable iron in the minus 150μm fraction

Diagrammes tridimensionnels montrant la distribution des teneurs de fer obtenues par analyse totale et après mise à froid de la fraction granulométrique < 150μm

a) Total Fe ***(Fe total)***; b) Cold-extractable Fe ***(cxFe)*** bedrock generally have fairly high cxFe contents. The poor delineation of the iron mineralisation is considered to be due to the stability of the magnetite during weathering in the semi-arid climate.

b - Cobalt and Nickel

The distribution of cobalt and nickel are similar, with a group of anomalous samples occurring in the north-east of the study area where they reflect the serpentinite massif. The highest concentrations are found in samples collected from ephemeral streams where dispersion trains do not exceed 1000 m. Downstream dilution is probably due to barren material derived from the sides of the mountains. Values of these elements do not exceed the regional threshold in the water-bearing rivers. The bulk of Ni is incorporated in the serpentine mineral, where nickel substitutes for Mg (Deer *et al.*, 1972) whereas cobalt is incorporated in the serpentine. cxCo and total Co values show a good correlation (sr = 0.67). This is confirmed by their similar areal distribution (Figs. 6a and 6b). As regards nickel, the majority of cxNi values are below the detection limit for background sample population, and the anomalous samples for both analytical methods are found only in samples underlain by the serpentinite bedrock. Ni and cxNi regional distributions are very similar (Figs. 6c and 6d) with sr = 0.73. Ratio values are very variable, ranging from 0-85.71% for Co and from 0-61.1% for Ni; the highest values being found in samples underlain by the serpentinites. Cold-extractable Co and Ni values are generally low, suggesting that these elements occur mainly in the resistate fraction.

Co, Ni, cxCo and cxNi adequately delineated the serpentinite massif. Bounessah (1993) demonstrated that the outlining of the Cr mineralisation was of limited success, when using the -150µm, with only one pod being detected. This is probably related to the fact that chromite was found to concentrate in the -600+150 µm grain fraction. As a consequence, it is suggested that cxCo and cxNi in addition to Co and Ni may be used for the geochemical mapping of underlying ultramafic bedrocks which may be the host of Cr mineralisation. Heavy mineral concentrates would normally be used when prospecting for Cr but the use of this technique in the ephemeral streams is not possible due to the relative small amounts of sediment and the absence of water for in-situ panning.

c - Lead, Zinc and Copper

Lead, zinc and copper were found to have a similar areal distribution, forming a northeastern trend (Figs. 7a-7f) of anomalous samples. In addition to these anomalies, a few anomalous samples were found along the northern and northeastern coast where Pb anomalies were reported by Thiebaut (1949; p.50) after a heavy mineral concentrate investigation. Anomalies mainly occur in samples collected from ephemeral streams. It was found that dispersion trains extended between 1000 and 1300 m downstream of known mineralised veins. The total lead content of the samples varies from 7 to 707 ppm (median = 36 ppm) whereas cxPb varies from <5 to 300 ppm (median = 11 ppm) with 20.9% as median value of the amount of metal extracted. In addition to the northeastern trend, a few moderately high Pb and cxPb values occur along the north and northeastern coast. Areal distribution of total and cold-extractable lead (Figs. 7a and 7b) are very similar with sr = 0.79.

Zinc values are very variable (Zn: 8-3177

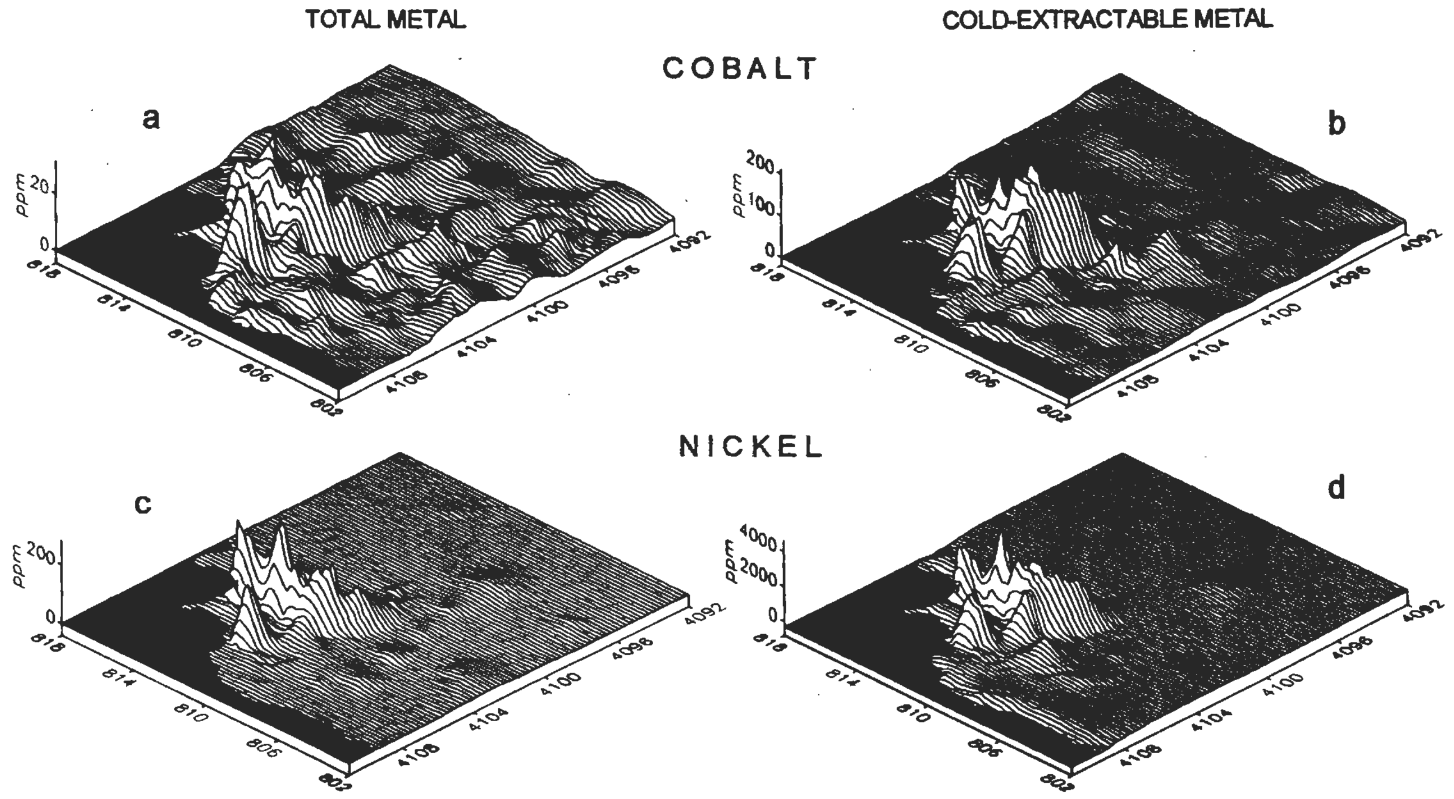

Fig. 6 - 3D - surface plots showing the geochimical relief of total and cold - extractable cobalt and nickel in the minus 150µm fraction
Diagrammes tridimensionnels montrant la distribution des teneurs de cobalt et de nickel obtenues par analyse totale et après mise à froid de la fraction granulométrique < 150µm

a) Total Co ***(Co total)***; **b)** Cold - extractable Co ***(cxCo)***; **c)** Total Ni ***(Ni total)***; **d)** Cold-extractable Ni ***(cxNi)***

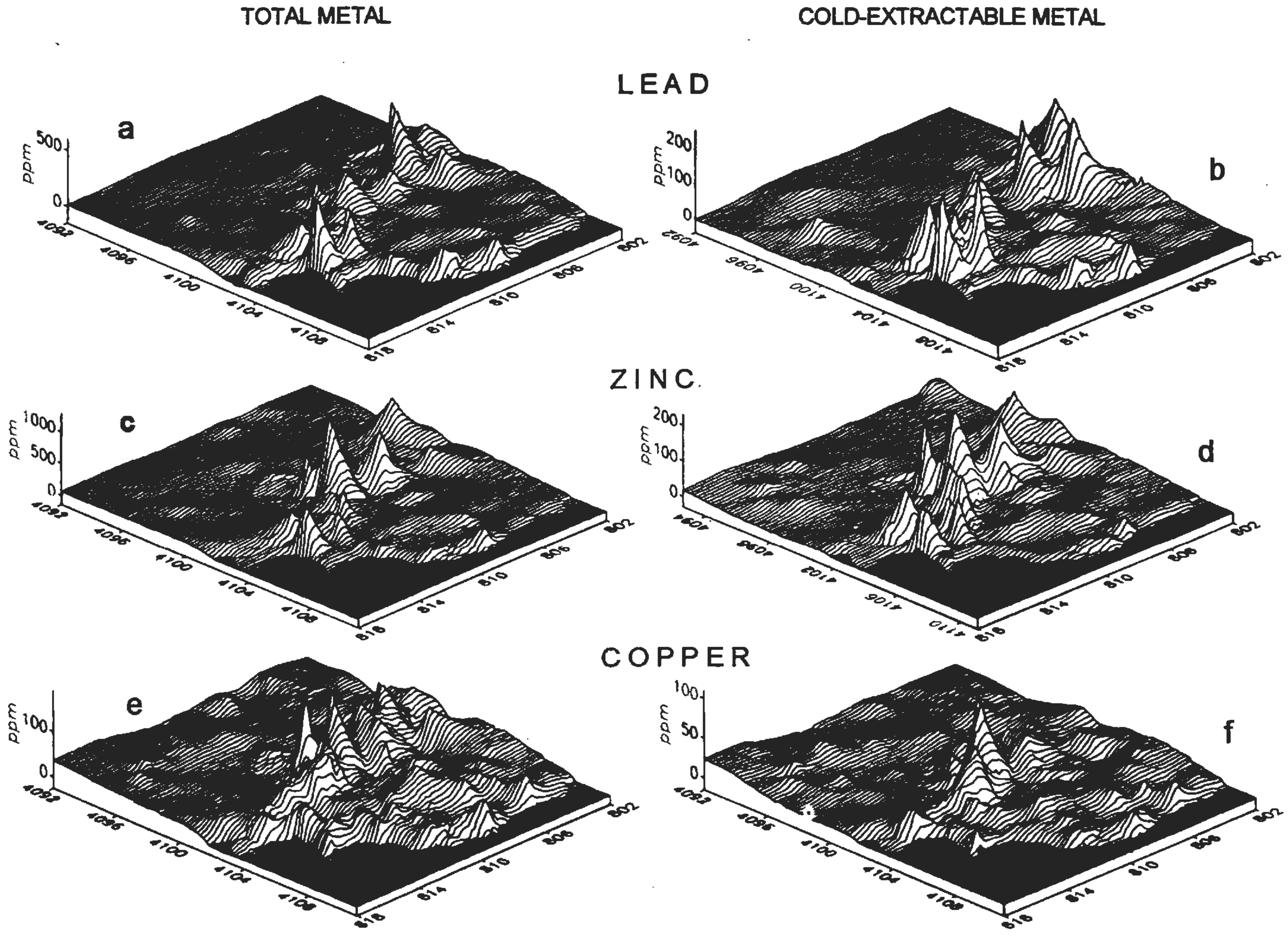

Fig. 7 - 3D - surface plots showing the geochimical relief of the total and cold - extractable lead, zinc and copper in the minus 150μm fraction
Diagrammes tridimensionnels montrant la distribution des teneurs de plomb, zinc et cuivre obtenues par analyse totale et après mise à froid de la fraction granulométrique < 150μm

a) Total Pb ***(Pb total)***; **b)** Cold - extractable Pb ***(cxPb)***; **c)** Total Zn ***(Zn total)***; **d)** Cold- extractable Zn ***(cxZn)***; **e)** Total Cu ***(Cu total)***; **f)** Cold - extractable Cu ***(cxCu)***

ppm; cxZn: 1-866 ppm) with a regional threshold value of 257 and 46 ppm for total metal and cold extractable metal respectively. Ratio values are very variable (2.4-85.1, median = 13.9%). The areal distribution of zinc, particularly in relation to the anomalous samples, is similar (Figs. 7c and 7d) with sr = 0.70.

Copper values range from 3 to 228 ppm (median = 32 ppm) for total results and from <3 to 120 ppm (median = 15 ppm) for the cold-extractable data. The average amount extracted is 19.4% (median). The lowest values are found in samples collected from the microgranites, the Numidian, the post-nappe sedimentary formation and the Kabyle Oligo-Miocene unit. These levels rarely exceed the 75th percentile (47 ppm) but samples collected over the serpentinite, gneiss and the Bougaroun Cape granite contain significantly higher contents. The correlation between total and cold-extractable results is good (sr = 0.73) as shown by the geochemical maps (Figs. 7e and 7f). Both total and partial extraction results adequately reflect the occurrence of known sulphide veins. However, a few samples yielded anomalous values in the cold-extraction data set but were not anomalous in the total analysis data set. This may suggest a difference in the degree of weathering. The most outstanding feature of the Cu-Pb-Zn association is their occurrence along a NE-SW trend. This starts in the north-east, at the boundary between the serpentinite massif and the post-nappe sedimentary formation and ends in the south-west, at the boundary between the Bougaroun Cape granite and the Kabyle Oligo-Miocene formation. However, in the west of the study area, no mineralisation has been reported and the newly discovered anomalies appear to be similar to those related to known Pb-Zn-Cu mineralisation hosted in granophyre. It is suggested that, for follow-up work in the west, the cold-extraction analysis of Pb, Zn and Cu may be used as an alternative to the total analysis of these elements.

V - DISCUSSION AND CONCLUSIONS

The results of both analytical methods (total and 3% HCl extraction analysis) used in this study reflected known sulphide mineralisation, serpentinite bedrock as well as indicating new anomalous zones. Distribution of anomalies for Co, Ni and the base metals for both analytical methods are very similar (Figs. 8a and 8b). The main exceptions to this are the chromite mineralisation, which was not confirmed by either analytical technique and the iron mineralisation that was not adequately confirmed by the cold-extraction technique. In the case of the chromite mineralisation, Bounessah (1993) indicated that a coarser fraction (-600 +150µm) would be more suitable for detecting the mineralised pods in the serpentinite massif. However, this study has shown that an indirect approach towards investigating the location of the chromite mineralisation, involving the use of Co, Ni as well as cxCo and cxNi to delineate the outcrop of the ultramafic massifs, is worthy of further consideration. Dilution in the ephemeral streams and water-bearing rivers is the main drawback for exploration in the study area. In the ephemeral streams this may be due to material consisting of rock debris and scree, creeping into the stream beds aided by the steep sides of the mountains. In addition to this material, a significant amount is accounted for by material derived from banks during flash floods. Dilution by barren material thus occurs and at a distance of 1000-1300 m anomalies are very weak or tend to reach background concentration levels. Samples collected in the rivers are also diluted and do not seem to show

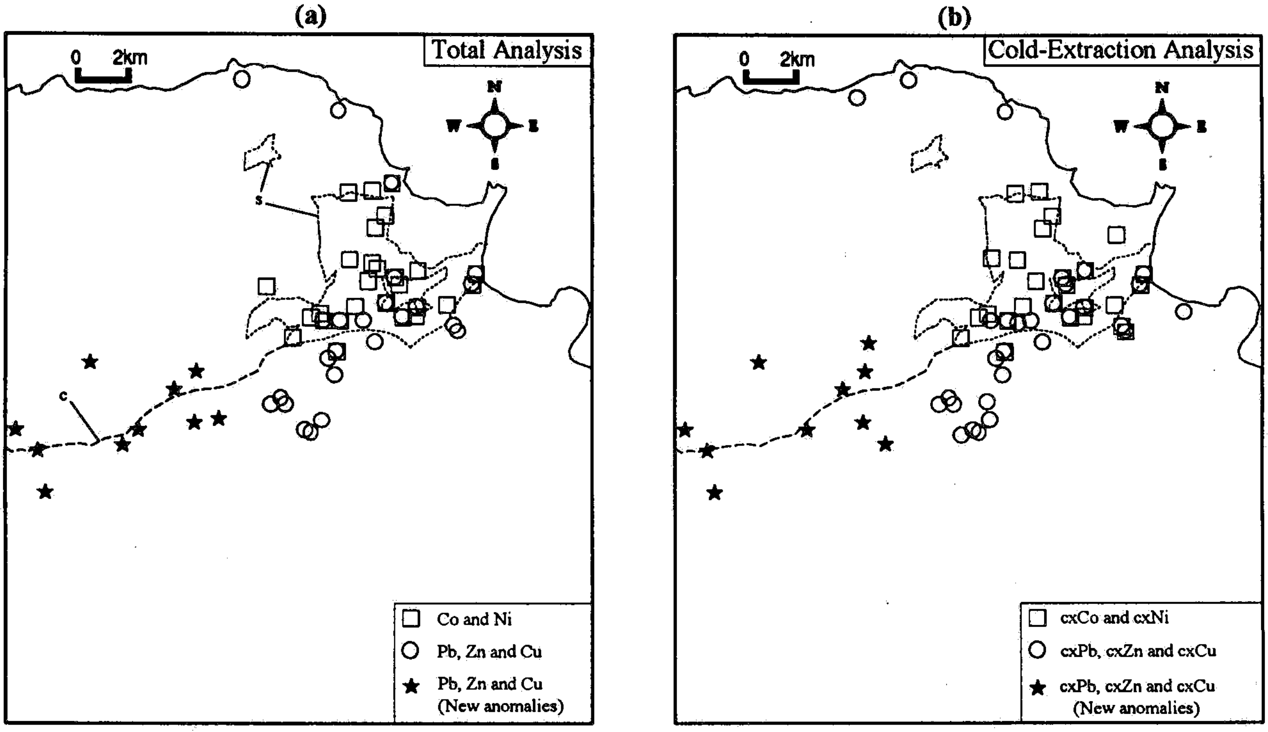

Fig. 8 - Comparison between the distribution of anomalies shown by total and cold-extraction results.
Comparaison entre la distribution des anomalies obtenues par analyse totale et après mise à froid

a) total anlysis "XRF" ***(analyse totale "Fluoréscence X")***; b) 3% HCl extraction analysis "AAS" ***(analyse après mise à froid avec 3% HCl "Absorption Atomique")***; s: serpentinite boundaries ***(bordure des serpentinites)***; c: southern border of the Bougaroun Cape granite ***(bordure méridionale du granite de Cap de Bougaroun)***.

any enrichment. This may be due to the following reasons:

i) the amount of clays is low in comparison to that of silt and fine-grain sand which may be attributed to losses during sampling,

ii) illite and kaolinite, which do not have high adsorption capacity (Bronlow, 1979; Degens, 1965; Garrels and Christ, 1965), are the main clay components;

iii) dilution;

iv) scavenging of transition metals by Fe and Mn oxides was found to be negligible (Bounessah, 1993).

The relative success of the cold-extraction technique, particularly for delineating the base-metal veins and in delineating the serpentinite bedrock, indicates that chemical remobilisation/weathering has taken place which has led to the deposition of elements in a readily extractable form. Anomalous values occur almost exclusively in ephemeral streams and are rarely found in samples from rivers. This is thought to be largely due to the lower dilution of detrital material in the ephemeral streams although the relative short length of the ephemeral streams and therefore the proximity of samples to the mineralised bedrock must also play a part. In conclusion, it is thought that the analysis of cxCu, cxPb and cxZn may be a cheap and rapid alternative to total analysis and can be used for the location of base metal mineralisation in semi-arid regions, whereas Co, Ni, cxCo and cxNi may assist in the mapping of ultramafic bedrocks in similar terrains. However, one has to emphasise that the best anomalies are found in sediments collected from the ephemeral streams rather than rivers. The limited length of the ephemeral streams has proved to be a major drawback to the use of stream sediment surveys in the study area. Both total and cold-extraction contents were found to decay after 1000-1300 m downstream of mineralised veins in the ephemeral streams and rapidly reached the background levels in sediments from water-bearing rivers. However, stream sediment surveys involving the analysis of base metals and Co and Ni by a cold-extraction technique on the -150 mm fraction, can be used as a cheap and rapid method of exploration geochemical surveys in semi-arid regions.

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