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GEOCHEMICAL INVENTORY IN THE STREAM SEDIMENTS OVER THE PALEOZOIC FORMATIONS OF BELGIUM

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ABSTRACT. - As a continuation of a stream sediment reconnaissance for uranium in the Palaeozoic of the Belgian Ardennes, a multielement survey is now carried out in the same region.

The mean density is one sample per km^2 and the area covers 12,000 km^2 . Dried samples are crushed and sieved and the minus 80-mesh fraction is retained for analysis. After a hot acid digestion, samples are analysed for twenty elements by direct current plasma emission spectrometry. Organic matter content and pH of samples are also determined. In selected anomalous areas, selective chemical extractions are carried out on an equal number of background and anomalous samples. The aim of this study is to better understand the control of anomalies and is an attempt to enlarge them. Statistical treatments of the data include uni- and multivariate technics; special attention is paid to lithological influence for thresholds determination.

Data are reported on topographic maps, at a scale of 1 : 100,000 and anomalies are also presented based on regression and factor analysis of the data. Each report includes a description of geological and drainage conditions, known mineralisations, description of main anomalies and recommandations for future work.

INTRODUCTION.

In the years 1979-1981 the Geological Survey of Belgium and the Commission of European Communities (DG XVII) sponsored a prospection campaign for Uranium in the Palaeozoic formations of Belgium (CHARLET *et al.*, 1983). This campaign included three different surveys :

- an hydrogeochemical survey in stream and spring waters;
- a carborne radiometric survey;
- a geochemical stream sediment survey.

In extension to the last one, the Ministery of Economy of the Region Wallonne decided in 1981 to undertake a multielement geochemical inventory of the same region and committed the leading of this survey to the Laboratory of Geochemistry of the University of Louvain.

The aim of this paper is to present the framework of this inventory and the treatments of the data through some preliminary results.

GEOLOGICAL CONTEXT.

The investigated area comprises all the Palaeozoic formations of Belgium which cover the central and southern part of the country and are overlapped in the north and in the south by the Meso-Cenozoic (Fig. 1).

The lower Palaeozoic consists of isolated Caledonian massifs with quartzopelitic lithology and local low grade metamorphism. The stratigraphic serie range from lower Cambrian to upper Silurian, although the Silurian is lacking in the southern massifs.

In the upper Palaeozoĩc, sediments are terrigenous at the base (lower Devonian) and change gradualy into a carbonate lithology (middle and upper Devonian, Dinantian).

The serie ends with the Silesian in the coal basin of Central Belgium.

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Fig. 1 - Location of studied zone and geological sketch.

FIELD AND LABORATORY WORK.

The prospected area, covering about 12,000 $\rm km^2$, was sampled with a mean density of one sample per $\rm km^2$. The samples were collected with an auger along the banks of the streams, below water level. This sampling method was adopted, after orientation surveys, due to fre-quent lack of fine material in the middle of the streams. After drying at 60°C, the samples were crushed and sieved and the minus 80-mesh fraction was retained for analysis.

The samples are dissolved by a mixed acid (HC1 - HNO3 - HF) digestion at 150°C and analysis is performed by direct current plasma emission spectrometry (Spectrametrics Instrument Model Spectraspan III with dynamic background compensation) for the following elements : Mn, Zn, As, Cd, Ti, Sb, Fe, Ni, Cu, Nb, Mo, Co, Y, Pb, V, La, Sr, Ba, Ag, and Ce. Organic matter content and pH of samples are also determined.

In selected anomalous areas, selective chemical extractions are carried out on an equal number of background and anomalous samples. The procedure uses a five steps extraction sequence (Table 1) and aims at better understand-ing the control of anomalies and possibly at enlarging them (SONDAG, 1981; MARTIN et al., 1983).

TABLE 1 SELECTIVE EXTRACTION SEQUENCE

| Reagent | Dissolved species | | | |
|--|----------------------------|--|--|--|
| Ammonium acetate 1 M, pH 4.5 | Exchangeable cations | | | |
| Hydroxylamine hydrochlo- ride 0.1 M, pH 4.5 | Manganese oxides | | | |
| Ammonium oxalate 0.175 M - oxalic acid 0.1 M, pH 3.3 (Tamm's reagent) in the dark | Amorphous iron oxides | | | |
| Tamm's reagent under U.V. light | Crystalline iron oxides | | | |
| Hydrochloric - nitric - hydrofluoric digestion | Clay and silt residue | | | |

(The time required for full achievment of the different steps was determined by a preliminary kinetic study).

For data handling, an APPLE-II computer is connected to the DCP Spectrometer; specific softwares were developped for :

- spectral backgrounds study.
- acquisition and correction of analytical data,
- list editing, data storage on floppy disks,
- preliminary statistical treatments on small data sets.

The APPLE-II computer is interfaced with an IBM 370/158 computer, so that all the data can be transfered on hard disks and magnetic tapes for statistical treatments and automatic mapping.

STATISTICAL TREATMENTS.

Statistical data processing includes distribution studies and threshold determinations, regression analysis and factor analysis.

DISTRIBUTION STUDY

For distributions study, cumulative probability graphs are drawn using a great number of intervals (i.e. 100-200) instead of 20-40 in classical treatments. This method allows a more precise definition of inflexion points since the curve is drawn in a quite continuous way (MARTIN et al., 1982). Probability curves drawn in this way often present several inflexion points, some more pronounced then others. However, experience has shown that it could be very informative to examine them all carefully because they could be related to different sub-populations which are meaningful in interpretation. Fig. 2 shows the probability plot obtained with 120 intervals for 975 values of Ti in the Bastogne area. An inflexion point appears clearly at a cumulative frequency of 46 % corresponding to 1700 ppm. Separation of a low and a high population has been made on the basis of this threshold and mapping of both populations indicates that the extend of the high population corresponds closely to the Gedin-nian and lower Siegenian (Fig. 3). On this figure, downstream displacement of

high values towards upper formation can also be observed, especially in the south of the area.

This example reveals that lithostratigraphy is an important factor to take into account in threshold determination. Therefore, subsets of samples originating from the same lithostratigraphic environment are studied separately and the distribution of frequencies, mean values and standard deviations examined to check eventual discrepancy between the subsets.

FACTOR ANALYSIS.

Influence of secondary environment (pH, Fe-Mn enrichments, organic matter) is investigated using multivariate Factor analysis in particular technics. is a powerfull method for defining associations of metals. Table 2 gives the significative scores calculated by the PA2 program (principal factoring with iteration) of S.P.S.S. (NIE, 1975) after a VARIMAX rotation. Factor 1, accounting for about one half of explained variance, regroups metals frequently associated in the Fe-Mn oxydes-hydroxydes resulting from weathering of the bedrock and scavenging trace elements in stream sediments. This factor would thus reflect the influence of the secondary environment on metal dispersion. This is furthermore confirmed by the slight but significative score of pH (0.40) on this factor.

Factor 2 associates the three R.E. elements analysed (La, Y, Ce). This association may result from primary minerals like monazite or xenotine, partly



Fig. 2 - Log probability curve of Titanium, Bastogne area (N = 975).



Fig. 3 - Mapping of low and high populations for Titanium, Bastogne area (N = 975).

TABLE 2 FACTOR LOADINGS (Bastogne area, N = 975)

| | Factor 1 | | Factor 2 | | Factor 3 | | Factor 4 | |
|------------------------------|----------|------|----------|------|----------|------|----------|-------|
| | Ni | 0.83 | La | 0.94 | Ba | 0.69 | Ce | 0.41 |
| | Fe | 0.77 | Y | 0.84 | Sr | 0.68 | Ti | -0.85 |
| | Со | 0.67 | Ce | 0.68 | Pb | 0.63 | | |
| | v | 0.64 | | | v | 0.48 | | |
| | Cu | 0.61 | | | | | | |
| | Mn | 0.59 | | | | | | |
| | Zn | 0.56 | | | | | | |
| | pН | 0.40 | | | | | | |
| Eigenvalue | ···-;;- | 5.85 | | 2.63 | | 1.79 | , | 1.04 |
| Explained Variance (%) | | 47.0 | | 21.1 | | 14.4 | | 8.4 |

dissolved by the hot acid digestion. This factor would thus be related to the presence of a residual phase.

Factor 3 may be interpreted as reflecting the influence of a carbonate phase associating Ba and Sr and characterized by particular Pb and V content. However, as carbonate rocks are very scarce in this area (maximum pH value of samples is 6.5), it seems unlikely they could give rise to an individual factor. So this factor is more probably related to the clay minerals content of the samples. Factor 4 is a lithological factor, reminding that Ti presents a population of high value corresponding to particular stratigraphic series. Furthermore, mapping of Ce values gives a rough inverse image of that of Ti.

MAPPING AND REPORTING.

Data are reported on maps at a scale of 1 : 100,000. The most interesting elements are presented individualy either with metal value at each sample location or with point-symbol representation. The last one aims also at interpreting of regional variations and at delimiting potential mineralized zones.

Regional trends are examined by manual contouring of lineprinter maps produced after gridding. The gridding algorithm used is a weighted moving average method with iterations (DAVAUD, 1975).

Anomalies are presented on maps of single element but regrouping on the basis of results of factor analysis will also be used.

Reports of the results will be published on the basis of the 1/100,000 maps and will comprise a description of geological context, known mineralisations, comments on the main anomalous zones and recommendations for follow-up operations. Raw data will be included on microfilm.

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