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**PRACTICAL APPLICATIONS OF
MULTIVARIATE STATISTICS IN
EXPLORATION GEOCHEMISTRY**

S.P. VRIEND

**PRACTICAL APPLICATIONS OF
MULTIVARIATE STATISTICS IN
EXPLORATION GEOCHEMISTRY**

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STATISTIEK IN DE EXPLORATIE GEOCHEMIE**

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Trace-element behavior in the W-Sn granite of Regoufe, Portugal.

S.P. Vriend, M.G. Oosterom, R.W. Bussink and J.B.H. Jansen.

Journal of Geochemical Exploration, 23: 13-25, 1985.

Chapter III

Assessment of mineralogical influences on the element mobility in the W-Sn enriched granite of Regoufe and its derivatives (Portugal) by means of XRF analysis of unpolished rock sections.

P.F.M. van Gaans, S.P. Vriend, R.P.E. Poorter and J.B.H. Jansen.

In: Mineral Deposits within the European Community (ed. by J. Boissonnas and P. Omenetto). S.G.A. Special Publication no. 5, Springer Verlag, 135-149, 1988.

Chapter IV

The application of fuzzy c-means cluster analysis and non-linear mapping to geochemical datasets: examples from Portugal.

S.P. Vriend, P.F.M. van Gaans, J. Middelburg and A. de Nijs.

Applied Geochemistry, 3: 213-224, 1988.

Chapter V

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S.P. Vriend, M.J. Dekkers, M. Jansen and J. Commandeur.

Presented at the XIII International Geochemical Exploration Symposium, 1989, Rio de Janeiro, Brazil and accepted for publication in the Journal of Geochemical Exploration.

Chapter VI

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M.J. Dekkers, S.P. Vriend, C.H. van der Weijden and Ph. van Diest.

Uranium, 2: 261-277, 1986.

Chapter VII

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M.J. Dekkers, S.P. Vriend, C.H. van der Weijden and P.F.M. van Gaans.

Applied Geochemistry, 4: 375-394, 1989.

Abstract

The search for new economic ore-deposits becomes increasingly difficult. A sophisticated approach is required to locate new ones. In exploration geochemistry the use of uni- and multivariate statistics is often advocated. In this series of studies it is shown how techniques such as factor analysis, discriminant function analysis, non linear mapping and cluster analysis can be of use to the exploration geochemist. Applications are presented to geochemical rock, sediment and water surveys.

Samenvatting

Het wordt steeds moeilijker nieuwe economische ertslichamen te ontdekken. Steeds verfijndere opsporingsmethodes zijn daarom noodzakelijk. In de exploratie geochemie wordt het gebruik van multivariate statistische technieken vaak aangeraden. In deze serie studies wordt getoond hoe technieken, zoals factor analyse, discriminant functie analyse, non-linear mapping en cluster analyse gebruikt kunnen worden door de exploratie geochemicus. Toepassing op geochemische surveys gebaseerd op gesteente-, sediment- en waterbemonstering worden gegeven.

CHAPTER I

INTRODUCTION

GENERAL CONSIDERATIONS

Rose et al. (1979) give the following definition of geochemical exploration: "Geochemical prospecting for minerals includes any method of mineral exploration based on systematic measurement of one or more chemical properties of a naturally occurring material". The measurement of properties of naturally occurring materials in exploration campaigns commonly entails the collection and analysis of several tens, up to hundreds of thousands of samples. While in the earlier years of the science it was common practice to only "eyeball" for high or anomalous values of single elements, nowadays a more sophisticated approach is often required, as the "easy" mineral deposits have long been found. It is more and more necessary to detect the less obvious anomalies in a rough geochemical landscape. To recognize these anomalies the setting of the individual sample in its immediate surroundings must be studied (Roquin, 1985). This means that, in the interpretation of the geochemical results, all information available in an area must be incorporated. Given the size of geochemical surveys, it is natural that exploration geochemistry was one of the first disciplines in the earth sciences to extensively use computerized data treatment techniques. In the beginning techniques like moving average or rolling means, trend surface analysis, cluster analyses etc. were rather indiscriminantly and sometimes incorrectly applied (e.g. I.

Nichol et al., 1969; Zielinski R.A. et al., 1987). Recently, at least in some textbooks, the dangers in blindly applying these techniques are treated (Howarth, 1983). A consequence of the awareness of these dangers is that the application of sophisticated computerized techniques does not speed up but in fact greatly slows down the interpretational process. In return one gets an in-depth understanding of the geochemical processes in a given area and one may discover anomalous situations that may go unnoticed otherwise. It also means that an exploration geochemist, who may collect widely varying types of sample materials (e.g. rock, soil, water, air etc.) and often works closely together with experts of different disciplines, must have a working knowledge of many fields in the geosciences in order to reach an optimal interpretation of his results. Unfortunately, although the total cost of geochemical surveys is generally considerable, in industry it is often difficult to find the limited though necessary funds for an adequate interpretation.

As exploration geochemistry is not a science to develop methods in data interpretation, this task is mostly left to other branches in science. The correct usage of these methods, the combination of procedures, together with what can be learned from them is rather unique for the exploration discipline. Of course many of the field and data-interpretation experiences gained in exploration have a direct application in environmental studies, a fact that largely has gone unnoticed in many countries.

In the following chapters some examples are given of the correct application of multi-variate data treatment techniques. Also techniques that recently appeared in the statistical literature are tested in geochemical exploration.

CASE HISTORIES

Chapter II and III are studies in litho-geochemistry. The Regoufe granite, a W-Sn specialized granite in Northern Portugal, was sampled conventionally and by the new integral rock analytical approach (IRA) (van Gaans et al., 1987). The interpretation of the multi-element geochemical data together with the field observations was mainly based on factor analysis. The analysis of the conventional data gave a clear reflection of (auto)metasomatic processes, operative during and after the emplacement of the granite. The intensity of the albitization and greisenisation process coincides with the disappearance of biotite, tourmaline and K-feldspar megacrysts and the appearance of sulphides. The influence of mineralizing fluids is mostly found near known W-Sn deposits and is much stronger near disseminated wolframite mineralization than near quartz vein type mineralization. Finally a factor of the incompatible elements Cs, Li and U points towards late stage hydrothermal activity (Voncken et al., 1986, Konings et al., 1988). In the IRA research small drillcores of different parts of the Regoufe granite were collected. These drillcores were subsequently sawn into 1 cm thick slices that were without further preparation analyzed by X-ray fluorescence spectrometry. This procedure has some clear ad-

vantages that are hardly offset by negatives. Outside speed and cost effectiveness, mineralogical and geochemical details can directly be studied that otherwise may be lost in the sample preparation. A first result is that in the Regoufe granite it is clearly shown that surface weathering has no influence on the chemical composition of the granite as long as the physical rock structure is retained. Through an electron microprobe study of some slices that exhibited extreme concentrations for certain elements, minerals that were unknown to occur in the Regoufe granite were effortlessly discovered. Especially the identification of the important ore-mineral columbo-tantalite which is often recovered from placer deposits around specialized granites is noteworthy. The detailed multivariate study of the bulk of the data showed that the hydrothermal processes left a distinct imprint in all parts of the Regoufe granite and its derivatives, showing thereby their pervasive nature. Their interaction with "existing" mineralogy was identified in factor analysis by element associations that point towards distinct minerals such as apatite, mica etc. The trace element signature of such factors are diagnostic concerning the processes that were active on these minerals. The element Sr is an interesting illustration of the power of the IRA approach. In the conventional study no satisfactory explanation of the behavior of Sr was forthcoming. In the IRA study it was found that in the western and least altered part of the Regoufe granite Sr is linked to feldspars, while in the eastern part it is mainly governed by apatite.

Chapter IV and V describe studies on mainly sediment material. Chapter IV deals with the problem of how to soundly interpret relatively small multivariate datasets. In situations whereby the use of techniques based on the correlation matrix are doubtful, owing to inhomogeneity of the dataset, the use of cluster analysis and pattern recognition techniques is advocated. The grouping obtained in such analysis may provide an adequate understanding of the case at hand. Especially the combination of two techniques which are fundamentally different is useful to arrive at a satisfactory model. A recurrent phenomenon in the study of naturally occurring materials is that groupings are not well separated but often show varying degrees of overlap. Conventional clustering techniques are not well suited for such situations. However clustering techniques based on the concept of fuzziness (Zadeh, 1965) may then perform better (Bezdek, 1981). The applicability of such fuzzy-clustering is illustrated in two case studies of water and sediment compositions in a region of Northern Portugal. It is shown to perform well in combination with the pattern recognition technique of non-linear mapping (NLM), whereby the NLM is mainly used to decide on the correct number of groupings to extract from the datasets. NLM provides a two-dimensional image of a multivariate dataset whereby the distances between sample points in the multivariate space are minimally distorted (Sammon, 1969). In chapter V the potential of well sediments for geochemical exploration purposes is assessed. A case study was conducted in a granite/schist contact zone, hosting a wide range of mineralizations, close to Nisa, Portugal. If

well sediments are indeed suitable for prospecting purposes, they must interact with their geological and geochemical environment. Through discriminant function and factor analysis studies it was shown that these sediments are indeed geochemically active media that reflect bedrock composition as well as the common geochemical processes that are active at the rock-atmosphere interface. Effects of contamination are minor and are easily recognizable. This confirms their general suitability as sampling medium. The subsequent anomaly evaluation demonstrates that the sediments give an excellent response to mineralization. At places where nowadays wells are found, the water is close to the surface. This is generally the case in joint and fracture zones. These are also zones most favorable for mineralization. It is therefore postulated that nature has already helped in the search for deposits by eliminating dry and thus commonly barren ground from the sampling realm.

Chapter VI and VII are hydrogeochemical studies in exploration geochemistry. They focus on the search of uranium deposits. In either chapter it is shown that a thorough understanding of the water chemistry in a certain region is mandatory for the interpretation of the uranium contents observed in the waters. In the case of the São Pedro do Sul granite, a granite enriched in radio-active elements, but void of any known mineralizations, no high U-tenors are encountered in surface or groundwater. Through a multivariate analysis it is made plausible that many of these waters reach deeper levels before surfacing again. It was therefore concluded that in this region which was

long considered favorable ground for U-deposits (Fernandez, 1970) the chance on finding such a deposit at the surface or at some depth are slim. A similar conclusion is reached if the mineralogy of uranium in the granite is considered. Uraninite is reported as a common accessory mineral in the granite (Basham, 1982). Normally uranium is easily leached from uraninite during hydrothermal activity. If a suitable geochemical barrier is reached it may reprecipitate and eventually form an ore-deposit. However the uraninite of the São Pedro do Sul granite contains 3-7% ThO₂, which implies that this type uraninite is not easily leached (Granstaff, 1976), thus precluding the formation of deposits.

The second case study, presented in chapter VII, was carried out in the same area as the well sediment study of chapter V. Sizeable vein type and disseminated U-deposits occur in this granite/schist contact zone. Prior to tackling the uranium distribution pattern in spring and well waters, a detailed and extensive study was made of the water chemistry in the area. Discriminant function analysis proves the significant impact of bedrock differences on the water composition. Factor analysis carried out separately on the data sets originating from granite and schist terrains indicate that basically the same processes influence the water chemistry. These are evapotranspiration, land-use, oxidation/reduction and water-rock interaction. However, the extent and signature differ. Similar processes were also found in related studies (Chapter VI, ten Haven et al., 1985, Comans et al., 1987). Through Q-mode cluster analysis it was possible to classify the waters in genetic groups, such as surface runoff, agri-

culture and village pollution types. Mapping of these types showed that their distribution pattern is not disrupted by the granite schist contact. Thermodynamic calculations marked UO₂(HPO₄)₂²⁻ as the predominant U-species and excluded the possibility of supersaturation of some U mineral. Supersaturation may severely distort the uranium distribution pattern (Runnels, 1981). The U contents vary widely between clusters, indicating that the definition of anomalies is best carried out within each cluster. A comparison of the results of such a definition with "simpler" definitions shows that bias introduced through changing bedrock or through evapotranspiration is virtually eliminated. All radiometric anomalies are reflected in the anomaly pattern. The interpretation of these anomalies together with some new discoveries within the hydrogeochemical framework allows for a refined priority classification for eventual follow-up research.

CONCLUDING REMARKS

In all studies multivariate procedures were helpful or even indispensable in the interpretation of the data at hand. A time consuming and difficult part of the multivariate analysis is the elimination of the distorting influences of deviations of normality owing to multimodality, skewness and outliers. Recently these problems have been recognized and so-called robust techniques gain rapidly in popularity. The fuzzy concept has already been mentioned. Other interesting developments are bootstrapping (Diaconis and Efron, 1983), jackknifing and the multivariate selection of outliers through the calculation of the Mahalanobis distance (Di Zhou, 1989).

Occasionally application is already found in geochemical literature (e.g. Oostindiër et al., 1988, van Gaans, 1990). Other techniques, which require a high sampling density are neighborhood regression (Roquin and Zeegers, 1987). This technique could be considered as an automated variant of part of the approach applied in the hydrogeochemical study in the Nisa region. In fact both techniques underline the importance of considering the contents of an element or compound in its own geochemical setting. In a simpler form Lepeltier (1969) already stated that geochemical parameters should be determined for each geochemical setting separately. This fact was independently, and somewhat later, noticed by the ministry of the environment of the Netherlands (Anonymous, 1986). The case studies presented here show that a thorough knowledge of both the geochemical and the statistical aspects is required to reach a sound interpretation. Especially the blind application of cookbook recipes may lead to inferior results. The new developments in data treatment will undoubtedly lead to a situation wherein sophisticated multivariate statistical techniques are easier to apply and will become routine tools for the interested scientist.

REFERENCES

Anonymous, 1986. Discussienotitie Bodemkwaliteit (VTCB A86/02-II), Staatsuitgeverij, Den Haag.

Basham, I.R., Ball, T.K., Beddoe-Stephens, B. and Michie, U. McL, 1982. Uranium bearing accessory minerals and granite fertility, II. Studies of granites from the British Isles. Proc. Symp. on Uranium

Exploration Methods. Review of the NEA/IAEA R & D Programme. Paris 1982. Nucl. Energy Agency, Paris, pp. 398-411.

Bezdek C.J., 1981. Pattern Recognition with Fuzzy Objective Function Algorithms. Plenum Press.

Comans, R.N.J., van der Weijden, C.H., and Vriend, S.P., 1987. Geochemical studies in the drainage basin of the Rio Vouga (Portugal). IV. Impact of land use on the hydrogeochemistry of natural waters in the Vouzela region. Environ. Geol. Water Sci., 9 (2): 119-128.

Diaconis, P. and Efron, B., 1983. Computer-intensive methods in statistics. Sci. Am., 248: 96-108.

Di Zhou, 1989. ROPCA: a fortran program for robust principal components analysis. Computers & Geosciences, 15: 59-78.

Fernandez, A.P., 1970. Contribuicao para o estudo da regio dos granitos radioactivos de S. Pedro do Sul. Junta de Energia Nuclear, Lisbon.

van Gaans, P.F.M., Vriend, S.P. and Schuiling, R.D., 1987. Integral Rock Analysis; a new approach in lithochemical exploration with use of X-ray fluorescence spectrometry. Geol. Mijnb. 65: 205-213.

van Gaans, P.F.M., Vriend, S.P., 1990. Multiple linear regression with correlations among the predictor variables. Theory and computer algorithm RIDGE (Fortran 77), Computers & Geosciences, in press.

Granstaff, D.E., 1976. A kinetic study of the dissolution of uraninite. Econ. Geol., 71: 1493-1506.

ten Haven, H.L., Konings, E., Schoonen, M.A.A., Jansen, J.B.H., Vriend, S.P., van der Weijden, C.H., Buitenkamp, J., 1985.

- Geochemical studies in the drainage basin of the Rio Vouga (Portugal). II. A model for the origin of hydrothermal water in the Vouzela region. *Chem. Geol.*, 51: 225-238.
- Howarth, R. J., 1983. Handbook of Exploration geochemistry (G. J. S. Govett, ed.), Volume 2. Statistics and data analysis in geochemical prospecting. Elsevier, Amsterdam, 437 pp.
- Konings, R.J.M., Boland, J.N., Vriend, S.P. and Jansen, J.B.H., 1988. Chemistry of biotites and muscovites in the Abas granite, northern Portugal. *Am. Min.* 73: 754-765.
- Lepeltier C., 1969. A simplified statistical treatment of geochemical data by graphical presentation. *Econ. Geol.* 64, 538-550.
- Nichol I, Garrett R.G. and Webb J.S., 1969. The role of some statistical and mathematical methods in the interpretation of regional geochemical data. *Econ. Geol.* 64, 204-220.
- Oostindiër J, Taufen P.M. and Vriend S.P., 1988. An application of litho-geochemistry to the evaluation of the Ni-sulphide ore potential of weathered serpentinites in the Fortaleza de Minas Greenstone Belt, Minas Gerais Brazil. *J. Geochem. Explor.*, 31: 57-73.
- Roquin C., 1985. Traitement des données en prospection géochimique: facteurs de variation du signal et sélection de la composante anormale, Documents du BRGM. no 86, 315 pp.
- Roquin, C., Zeegers, H., 1987. Improving anomaly selection by statistical estimation of background variations in regional geochemical prospecting. In: R.G. Garrett (ed.), *Geochemical Exploration 1985*. *J. Geochem. Explor.*, 29: 295-316.
- Runnells, D.D. and Lindberg, R.D., 1981. Hydrogeochemical exploration for uranium ore deposits: use of the computer model Wateqfc. In: A.W. Rose and H. Gundlach (eds.), *Geochemical Exploration 1980*. *J. Geochem. Explor.*, 15: 37-50.
- Rose A.W., Hawkes H.E., Webb J.S., 1979. *Geochemistry in mineral exploration*, Academic Press London, 657 pp.
- Runnells D.D. and Lindberg, R.D., 1981. Hydrogeochemical exploration for uranium ore deposits: use of the computer model WATEQFC. In: A.W. Rose and H. Gundlach (Eds), *Geochemical Exploration 1980*. *J. Geochem. Explor.*, 15: 37-50.
- Sammon, J.W., 1969. A nonlinear mapping for data structure analysis, *IEEE Trans. Comput.* C18, 826-829.
- Voncken, J.H.L., Vriend, S.P., Kocken, J.W.M. and Jansen, J.B.H., 1986. Determination of Beryllium and its distribution in rocks of the Sn-W granite of Regoufe, N-Portugal. *Chem. Geol.*, 59: 93-103.
- Zadeh L.A., 1965. Fuzzy sets. *Inf. Control* 8, 338-353.
- Zielinski R.A., Otten J.K., Wanty R. B. and Pierson C.T., 1987. The geochemistry of water near a surficial organic-rich uranium deposit, Northeastern Washington State, U.S.A. *Chem Geol.* 62, 263-289.

CHAPTER II

TRACE-ELEMENT BEHAVIOR IN THE W-Sn GRANITE OF REGOUFE, PORTUGAL

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ABSTRACT

Vriend, S.P., Oosterom, M.G. Bussink R.W. and Jansen, J.B.H., 1985. Trace-element behavior in the W-Sn granite of Regoufe, Portugal. *J. Geochem. Explor.*, 23: 13–25.

Vein-type W-Sn deposits occur both in and around the Regoufe granite. The muscovite-albite granite hosts several roof pendants of schist along its eastern and northern margins. Biotite, tourmaline and K-feldspar megacrysts are virtually absent from the roof zone of the granite but sulphides are abundant. These sulphides disappear through a transition zone and the granite becomes a tourmaline-bearing porphyritic two-mica granite. Fifty-five rock samples were collected within the granite resulting in a sample density of about 10 samples per km². The analytical results show that the granite is extremely rich in Sn, W, Li and Cs, rich in P, Ta, Rb, F and U, about normal in Cu, Zn and Nb and low in Sr, Ti and Zr in comparison with the global averages for low-Ca granites. Factor analysis was applied to the data and the resulting three factor model could be correlated to the field relations. Factor 1 reflects greisenization and albitization processes. Factor 2 scores are high in the mineralized areas and factor 3 appears to be connected with the transition zone.

INTRODUCTION

The Regoufe granite is located around latitude 40° 52' 57" north and longitude 0° 58' 56" east of Lisbon. It is situated about 200 km north of Lisbon on the boundary of the provinces of Douro Litoral and Beira Alta. Geologically the Regoufe area belongs to the Hercynian massifs which are exposed over large parts in the northwest of the Iberian peninsula. Numerous tungsten-bearing quartz-vein deposits are found in and around the Regoufe granite. Most of these deposits have been mined in the past.

The purpose of this study was to discern the trace-element trends within this granite and determine their relationship to magmatic differentiation processes, post-magmatic mineralization and late alteration.

GEOLOGY

The geology of the region has been studied in detail by Sluyk (1963). According to Oen (1970) the Regoufe granite belongs to the Younger Hercynian granites. Pinto (1979) determined with the Rb-Sr whole-rock isochron method an age of 280 ± 9 Ma. The granite is oval-shaped in outcrop and has a surface expression of about 6 km². It is discordantly intruded into the metasedimentary rocks of the Beira Shale Complex, a group of low-grade metamorphic rocks, composed of sericitic phyllites and quartzites with intercalated conglomerates. The granite contact is steep in the east and dips away at a low angle in the west. A contact-metamorphic aureole of spotted phyllites with biotite, cordierite and andalusite occurs around the granite, which is much wider in the west than in the east (Fig. 1). In the eastern and northern parts of the granite schist roof pendants are found (Fig. 1). Sluyk (1963) describes the rock type as a

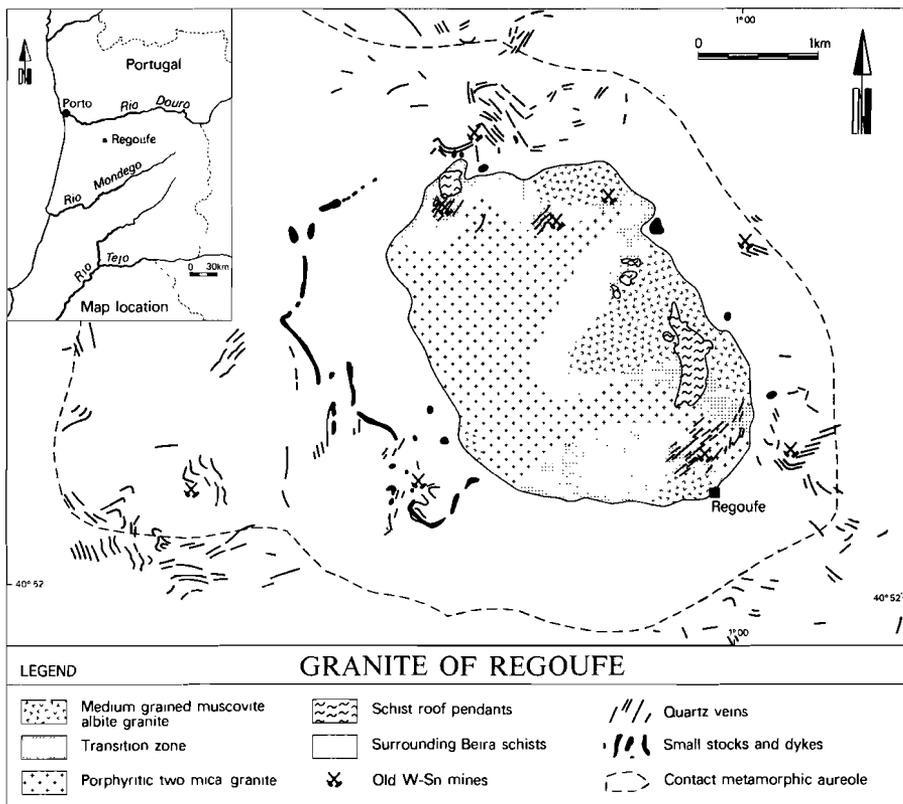


Fig. 1. Petrological sketch map of the Regoufe granite (modified after Sluyk, 1963).

muscovite-albite granite with a porphyritic texture. The following average composition is given: 25–30% albite; 30–40% quartz; 10–20% microcline; 15–20% muscovite. Apatite is a minor component. Biotite, tourmaline and arsenopyrite occur in certain parts of the granite. Accessories are zircon, ilmenite, anatase, monazite, xenotime and rutile.

MINERALIZATIONS

Several tungsten-tin deposits occur in and around the granite body. The areas where mining activity took place in the past are indicated in Fig. 1. At present none of these deposits are being exploited and no production data, or ore reserve estimates, are available. The most important mine in the area was the Minas de Regoufe, located near the village of Regoufe. Exploitation of the mine stopped in the late fifties. Mineralization occurs mostly in quartz veins where the important ore minerals are wolframite and some cassiterite. Sphalerite is often encountered in close association with these minerals. The wall rock around the veins in the granite is often altered into a quartz-muscovite greisen with cassiterite, late apatite and tourmaline (Sluyk, 1963).

SAMPLING AND ANALYTICAL TECHNIQUES

Fifty-five rock samples (Fig. 2) were collected in July 1981. As far as was practical and possible, the sample locations were chosen to reach a sample density of about 10 per km². This high density was chosen to show

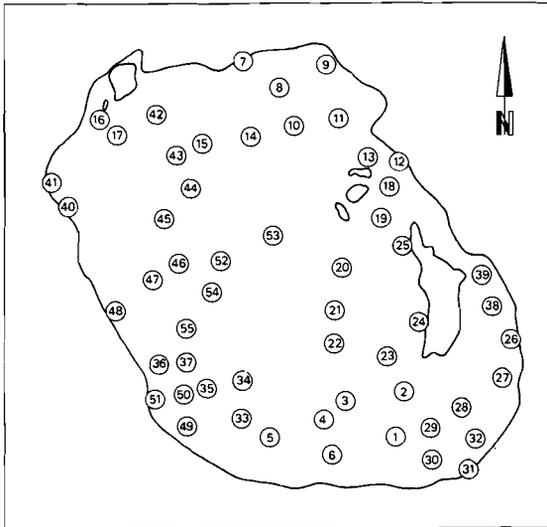


Fig. 2. Sample site map of the Regoufe granite.

the interelement associations and to accurately map the element distributions within the granite. At each sample location about 10 chips of approximately 100 g were collected over an area of about 500 m². The freshest rock obtainable at each location was accepted for samples. A finer-grained aplitic rocktype sometimes occurs in the granite. This type of rock was not included in the sample series. The mineral composition and grainsize of each sample was estimated by one of the authors who did not participate in the sampling. The whole rock sample was crushed, split and pulverized to -250 mesh in Ni-Cr steel equipment. Rb, Sn, W, Sr, Ta, Cs, Nb, P, Ti, Zr and U were determined by XRF in pressed powder briquettes; Cu, Zn and Li by AAS after a HF-HClO₄-HNO₃ sample decomposition; and F by ISE after a fusion with Na₂CO₃. The quality of the analyses was monitored by the inclusion of international standard samples of appropriate composition. The results were interpreted with the aid of the computer packages SPSS (Nie et al., 1975) and Symap (Dougenik and Sheehan, 1976).

RESULTS AND DISCUSSION

Mineralogical observations

The contour maps (Fig. 3) of our mineralogical observations show some interesting general features. For easy comparison between these maps and also those shown in Figs. 4 and 5 the mineral composition and grainsize ranges are divided in ten intervals. In the zone where arsenopyrite is present, tourmaline and biotite are mostly absent and potassium feldspar megacrysts are less abundant than in the rest of the granite. Though somewhat vague it also seems that the grainsize in the sulphide-rich zone is smaller than in the other parts. Muscovite is a major mineral component throughout the granite and is more abundant in the eastern than in the western part. In the northern and eastern parts the granite is sulphide-bearing, medium grained and only contains muscovite. Then through a transition zone wherein the mineralogical composition is not always uniform, it becomes a tourmaline-bearing porphyritic two-mica granite. A petrological sketch map (Fig. 1) was drawn with the aid of the mineralogical maps. This map differs in some important details with the one presented by Sluyk (1963).

Trace- and minor-element distribution

The distribution of the elements within the granite is shown in Fig. 4. Table 1 gives the arithmetic mean, standard deviation and range of the concentration of the different elements together with global average concentrations for low-Ca granite (Rösler and Lange, 1975). The ratio between the concentrations in the Regoufe granite and the global average for low-Ca gran-

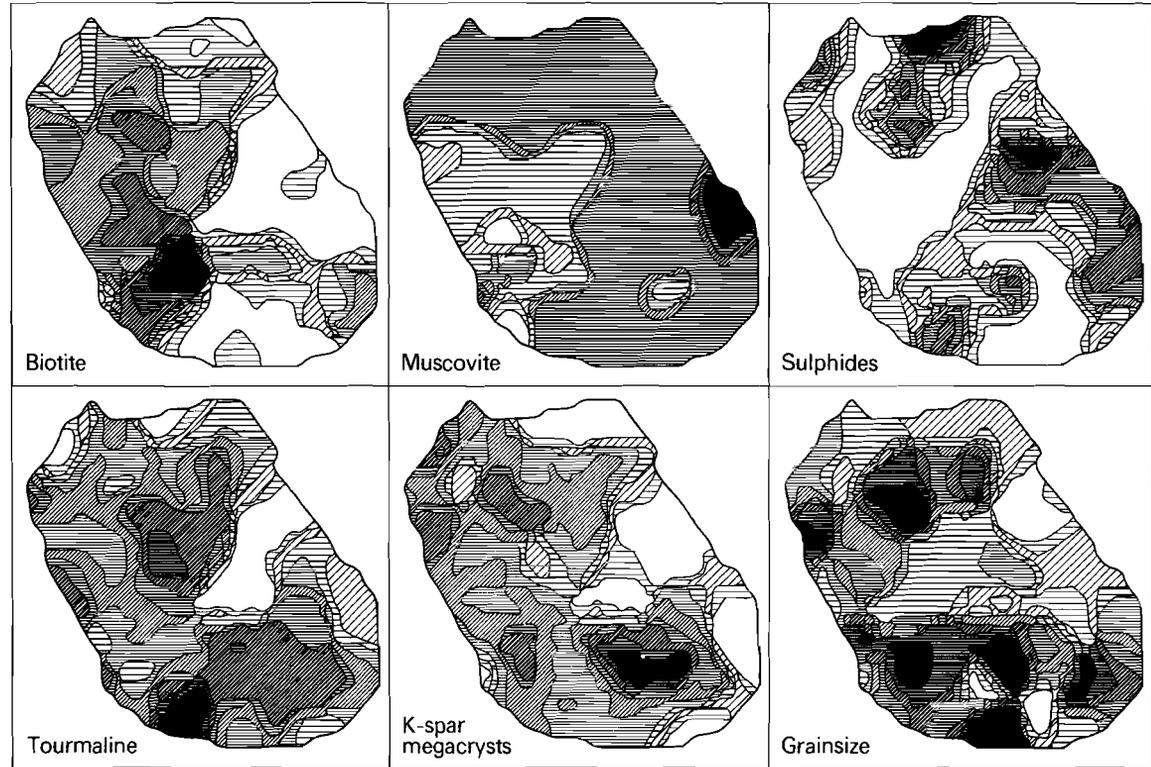


Fig. 3. Distribution of estimated mineralogical parameters in the Regoufe granite. Ranges of the estimates are: biotite 0–5%; muscovite 5–25%; sulphides 0–2%; tourmaline 0–3%; K-spar megacrysts 0–10% and grainsize 3–15mm. The contours are equal interval. Values increase from white to black.

ites shows that the granite is: extremely rich in Sn, W, Li and Cs; rich in P, Ta, Rb, F and U; about normal in Cu, Zn and Nb; and low in Sr, Ti and Zr. These characteristics are quite common for "specialized granites" affiliated with Sn and W mineralizations (Tischendorf, 1977). The trace- and minor-element contour maps correspond in several aspects with the mineralogical contour maps. In the sulphide-bearing zone Rb, P, Nb and Ta are relatively high and Zr and Ti are relatively low. Also in this zone, Sn and F are locally higher, though less conspicuously than the Rb group elements. Li and Cs show their highs mainly in the transition zone. The distributions of W, U and especially Sr are difficult to interpret.

Factor analysis

R-mode factor analysis was applied to the data in order to investigate the interrelation of the elements. R-mode factor analysis is based on the correlation matrix. Correlations are adversely affected if the distributions of the variables are highly skewed, multimodal, or contain outliers. The gap statistic (Miesch, 1981) did not show any significant gaps at the 0.20 probability level except for Cu, Zn and F (significant at about the 0.01–0.02 probability level). The gaps in the Cu and Zn distributions are induced by rounding off during the analytical procedures. This conclusion is corroborated by the absence of an inflection point in the cumulative frequency curves of these elements. The gap in the F distribution appears to be genuine. Skewnesses of the distributions of the variables were compared with those of the distributions of the logarithmically transformed variables. The average of the absolute of the skewnesses of the non-transformed data was 0.95, while the average for the log-transformed data was 0.40, clearly an improvement. The log-transformation increased the skewness only for Li and U. Finally the calculation of the standardized scores for the different variables (i.e. $z_i = (x_i - \bar{x}_i)/s_i$ where z_i is the standardized score and x_i and s_i the mean and standard deviation of variable x_i) showed that for the non-transformed data 15 results were outside the mean ± 2.5 standard deviation range and 9 outside the mean ± 3.0 range. For the log-transformed data these figures were respectively 10 and 4. These latter figures are in close agreement with those theoretically expected. Taking the above considerations into account it was felt that, although some deviations occurred, a logarithmic transformation of all variables would provide an adequate starting point for the factor analysis. Considering that the study of the processes that led to the present day composition of the granite was one of the main interests of this research, it was decided that factor analysis rather than component analysis (respectively indicated by PCA2 and PCA1 in the SPSS) was the appropriate approach. Factor analysis is aimed at the explanation of the interrelation of the variables, while component analysis is more variance oriented (Jöreskog et al., 1976). Study of the eigenvalues and different factor models indicated that a three factor

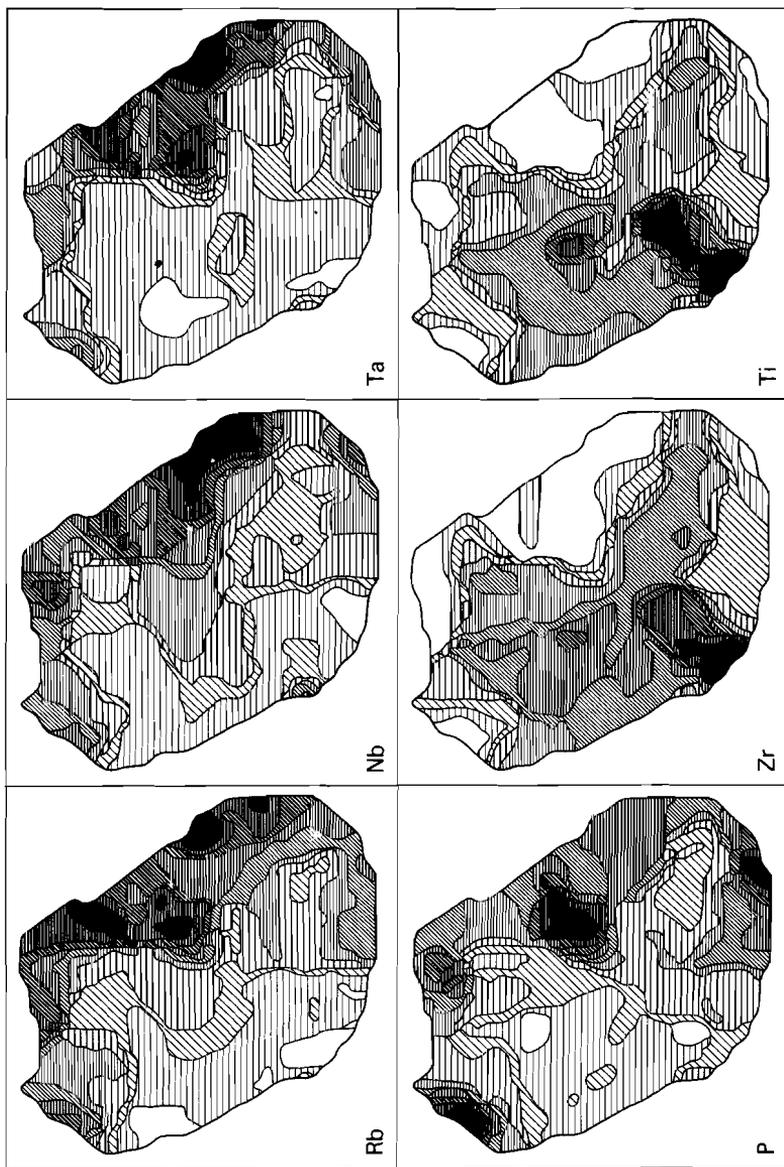
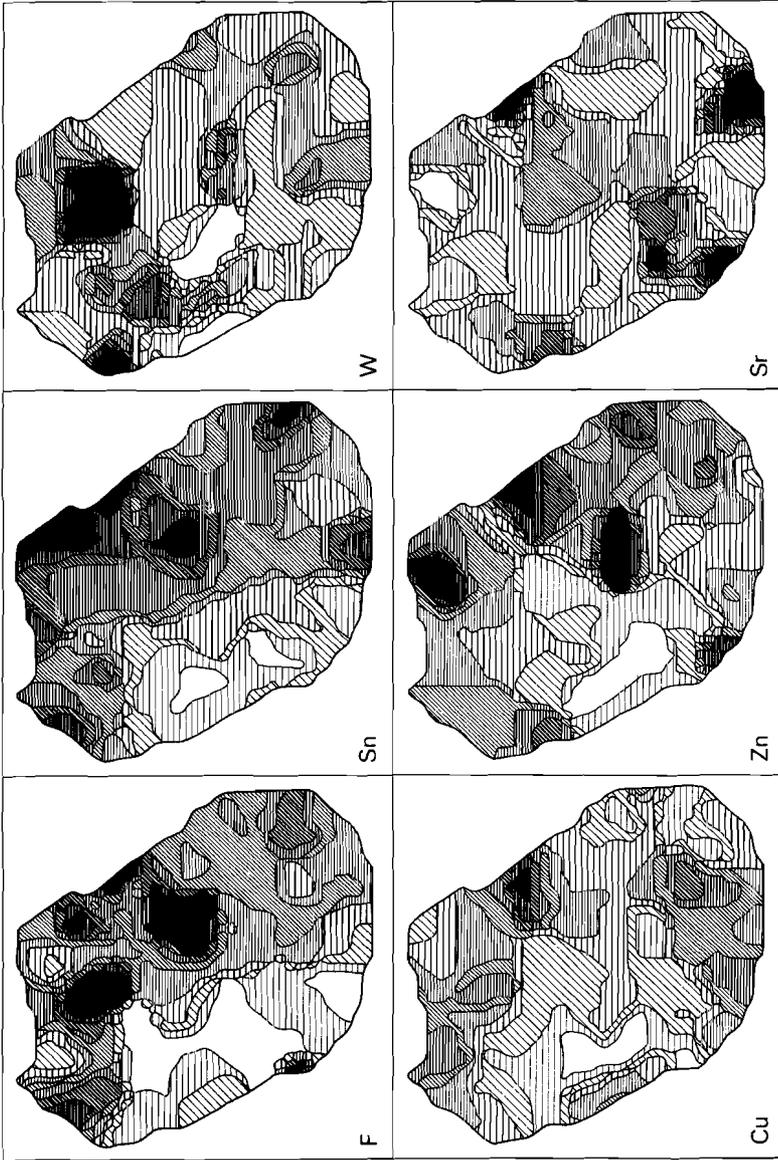


Fig. 4. For explanation see p.21.



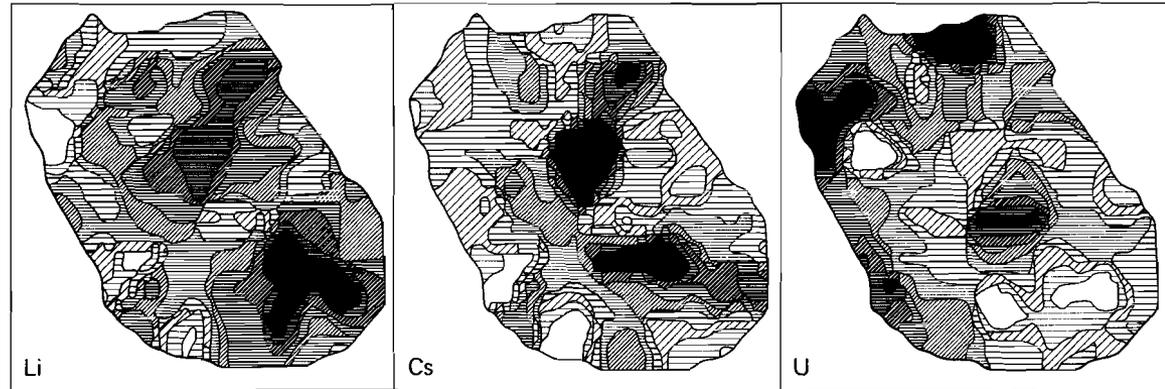


Fig. 4. Distribution of minor and trace elements in the Regoufe granite. The concentration ranges between white and black are: Rb 540–920ppm; Nb 27–59ppm; Ta 10–27ppm; P 1350–2900ppm; Zr 21–57ppm; Ti 145–770 ppm; F 2300–4700ppm; Sn 33–75ppm; W 7–25ppm; Cu 4.5–15ppm; Zn 47–117ppm; Sr 24–53ppm; Li 300–760ppm; Cs 37–93ppm and U 4.3–17ppm. In these ranges the contours are equal interval. The white and black intervals bracket these ranges and are limited by respectively the minimum and maximum values listed in Table I.

TABLE 1

Arithmetic averages (\bar{x}), standard deviations (s) and concentration ranges for the elements in the Regoufe granite. Global averages for low-Ca granites are given for comparison (Rösler and Lange, 1975). The ratio is the ratio between the columns 1 and 4. All concentrations are given in ppm

	\bar{x}	s	Range	Low-Ca granite	Ratio
Sn	54	15	28— 101	3	18
Li	555	145	240— 900	40	14
Cs	58	20	28— 118	5.0	12
W	16	5	7— 34	1.5	11
Rb	700	131	491— 965	150	4.5
Ta	15	6	7— 35	3.5	4.3
F	3410	1080	2000—6880	850	4.0
U	10	4	1— 21	3.5	2.9
P	1960	470	1160—3100	700	2.8
Nb	37	9	19— 59	20	1.9
Zn	80	26	30— 150	50	1.6
Cu	8	3	3— 17	15	0.53
Zr	35	13	17— 85	200	0.18
Ti	354	223	65—1280	2300	0.15
Sr	36	13	13— 109	300	0.12

TABLE 2

Kaiser varimax-rotated factor loadings for 55 samples of the Regoufe granite

	Factor 1	Factor 2	Factor 3
Rb	0.81	0.41	0.30
Nb	0.83		
Ta	0.90		
P	0.79	0.37	
Zr	-0.92		
Ti	-0.91		
Sn	0.51	0.72	0.30
W		0.59	
Cu		0.47	
Zn		0.71	
F	0.51	0.47	
Li			0.95
Cs			0.77
U			-0.46
Sr			
Eigenvalues before rotation			
	6.82	2.29	1.42

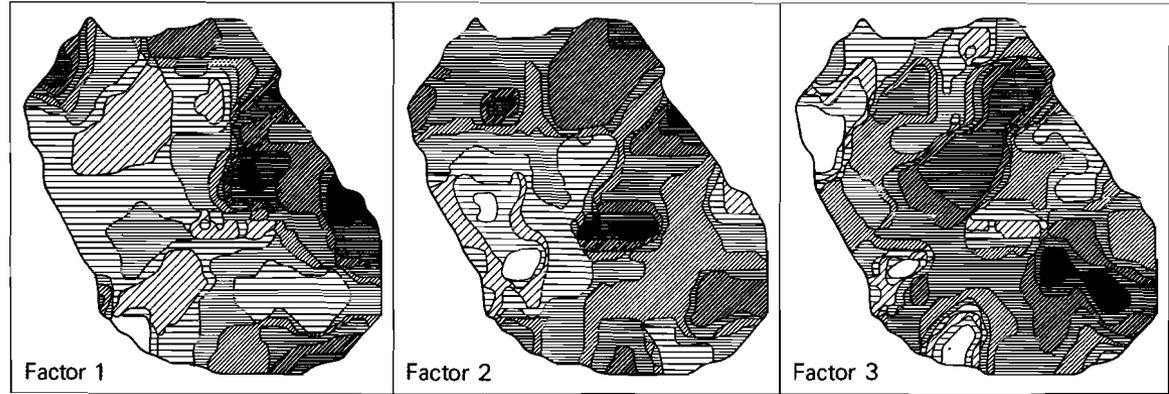


Fig. 5. Distribution of the factor scores in the Regoufe granite. The ranges are: factor 1 -2.17 to $+2.20$; factor 2 -2.24 to $+1.98$; and factor 3 -2.20 to $+1.87$. The contours are equal interval. In all figures, the lowest values are white, shading gradually towards black for the higher values.

model, explaining some 70% of the data variability, best described the different trends. A rerun of the factor analysis after deletion of the four cases that contained results deviating more than 3.0 standard deviations from the mean gave some slight shifts in the factor loading matrix; however, the three-factor model remained essentially the same. The Kaiser varimax-rotated factor loading matrix is given in Table 2. Contour maps of the factor scores of these three factors are given in Fig. 5. Factor 1 has high positive loadings for Rb, P, Nb and Ta and high negative loadings for Ti and Zr. Sn and F give only minor positive contributions. The map of the factor 1 scores outlines a zone in the roof of the granite which is sulphide-bearing, contains little or no biotite and tourmaline and is relatively fine grained and megacryst free. According to one of us (JBHJ) the processes described by this factor can best be related to greisenization and albitization. Factor 2 is controlled by the ore-related metal-elements Sn, Zn, W and Cu with Rb and F also contributing moderately. This factor mainly scores high in areas where W-Sn mineralization occurs within the granite. It therefore seems that the mineralization process had a distinct influence on the trace- and minor-element composition of certain parts of the granite. Factor 3 is dominated by Li and Cs with a moderately negative U loading. It seems to be related to the transition zone within the granite, and may reflect some deuteric alteration process that took place. Further investigations are required to better understand this factor. Sr does not load on any of the three factors.

CONCLUSION

The information gained from multi-element analysis and statistical interpretation elucidates which processes left a distinct imprint on the composition of the Regoufe granite. Even without prior knowledge of the existing mineralizations, the average trace and minor element concentrations clearly indicate that the granite strongly deviates from common low-Ca granites. For the exploration geochemist factor 2, found in the factor analysis, is the most interesting. It outlines zones where circumstances for mineralization are favourable and thus a target for more detailed prospecting.

ACKNOWLEDGEMENTS

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REFERENCES

- Dougenik, J.A. and Sheehan, D.E., 1976. Symap User's Reference Manual. Harvard University, Mass., 5th ed.
- Jöreskog, K.G., Klovan, J.E. and Reyment, R.A., 1976. Geological Factor Analysis. Elsevier, Amsterdam, 178 pp.
- Miesch, A.T., 1981. Estimation of the geochemical threshold and its significance. *J. Geochem. Explor.*, 16: 49–76.
- Nie, N.H., Hull, C.H., Jenking, J.G., Steinbrenner, K. and Bent, D.H., 1975. Statistical Package for the Social Sciences (2nd ed.). McGraw-Hill inc., New York, NY., 675 pp.
- Oen Ing Soen, 1970. Granite intrusion, folding and metamorphism in central and northern Portugal. *Bol. Geol. Min.*, LXXXI: 271–298.
- Pinto, M., Serrano, 1979. Geochemistry and geochronology of granitic rocks from the Aveiro and Viseu district (Northern Portugal). Unpub. Ph. D. thesis, University of Leeds.
- Rösler, H.J. and Lange, H., 1975. Geochemical Tables, (2nd ed). Deut. Verlag Grundstoffind, Leipzig, 674 pp.
- Sluyk, D., 1963. Geology and tin-tungsten deposits of the Regoufe area, northern Portugal. Thesis, University of Amsterdam, 123 pp.
- Tischendorf, G., 1977. Geochemical and petrographic characteristics of silicic magmatic rocks associated with rare-element mineralization. In: M. Stempok, L. Burnol and G. Tischendorf (Editors): MAWAM (Metallization Associated with Acid Magmatism) vol 2. Geologic Survey, Prague; Stuttgart, Schweizerbart, pp. 41–96.

CHAPTER III

Assessment of Mineralogical Influences on the Element Mobility in the W–Sn Enriched Granite of Regoufe and Its Derivatives (Portugal) by Means of XRF Analysis of Unpolished Rock Sections

P.F.M.VAN GAANS, S.P. VRIEND, R.P.E. POORTER, and J.B.H. JANSEN¹

Abstract

The relation of rock chemistry, mineralogy and geochemical processes was studied in the hydrothermally altered, W–Sn specialized granite of Regoufe, northern Portugal. To this end unpolished rock sections sawn from small drill cores were directly analyzed by X-ray fluorescence spectrometry, which is the basic aspect of an approach called Integral Rock Analysis (IRA). Chemical variation within the granite and its derivatives is mainly due to pervasive (auto)metasomatic activity. The effect of chemical weathering on the rock chemistry of this denuded granite is negligible. With the aid of factor analysis the imprints of albitization, muscovitization, apatitization and mineralization are traced throughout the granite and associated dyke system. Alteration generally increases from west to east. In the NE area the separate effect of disseminated wolframite mineralization, apart from the common W–Sn quartz-vein association, and late sericitization are recognized. The importance of mineralogy or major element chemistry in the response to the hydrothermal processes is typically evidenced by the element associations of Sr and of Ti and Zr. Sr preferentially substitutes for K in feldspar and mica in the western region, whereas it mainly substitutes for Ca in phosphates in the most altered eastern zone. As expected, Ti and Zr are closely related to biotite in the western part and appear to remain concentrated in the biotite alteration products. Depletion of Ti and Zr by leaching of refractory minerals is linked to Na₂O, P and metal enrichment through albitization, apatitization and mineralization. The IRA approach offers a rapid method for the acquisition of large quantities of detailed rock geochemical data. An additional advantage is that data are indicative of mineralogy. Selected rock sections were investigated microscopically and by electron-probe microanalysis, resulting, among others, in the discovery of the trace minerals columbotantalite and scorodite in the granite.

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1 Introduction

Not all W–Sn enriched granites have affiliated ore deposits. Understanding of the crystal-chemical parameters that lead to dispersion and concentration of elements may improve the discrimination between barren and productive granitoids (Stemprok 1979). The main rock-forming processes are reflected by rock chemistry. The composition of a sample of a particular granite may reflect the composition of the primary magma, metasomatic and post-magmatic processes, metamorphism, and in the case of surface samples, the effects of weathering (Govett and Nichol 1979). The impact of processes, however, is also determined by the mineralogical nature of the host rock itself. Especially trace element behaviour strongly depends upon the interaction of magma or fluid with existing host minerals (Mellinger 1984). The integration of rock chemistry, mineralogy and mineral chemistry is therefore a prerequisite to a full understanding of the history of the rock. Results of conventional chemical analysis and electron-probe microanalysis are often difficult to interrelate, owing to differences in scale and nature of the object studied. Integral Rock Analysis (IRA) is an attempt to fill this gap. This approach was applied to the granite of Regoufe, Portugal, an example of a 'specialized' granite (Tischendorf 1977), to gain insight in the interaction of mineralogy with metasomatic processes.

2 Geology

The granite of Regoufe, located about 200 km north of Lisbon, is a hydrothermally altered, W–Sn specialized granite of Hercynian age (280 ± 9 Ma, Pinto 1985). The geology of the region was studied by Sluijk (1963). The granite, with a surface expression of about 6 km², discordantly intruded the metasedimentary Beira Schist Formation. The contact is steep in the east and dips away at a low angle in the west. A petrological sketch map is given in Fig. 1. Vriend et al. (1985) distinguished two major rock types on the basis of mineralogical variation. A porphyritic two-mica (P2M) granite with tourmaline grades towards the east into a muscovite albite (MA) granite rich in arsenopyrite, with virtually no K-feldspar megacrysts, biotite or tourmaline (Fig. 1). The eastern part is the most altered. Granitic and aplitic rocks are exposed in rows of small outcrops W and SW of the granite and form a few ring-shaped dykes. Several tungsten-bearing quartz veins in and around the granite have been mined in the past. Post-magmatic processes, including mineralization, are related to various trace element trends within the granite (Vriend et al. 1985; Voncken et al. 1986). Schist roof pendants occur at the higher altitudes. Study of the chemical variation and the interaction of rock type and hydrothermal fluids at the direct contact of a schist inclusion (van Gaans et al. 1986a) revealed enrichment of the inclusion in W, Ta, Nb, Sn, Rb, Cs and K and depletion in P, Ca, Sr, Na, Ti and Zr, relative to normal schist concentrations, which is in accordance with the mineralization trend within

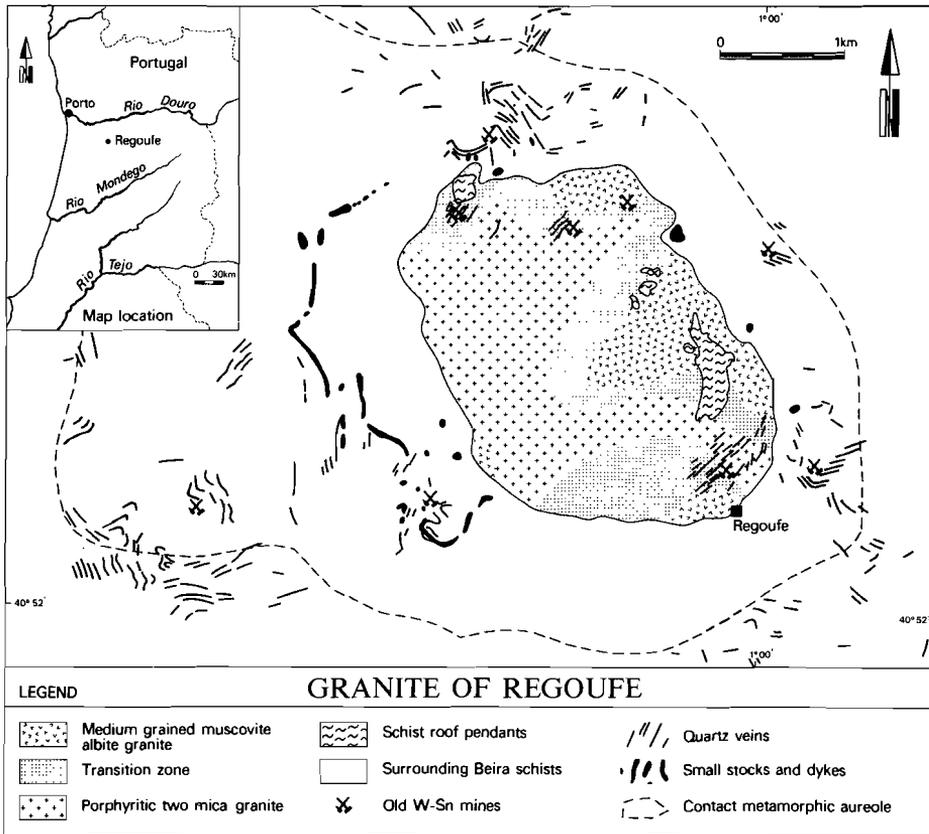


Fig. 1. Petrological sketch map of the Regoufe granite (After Vriend et al. 1985)

the granite itself (Vriend et al. 1985). The schist inclusion appeared to be a favourable deposition site for the ore-related elements. The effect of albitization and greisenization in the schist decreased steeply with increasing distance from the granite contact.

3 Sampling, Analytical and Statistical Techniques

Some 90 small drill cores, with a diameter of 24 mm and a length varying between 5 and 20 cm, were collected in the Regoufe granite and its associated dyke system. Detailed study in a number of subregions of the granite was thought to result in a better understanding of the rock-forming processes (Voncken et al. 1986). Therefore,

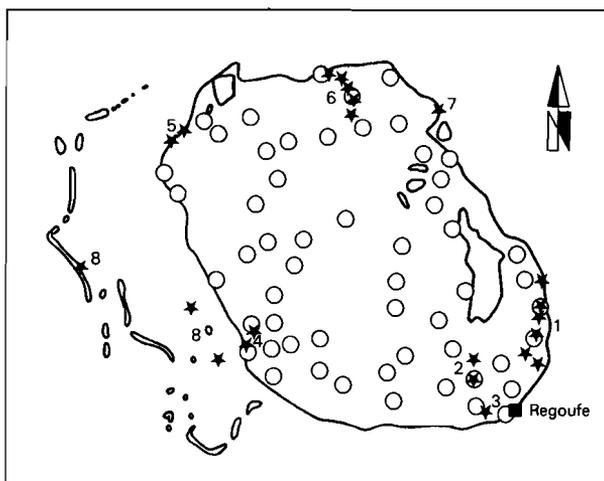


Fig. 2. Sample site map. Drill core locations are indicated by a star. Numbers denote the sampled subregions (number of cores per subregion); 1 MA-1 (6); 2 P2M-2 (5); 3 MA-3 (15); 4 P2M-4 (10); 5 P2M-5 (10); 6 MA-6 (14); 7 NEA (12); 8 WD (16). Open circles indicate conventional geochemical samples (After Vriend et al. 1985)

sampling was concentrated in eight subregions, representative of the variation within the granite and its derivatives (Vriend et al. 1985; Voncken et al. 1986). The main granite is covered by subregions 1 to 6, an aplite in the northeast by subregion 7 (NEA) and the dykes in the west by subregion 8 (WD) (Fig. 2).

Following the IRA method (see Appendix and van Gaans et al. 186a) cores were dissected into ca. 6-mm-thick slices by a diamond saw with a cut of about 3 mm. The terms core, slice and section are illustrated in Fig. 3. Ten to 15 sections per core provided sufficient data for the study of the granite on the various spatial scales. Calculations showed that 10 to 15 sections are sufficient to adequately estimate (trace) element contents, including those occurring in small discrete particles, and to give a reasonable chance of detecting trace minerals (Grassia 1986).

Some 1000 rock sections were analyzed by XRF for SiO_2 , Na_2O , K_2O , CaO , Cs , Sn , Ti , P , Ta , Nb , W , Rb , Sr and Zr using a Philips PW 1400 with automatic sample changer. The exposed part of the sections was 22 mm. Pressed powder tablets of artificial and international natural granite standards were included for calibration. As the focus of this study is inter-element correlations and not absolute tenors, for reasons of expediency, no further matrix corrections were applied.

Results of 55 conventionally analyzed samples of Regoufe granite were used for comparative purposes (Vriend et al. 1985; Vriend unpubl. data). The samples are composites of ten chips collected over an area of 500 m². Major elements were analyzed wet chemically (Shapiro 1967) and XRF analyses of pressed powder briquettes were made for trace elements. IRA concentration levels for most elements

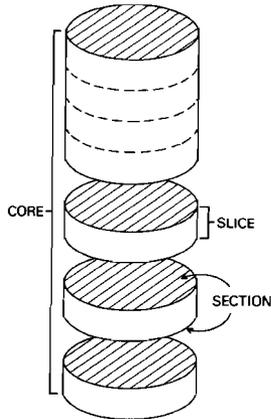


Fig. 3. Illustration of the terms core, slice and section

are, considering the spatially different sample coverage (Fig. 2), in agreement with the conventionally obtained results (Table 1). Significant differences in the concentration level between IRA and conventional results are due to uncorrected mineralogical matrix effects (de Jongh 1970; van Gaans et al. 1986b) which do not greatly influence correlation coefficients (van Gaans et al. 1986a). For all elements the displayed chemical variation among subregions within the granite is in accordance with the distribution maps of conventional results (Vriend et al. 1985, 'Vriend, unpubl. data). Thus, the IRA data set has an internally consistent, relative basis.

Data were interpreted with the aid of SPSS and BMDP statistical software (Nie et al. 1975; Hull and Nie 1981; Dixon 1981). The element association patterns were studied by means of component analysis, a type of factor analysis (Le Maitre 1982; Jöreskog et al. 1976). The number of factors was chosen with application of the Gutman criterion, i.e. only unrotated factors with eigenvalues greater than 1.0 are retained. Pearson correlations, used as a measure of association, are adversely affected by the presence of outliers and by skewness of the frequency distributions. Histograms showed that 3.7% of the analyzed sections significantly deviated from the main population for one or more elements. These outliers were removed from the data set. A selection of rock sections with outlying or extreme results was polished for electron-probe microanalysis (EPMA). For the main population a transformation of the general form $x' = \ln(x - \alpha)$, with α adjustment to obtain minimum skewness for the distributions (Miesch 1981; Selinus 1983), was applied to all variables.

Table 1. Results of Integral Rock Analysis (IRA); averages for the various subregions of the granite and its derivatives.^a

Subregion	Western dikes (WD)	Porphyritic two-mica granite (P2M)			mean P2M	Muscovite albite granite (MA)			mean MA	NE Aplite (NEA)	Mean main granite 1-6	Vriend et al. (1985)
	8	2	4	5		1	3	6		7		
W	13	15	13	14	14	16	15	15	15	23	15	16
Sn	54	56	39	55	47	66	58	54	58	85	54	54
Nb	27	18	19	20	19	31	33	33	33	41	29	37
Ta	32	28	24	23	25	32	38	35	36	37	33	16
Ti	170	309	322	361	331	153	90	102	108	82	187	354
Zr	24	31	30	36	32	20	14	17	16	15	21	35
Cs	46	55	29	31	34	48	32	28	34	57	34	49
Rb	635	662	532	513	557	727	739	661	708	963	663	683
K ₂ O	4.09	4.90	4.32	4.39	4.44	3.99	3.91	4.00	3.96	3.74	4.13	4.09
SiO ₂	76.8	74.2	74.3	74.7	74.4	73.4	75.1	74.2	74.4	77.0	74.4	73.1
Sr	46	38	38	41	39	35	50	43	44	64	42	36
CaO	0.27	0.11	0.20	0.22	0.19	0.24	0.40	0.25	0.32	0.24	0.27	0.27
P	1649	1386	1301	1246	1301	2062	2305	2036	2163	2164	1855	1958
Na ₂ O	4.39	2.90	3.46	3.27	3.31	3.68	4.42	4.03	4.13	2.60	3.83	3.53
N	247	47	132	68	247	100	200	175	475	144	722	55

^a The selection of elements measured reflects the major rock-forming processes. IRA data are on an internally consistent, relative basis. The conventional results for the main granite (Vriend et al. 1985; Vriend unpubl. data; see also Fig. 2) are added for comparison. Oxides are in wt%, elements in ppm. N is the number of rock sections or samples.

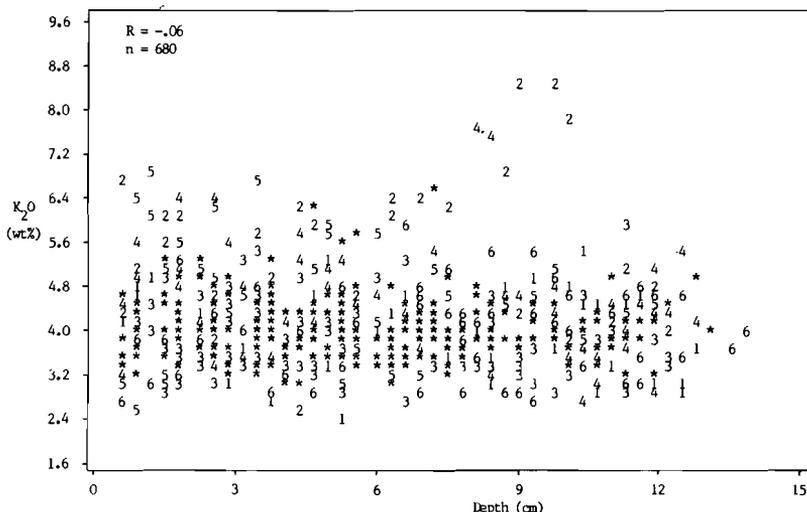


Fig. 4. Variation of K₂O with depth as an inverse measure of weathering for the main granite. The numbers in the plot indicate subregions, an asterisk is used for coinciding points

4 Litho geochemistry

4.1 Weathering

The Regoufe granite has a slightly weathered appearance, while generally a soil cover is lacking. Of the major oxides, K₂O is most sensitive to the weathering of granite (Chessworth 1979). No trend of K₂O content with depth is evident for the Regoufe granite (Fig. 4). Also, none of the other analyzed elements exhibit an obvious increase or decrease in concentration with depth. Clearly, erosion proceeds more rapidly than chemical weathering in the Regoufe environment. In the present study on (trace) element behaviour the influence of weathering on chemistry need not be considered and the collected cores can be used integrally. An additional conclusion is that conventional samples taken at the immediate surface also have no significant overprint of chemical weathering.

4.2 Spatial Element Distributions

The granite subregions 2, 4 and 5, located in the P2M granite and in the transition zone, are chemically distinct from subregions 1, 3 and 6 in the MA granite (Table

1), which is confirmed by Analysis of Variance (ANOVA) and subsequent pairwise contrast tests (van Gaans et al. 1985). The MA granite is higher in CaO, Na₂O, P, Rb, W, Ta and Nb and lower in K₂O, Ti and Zr than the P2M granite, which is interpreted as the result of hydrothermal alteration (Vriend et al. 1985; van Gaans et al. 1985). The composition of the WD is intermediate between the P2M and the MA granite compositions. High tenors of Sn, Cs, Rb and low concentrations of K₂O, Na₂O, Ti and Zr in the NEA are attributed to intense hydrothermal alteration (van Gaans et al. 1985).

4.3 Data Extremes

The rock volume represented by IRA is for single sections smaller than with a single conventional rock analysis. Averaging, inherent to the conventional sample preparation, whereby the effects of chemical extremes and mineral accumulations are diluted, does not occur. Outliers are aberrant for Si, P and Cs, probably because of their high mobility (van Gaans et al. 1986a). In contrast, no local enrichment or depletion outside the normal statistical range of concentrations is encountered for Sn and Zr, suggesting no secondary entrapment within the granite. The dominating mineralogical/structural factor causing an extreme can be determined, and interesting phenomena may be discovered in rock sections falling in the tails of the frequency distributions. Trace minerals that were unknown in the granitic rocks of Regoufe were discovered by EPMA of selected sections. Columbo-tantalite grains [(Nb_{1.38}Ta_{0.57}Ti_{0.07}Fe_{0.55}Mn_{0.44})O₆] were identified in a section of MA-6, which was highest in Ta and Nb (Plate 1). Scorodite [(Fe,Al)(As,P,Bi)O₄·2H₂O] was detected in the section highest in P₂O₅ (5.3%) of the NEA. A phosphorus outlier of 3.0% P₂O₅ from the eastern margin of the Regoufe granite (MA-1) (versus a maximum of 0.71% in conventional samples) was microscopically identified as an apatite bearing quartz veinlet, thus clearly showing the mobility of P.

4.4 Element Association Patterns Within the Main Granite

R-mode Component Analysis was applied to the analytical results of single sections, to the means per core and for comparison also to the conventionally analyzed samples of the main granite, to study the interrelation of the chemical elements. The Varimax-rotated factor-loading matrices for sections (F_{sect}), cores (F_{core}) and conventional bulk samples (F_{bulk}) are listed in Table 2. Ta was excluded from the factor model for sections because it showed no significant correlations with the other elements, due to the large relative random error for analytical values near the detection limit.

The mineralogical influence on the element association patterns is emphasized by the extracted factors for rock sections. CaO, Sr and P form an apatite factor

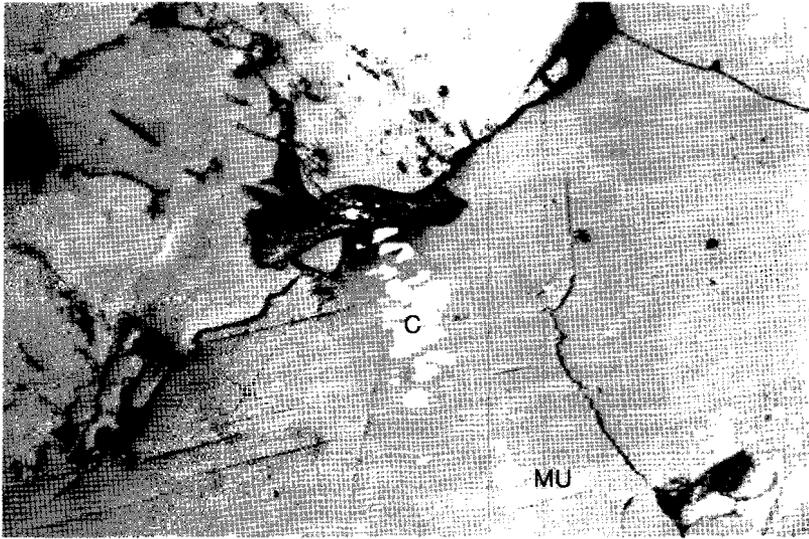


Plate 1. Example of columbo-tantalite (C) embedded in muscovite (MU). Incident light, width of photograph ca. 0.2 mm

$F3_{sect}$. Apatite occurs as primary magmatic inclusions and as a late hydrothermal mineral (Sluijk 1963; this study). This factor is therefore an expression of apatitization. The combination of CaO with Sr is present for all three types of samples in $F3_{sect}$, $F3_{core}$ and $F3_{bulk}$. K_2O , Rb and negative SiO_2 in $F4_{sect}$ may reflect muscovitization or the closure effect (Le Maitre 1982) between K-feldspar (muscovite, biotite) and quartz. The positive association of Rb with K for sections contrasts with their inverse association in $F1_{core}$ and $F1_{bulk}$, which reflect the observed increase of Rb and decrease of K with alteration (Table 1). Evidently, the small-scale mineralogical association dominates for rock sections, whereas the larger scale alteration trend dominates for means per core and bulk samples. For similar reasons, the negative association of Ti and Zr with Nb, Ta and Rb in $F1_{core}$ and $F1_{bulk}$ is obliterated for sections where the chemical or spatial relation of all these elements to biotite takes its effects. $F1_{sect}$ has high positive loadings for Ti and Zr and negative loadings for Na_2O and also P; it links the leaching of refractory minerals to processes like albitization and apatitization. Its mirror image forms part of $F1_{core}$ and the almost identical $F1_{bulk}$, which have a more pronounced apatite component. The loadings of Ta, Nb and Rb, and for bulk samples also Sn, on $F1_{core}$ and $F1_{bulk}$ relate leaching of refractories to mineralization. $F2_{sect}$ with high positive loadings for Nb, W, Cs, Sn and Rb obviously describes a mineralization process. $F2_{core}$ is similar to $F2_{sect}$ with only a moderate Nb contribution. $F2_{bulk}$ is a simple W-Sn mineralization factor; here, the relation of mineralization to the other processes is expressed more explicitly in $F1_{bulk}$.

Table 2. Varimax-rotated factor-loading matrices for the Regoufe main granite (only loadings of over 0.4 are given)

A. IRA data of sections				B. IRA mean data per core			C. Conventional data (after Vriend et al., 1985)				
	F1 _{sect}	F2 _{sect}	F3 _{sect}	F4 _{sect}	F1 _{core}	F2 _{core}	F3 _{core}	F1 _{bulk}	F2 _{bulk}	F3 _{bulk}	F4 _{bulk}
W		0.67			W	0.70		W	0.91		
Sn		0.88			Sn	0.85		Sn	0.63	0.51	
Nb		0.79			Nb	0.69	0.55	Nb	0.87		
					Ta	0.69		Ta	0.82		
Ti	0.86				Ti	-0.92		Ti	-0.94		
Zr	0.91				Zr	-0.92		Zr	-0.93		
Cs		0.73			Cs		0.82	Cs			0.83
Rb		0.67		0.61	Rb	0.47	0.71	Rb	0.86		
K ₂ O				0.88	K ₂ O	-0.70		K ₂ O	-0.63		0.48
SiO ₂				-0.75	SiO ₂		0.75	SiO ₂			-0.58
Sr			0.76		Sr		0.80	Sr		0.91	
CaO			0.82		CaO	0.64	0.47	CaO		0.78	
P	-0.44		0.73		P	0.82		P	0.88		
Na ₂ O	-0.63				Na ₂ O	0.84		Na ₂ O	0.71	-0.43	

Table 3. Varimax-rotated factor-loading matrices for the sampled subregions (IRA data of sections; only loadings of over 0.4 are given)^a

	WD				P2M-2			P2M-4				P2M-5			
	F _{min}	F _{biot}	F _{ap}	F _{mu}	F _{min}	F _{ap}	F _{mu}	F _{min}	F _{biot-alb}	F _{ap}	F _{mu}	F _{min}	F _{biot}	F _{ap}	F _{mu}
W	0.74				W	0.61		W	0.72			W	0.71		
Sn	0.72				Sn	0.96		Sn	0.90			Sn	0.81		
Nb	0.67				Nb		0.95	Nb	0.92			Nb	0.78		
Ti		0.86			Ti	0.91		Ti	0.63	0.57		Ti	0.64	0.69	
Zr		0.91			Zr	0.52		Zr		0.86		Zr		0.90	
Cs		0.68		0.48	Cs		0.84	Cs	0.66	0.50		Cs	0.62	0.56	
Rb				0.88	Rb		0.88	Rb	0.46		0.82	Rb			0.87
K ₂ O				0.90	K ₂ O		0.92	K ₂ O			0.90	K ₂ O			0.91
SiO ₂				-0.72	SiO ₂		-0.84	SiO ₂		0.48	-0.56	SiO ₂			-0.81
Sr			0.66		Sr		0.87	Sr			0.68	Sr	-0.53		0.66
CaO			0.85		CaO		0.81	CaO		0.94		CaO			0.92
P			0.89		P		0.88	P		0.93		P			0.88
Na ₂ O			0.70		Na ₂ O		0.87	Na ₂ O		-0.43	0.63	Na ₂ O			0.87

	MA-1				MA-3			MA-6				NEA					
	F _{min-mu}	F _{biot}	F _{ap}	F _{alb}	F _{min}	F _{ap}	F _{mu-alb}	F _{min1}	F _{ap}	F _{ser}	F _{min2}	F _{alb}	F _{min1-alb}	F _{ap}	F _{ser}	F _{min2}	F _{alb}
W	0.71				W	0.59		W	0.49		0.64		W				0.75
Sn	0.84				Sn	0.85		Sn	0.90				Sn	0.79			0.50
Nb	0.77				Nb	0.78		Nb			0.87		Nb				0.75
Ti	0.42	0.85			Ti	0.89		Ti	0.86				Ti	0.92			
Zr		0.90			Zr	0.56		Zr	0.58	-0.53			Zr	0.50	-0.64		
Cs	0.58	0.66			Cs	0.72	0.49	Cs	0.65	0.67			Cs		0.69		
Rb	0.94				Rb	0.54	0.74	Rb		0.94			Rb		0.97		
K ₂ O	0.74				K ₂ O		0.85	K ₂ O		0.89			K ₂ O		0.90		
SiO ₂	-0.64			0.49	SiO ₂		-0.86	SiO ₂			-0.69		SiO ₂				-0.88
Sr				0.59	Sr		0.80	Sr		0.60			Sr	0.64	0.42		
CaO			0.92		CaO		0.93	CaO		0.96			CaO	0.86			
P			0.91		P		0.92	P		0.93			P	0.91			
Na ₂ O				-0.86	Na ₂ O	-0.55	0.44	Na ₂ O			0.74	Na ₂ O	-0.52				0.69

^a The tentative geochemical interpretation of the factors is indicated by the suffixes: *min* mineralization; *min1* Sn(W) quartz-vein type mineralization; *min2* disseminated W mineralization; *biot* biotite; *ap* apatite/apatitization; *mu* muscovitization; *alb* albitization; *ser* late sericitization.

4.5 Element Association Patterns Within the Subregions

Component Analysis was applied to rock section data for the subregions (Table 3). A sufficient number of analyses (Howarth and Sinding-Larsen 1983) per subregion is available (Table 1).

A mineralization factor F_{\min} is present for all subregions, commonly composed of Sn, W, Nb, Cs, Rb and mostly Ti. For the WD this association is more or less divided over a simple mineralization factor and the biotite factor. For MA-6 and NEA an Nb–W factor $F_{\min 2}$, with only a minor Sn contribution in NEA, is found separate from the major Sn-related factor $F_{\min 1}$. The two factors probably express different mineralization types. In the NE part small disseminated wolframite mineralizations occur within the granite (this study) which is in contrast to the common quartz-vein, W–Sn type mineralization.

Zr and Ti, which are depleted in the Regoufe granite (Vriend et al. 1985), invariably combine in F_{biot} . Except for the NEA, they load on the same factors as Cs, which is highly enriched. Zr–Ti depletion may be related to albitization or apatitization (see above). The association with the incompatible element Cs probably stems from the close association of Ti and Zr with biotite or its alteration products (van Gaans et al., in prep.). In the three-factor models (P2M-2 and MA-3) Ti, Zr and Cs load positively on F_{\min} , indicating that the ore elements have some spatial relation to (altered) biotite. In the factor models for the MA-6 and NEA, Zr loads on two different factors. Outside the Zr–Ti association on F_{\min} , an alkali factor F_{ser} with a negative Zr loading is present. This alkali metal versus Zr factor points towards the leaching of Zr with late sericitization which is largely restricted to the NE part of the Regoufe area.

SiO_2 inversely associates either with Na_2O in F_{alb} (MA, P2M-4, NEA) or with K_2O , Rb and Sr or Cs in F_{mu} (P2M-2, P2M-4, MA-1, WD), in MA-3 with both in one factor $F_{\text{alb-mu}}$. This may reflect albitization and muscovitization respectively, or the predominance of either albite or K-feldspar as the most abundant mineral next to quartz. Although the Na_2O content of the NEA is relatively low (Table 1), the relative importance of albite over K-feldspar, as observed in thin section, is confirmed by F_{alb} in the component analysis.

K_2O and Rb generally load on the same factor, either F_{mu} or F_{ser} , in the WD, the MA granite and the NEA together with Cs, in the P2M granite and the NEA with Sr. In F_{mu} they oppose SiO_2 , in F_{ser} (MA-6, NEA) Zr.

CaO and P consistently form an apatite factor F_{ap} , in the P2M granite together with Na_2O , in the MA granite and the northeastern aplite commonly together with Sr (MA-3, MA-6, NEA) and in the western dykes (WD) with both.

The Sr affinities thus vary among subregions. Sr associates with K_2O and Rb and inversely with SiO_2 for the P2M granite (F_{mu}). In the factor model for P2M-5 Sr also loads negatively on F_{\min} . Sr loads on F_{ap} in the WD and the NEA and in part of the MA granite (MA-3 and MA-6), in MA-1 Sr and SiO_2 together oppose Na_2O in F_{alb} . In the NEA Sr also loads on F_{ser} . The above indicates that Sr acts mainly as a substitute for K in the P2M granite and mainly as a substitute for Ca in the MA granite and the aplites and dykes. In the NEA both substitutions appear

to be of importance. This ambiguous behaviour of Sr explains why the conventional general study of Vriend et al. (1985) failed to explain the Sr variance.

5 Discussion and Conclusions

Owing to the small rock volume, mineralogically determined element associations greatly affect the association patterns for rock sections. Larger scale processes and features are stressed if mean concentrations per core are considered. Their association patterns therefore more closely resemble the patterns obtained on conventional samples. The expression of metasomatic and ore-forming processes varies with the scale of observation. Therefore, the resolution of rock chemical data is different for each scale. Mineralogical and local phenomena may go unnoticed if only bulk chemistry is considered. Integration of the association patterns of all scales, including results of conventional chemical analysis and microscope techniques, elucidates the interaction of the various rock-forming phenomena.

The influence of weathering on rock chemistry of the Regoufe granite is negligible for major and trace elements, provided that the physical rock structure is retained. Erosion is obviously faster than chemical weathering in this type of environment.

The effects of the hydrothermal processes on rock chemistry are recognized throughout the Regoufe granite and its derivatives. Albitization, W–Sn quartz-vein type mineralization, muscovitization and apatitization and in the NE, also disseminated W-mineralization and late sericitization, are distinguished. Although the exact compositions and relative importance of the various factors differ among subregions, association patterns of the individual subregions, based on rock sections, basically describe the same features and processes as identified for the whole main granite. The post-magmatic processes obviously not only induced chemical variation *among*, but also *within* subregions. Therefore, despite local variation, the detailed results presented here indicate the pervasive nature of the processes. The decrease in the extent of alteration from the roof zone towards the deeper parts of the granite is apparent from the gradually changing concentrations and by the shifts in the element association patterns, whereby the distinct patterns for the NE are noteworthy.

The element correlations clearly illustrate the impact of the mineralogical composition of the granite in hydrothermal alteration. The interaction of mineralogy with metasomatic processes can be identified and evaluated e.g., in an apatite factor, a biotite influence for Ti and Zr, mica, feldspar and quartz components. Sr illustrates both the importance of mineralogy or major element chemistry and the effect of varying alteration. It preferentially substitutes for K, in feldspar or mica, in the P2M granite and for Ca, in phosphate minerals, in the WD and the MA granite. In the NEA both substitutions are of importance.

Facilitated by the selection based on rock chemistry (IRA) of sections, interesting features, like an apatite-bearing quartz veinlet, and some trace minerals were

identified. Columbo-tantalite was detected in the MA granite, scorodite was found in the NEA.

Appendix: The IRA Approach

Flat rock sections cut from drill-cores are analyzed by XRF spectrometry as they are, without further sample preparation, yielding a total chemical analysis for each section. At the cost of some loss in accuracy and precision much is gained by: a better resolution of within-sample inhomogeneities, a more direct relation between rock chemistry and mineralogy, the availability of the sections for later investigation, e.g. ore microscopy and electron-probe microanalysis (EPMA) and effectiveness in time and costs. The IRA approach is described in detail by van Gaans et al. (1986a).

Evaluation of the IRA method (van Gaans et al. 1986b, c) showed that precision for repeat analysis of the same rock section at the 95% confidence level is normally within 8%. Precision of XRF analysis of pressed powder tablets is only 25 to 50% better. Accuracy of the method mainly depends on the type of matrix correction applied. Insufficient matrix correction usually causes approximately linear systematic deviations which can be empirically corrected. However, for exploration purposes and for the study of geochemical processes, relative figures are more important than absolute values (Levinson 1974; Fletcher 1981) and in these instances elaborate matrix corrections are rarely needed. Within a geochemical setting of volcanic rocks with associated sulphide deposits (van Gaans et al. 1986c), correlations between IRA and conventional results were better than 0.94 (van Gaans et al. 1986c).

In the same study a considerable reduction of 60% in analyst time was achieved compared to conventional routine XRF analysis of trace and major elements. Instrument time is generally ten times longer using a sequential spectrometer. However, the consequent ten-fold increase of data allows the study of rock chemistry on 'conventional' as well as on smaller, within-sample, down to mineral scales. Moreover, sample throughput is fully automated and if necessary can be greatly increased with a simultaneous spectrometer. For subsequent study by more expensive and more labour-intensive techniques, such as microscopy, X-ray diffraction, electron-probe microanalysis, scanning electron microscopy or neutron activation-induced beta-autoradiography, sections of interest can be selected on the basis of the IRA data, providing a more (cost-)efficient use of these methods.

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References

- Chessworth W (1979) The major element geochemistry and the mineralogical evolution of granitic rocks during weathering. *Phys Chem Earth* 11:305–313
- Dixon WJ (ed) (1981) *BMDP Statistical software 1981*. University of California Press, Berkeley, Calif
- Fletcher WK (1981) *Analytical methods in geochemical prospecting*. Elsevier Scientific Publishing Company, Amsterdam, 255 pp. (Handbook of Exploration Geochemistry Govett, GJS ed) vol 1)
- Gaans PFM van, Vriend SP, Schuiling RD (1985) Integral rock analysis; a new approach to lithogeochemical exploration. Application: the granite of Regoufe. Report to the Commission of the European Communities, contract MSM-073-NL.
- Gaans PFM van, Vriend SP, Schuiling RD (1986a) Integral rock analysis; a new approach in lithogeochemical exploration with use of X-ray fluorescence spectrometry. *Geol Mijnbouw* 65:205–213
- Gaans PFM van, Vriend SP, Wal J van der, Schuiling RD (1986b) Integral rock analysis; a new approach to lithogeochemical exploration. Application: carboniferous sediments of a coal exploration drilling, Limburg, the Netherlands. Report to the Commission of the European Communities, contract MSM-073-NL
- Gaans PFM van, Vriend SP, Meyer HC, Finlow-Bates T, Wal J van der, Schuiling RD (1986c) Integral rock analysis; a new approach to lithogeochemical exploration: exploration for volcanogenic massive sulphides, the Pyrite Belt, Huelva, Spain. A pilot study based on Ti–Zr chemistry. Report to the Commission of the European Communities, contract MSM-073-NL
- Gaans PFM van, Vriend SP, Poorter RPE, Jansen JBH (in prep) Changing element association patterns with hydrothermal processes in the W–Sn enriched Regoufe granite and its derivatives, Portugal
- Govett GJS, Nichol I (1979) Lithogeochemistry in mineral exploration. In: Hood PJ (ed) *Geophysics and geochemistry in the search of metallic ores*. *Geol Surv Can Ec Geol Rep* 31:339–362
- Grassia A (1986) “Discovery” sampling in geological research Part 2. *Math Geol* 18:323–328
- Howarth RJ, Sinding-Larsen R (1983) Multivariate analysis. In: Howarth RJ (ed) *Statistics and data analysis in geochemical prospecting*. Elsevier Scientific, Amsterdam pp 207–286 (Handbook of Exploration Geochemistry, vol 2)
- Hull CH, Nie NH (1981) *SPSS update 7–9*. McGraw-Hill, New York
- Jöreskog KG, Klován JE, Reyment RA (1976) *Geological factor analysis*. Elsevier Scientific, Amsterdam (Methods in Geomathematics 1)
- Jongh WK de (1970) Heterogeneity effects in X-ray fluorescence analysis. *Philips Analytical Equipment Bulletin*
- Levinson AA (1974) *Introduction to exploration geochemistry*. Wilmette, Illinois, USA, 612 pp
- Maitre RW le (1982) *Numerical petrology. Statistical interpretation of geochemical data*. Elsevier Scientific, Amsterdam
- Mellinger M (1984) The application of correspondence analysis to the study of lithogeochemical data: general strategy and usefulness of various data-coding schemes. *J Geochem Expl* 21:455–469
- Miesch AT (1981) Estimation of the geochemical threshold and its statistical significance. *J Geochem Expl* 16:49–76
- Nie NH, Hull CH, Jenkins JG, Steinbrenner K, Bent DH (1975) *Statistical Package for the Social Sciences*, 2nd edition. McGraw-Hill, New York
- Pinto MS (1985) Carboniferous granitoids of Portugal: some geochemical and geochronological aspects. In: Lemos de Sousa MJ, Wagner RH (ed) *Papers on the Carboniferous of the Iberian Peninsula. Sedimentology, Stratigraphy, Paleontology, Tectonics and Geochronology* pp 15–33
- Selinus O (1983) Factor and discriminant analysis to lithogeochemical prospecting in an area of central Sweden. *J Geochem Expl* 19:619–642
- Shapiro L (1967) Rapid analysis of rocks and minerals by a single-solution method. *US Geol Surv Prof Pap* 575B:187–191
- Sluijk D (1963) *Geology and tin-tungsten deposits of the Regoufe area, northern Portugal*. Thesis, University of Amsterdam
- Stemprok M (1979) Mineralized granites and their origin. *Episodes* 3:20–24
- Tischendorf G (1977) Geochemical and petrographic characteristics of silicic magmatic rocks associated with rare-element mineralization. In: Stemprok M, Burnol L, Tischendorf G (eds) *MAWAM (Metal-*

- lization associated with acid magmatism), vol 2. Geologic Survey, Prague; Stuttgart, Schweizerbart, pp 41–96
- Voncken JHL, Vriend SP, Kocken JWM, Jansen JBH (1986) Determination of beryllium and its distribution in rocks of the Sn–W granite of Regoufe, N-Portugal. *Chem Geol* 56:93–103
- Vriend SP, Oosterom MG, Bussink RW, Jansen JBH (1985) Trace element behaviour in the W–Sn granite of Regoufe, Portugal. *J Geochem Expl* 23:12–25

CHAPTER IV

The application of fuzzy *c*-means cluster analysis and non-linear mapping to geochemical datasets: examples from Portugal

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Abstract—In the interpretation of relatively small multivariate datasets, deviations from homogeneity may cause severe problems. In these cases fuzzy *c*-means cluster analysis (FCM) and non-linear mapping (NLM) are conceptually suited to discern structure in the datasets. Particularly, the combined use of FCM and NLM furnishes a powerful method to find meaningful data groupings within a dataset. This is illustrated with two case studies, for water and combined water and stream sediment analyses, respectively, where FCM and NLM were applied. The results are easily related to geology, mineral occurrences and environmental factors.

INTRODUCTION

THE MULTI-ELEMENT analysis of geochemical samples has virtually become a routine procedure. In a single- or multi-pass analysis of the same sample preparation, techniques such as XRF, ICPE, INAA, AAS and ion chromatography, used alone or in combination, can easily yield data for up to 40 elements. The interpretation of the resulting data matrices requires a sound geochemical background, but often benefits from sophisticated statistical manipulations. An excellent review of many of the more popular statistical techniques is given by HOWARTH and SINDING-LARSEN (1983).

One recurrent problem is the requirement for population homogeneity by many classical multivariate statistical procedures. In order to use many statistical techniques to their full advantage the variables must be multivariate-normally distributed. For the interpretation of correlation coefficients, and the many techniques based on the analysis of the correlation matrix, strict adherence to the above is mandatory. The examination of datasets for deviations from normality is usually undertaken with the aid of histograms, cumulative frequency curves, and (principal) component and factor analysis. This may be a tedious iterative affair if the population is to be subdivided because of multimodality or outliers. In the case of multimodality, subpopulations, which are often difficult to define precisely, should be treated separately. Cases containing outlying values can be used in the final interpretation as their coordinates within a given model can be calculated. However, these cases must be omitted from the calculation of correlations, regression coefficients and other estimates of population parameters that are used to derive a generalized model for a certain dataset. Thus, adhering to the above guidelines, it is often impossible to establish in smaller sample sets (i.e. with size less than a hundred) a sufficiently large homogeneous

dataset with the needed requirements to build an initial general model.

In cases where inhomogeneity in a dataset is suspected due to *a priori* knowledge of a classificatory parameter, such as the geology at the sample point, discriminant analysis (DA) may be helpful in determining if such a classification has statistical significance. However, as has been shown by FOLEY (1971), DA is only effective if a large number of cases, relative to the number of variables, per group is available. Secondly, compositional overlap between various subgroups, an oft encountered phenomenon in geochemistry, is not adequately dealt with in conventional DA. When the differences between groups are large the above considerations are of no importance, however, in such cases only the obvious has been proven. Finally, it may be possible to confirm the influence of a known parameter with DA, whilst the influence of some important but unknown parameter goes unnoticed.

Clustering techniques are generally used to discover such unknown parameters. Hierarchical clustering yields a series of successive agglomerations of samples on the basis of successively coarser partitions. Iterative partitioning techniques, of which *c*-means clustering is an example, are used if a partition in a predetermined number of groups is appropriate (HOWARTH and SINDING-LARSEN, 1983). However, just as conventional DA, most conventional clustering techniques have the disadvantage that they are too rigid and do not consider compositional overlap between clusters.

Because of the above difficulties, which are particularly encountered in the interpretation of smaller datasets, techniques which neither require multivariate normality nor *a priori* knowledge of classificatory parameters and allow for a certain overlap seem the most appropriate for geochemical studies. We find that together with the standard univariate and bivariate techniques, the application of fuzzy

c-means cluster analysis (FCM) in combination with non-linear mapping (NLM) greatly facilitates the interpretation of data. The two techniques are based on different theoretical considerations, and thus any similarities between the data structures elucidated in the application of FCM and NLM are a strong indication for their true existence. The huge computer costs of similar techniques noted in the past (LEFEBVRE and DAVID, 1977) need no longer impede their utilization. For both techniques existing computer programs were modified to suit the present needs and adapted to run on inexpensive personal computers.

After a brief introduction into the theoretical background of FCM and NLM, two case studies will be presented. These illustrate the effectiveness of the approach, together with the pitfalls encountered and the reasoning required in reaching a satisfactory interpretation.

THEORETICAL BACKGROUND

Conventional (hard) *c*-means clustering (e.g. DIXON, 1981) is an iterative partitioning of cases among subgroups or clusters, which is directed to minimize the maximum distance of a case to its cluster center (ENGELMAN, 1980). Cases are unambiguously allocated to one cluster only, based on a notion of uncertainty in terms of the chance that this is the most likely configuration (stochastic or probabilistic approach). Consequently, cases that are really intermediate between two or more clusters, or outliers that belong to none of the clusters, are forced into a cluster. The influence of these misfits on the cluster to which they are allotted is too large and their influence on the other clusters is nil; the model is a distorted representation of the existing data structure.

The concept of fuzziness, introduced by ZADEH (1965), takes a different approach towards uncertainty. Some fuzziness or vagueness is allowed in the description of the cluster-model. Interest is not in whether chances are largest that a case belongs entirely to one specific cluster, but in the similarity between case and cluster and how much they are alike (BEZDEK, 1981). In fuzzy models, likeness or similarity is indicated by a continuous function (membership) between zero (completely different) and one (exactly the same). The memberships of a case to all clusters sum up to 1. Hence, FCM allows intermediate cases to be recognized as such by assigning similar memberships of the case to the clusters concerned. Outliers contribute equally to all clusters. In computing the cluster centers each case is weighed by its membership, thus outliers have less influence on the final cluster configuration in the fuzzy model than in the hard model.

Recently a new computer program for this type of multivariate clustering was published (BEZDEK *et al.*,

Table 1. Algorithms used in fuzzy *c*-means cluster analysis

In the case of *C* clusters for *N* cases analyzed for *V* variables (*x*) and a fuzzy exponent *q* then the cluster center (CC) of the *i*th cluster for the *j*th variable is:

$$CC_{ij} = \frac{\sum_{k=1}^N (u_{ki})^q \cdot x_{kj}}{\sum_{k=1}^N (u_{ki})^q}$$

and the membership (*u*) for the *k*th case to the *i*th cluster:

$$u_{ki} = \frac{[(d_{ki})^2]^{-1/(q-1)}}{\sum_{i=1}^C [(d_{ki})^2]^{-1/(q-1)}}$$

where the standardized distance (*d*) of the *k*th case to the *i*th cluster (with *s_j* as the standard deviation of the *j*th variable) is given by:

$$(d_{ki})^2 = \sum_{j=1}^V [(x_{kj} - CC_{ij})/s_j]^2$$

1984). The actual algorithm used is presented in Table 1. The exponent *q* controls the extent of membership sharing between fuzzy clusters (BEZDEK, 1981). The "fuzziness" of the model increases with *q*. For *q* ⇒ 1 the fuzzy *c*-means clustering converges to conventional hard *c*-means clustering. Cluster centers are then the normal centers of gravity of the cluster data cloud and memberships are either 1 or 0. For *q* ⇒ +∞, all cluster centers converge to the overall center of the data cloud, memberships of all cases to all clusters are equal (and thus equal to 1/*C*, where *C* is the number of clusters). According to BEZDEK *et al.* (1984), there is no theoretical basis for the choice of *q*. Generally, *q* is assigned a value between 1.5 and 3. Clustering is carried out in an iterative procedure, which starts with the generation of a series of random numbers initial cluster memberships. Thus, two runs on the same dataset do not necessarily yield the same result. However, any similarity of run results gives an indication of the stability of the solutions, and the reality of the revealed data structure.

The number of clusters, both in hard and fuzzy models, may either be predetermined on empirical grounds, or models for different numbers of clusters may be compared on the basis of a suitable validity functional (BEZDEK, 1981; BEZDEK *et al.*, 1984). For FCM the classification entropy *H* and the partition coefficient *F* are such functionals (Table 2). *F* is conceptually comparable to the *F*-ratio of the pooled within-cluster (co)variance and the between-cluster (co)variance. It is closest to one for the most significant clustering. *H*, which resembles mathematically the thermodynamic entropy, approaches zero for the most significant clustering. Both functionals describe properties of the model rather than of the initial raw data. The limiting values for both functionals are dependent on the number of clusters (Table 2). Often when these parameters do not give conclusive evidence, the number of clusters is decided on the basis

Table 2. Classification entropy H and partition coefficient F functions and their limiting values

$H = - \sum_{k=1}^N \sum_{i=1}^C [u_{ki} \cdot \log (u_{ki})/N]$	$0 \leq H \leq \log (C)$
$F = \sum_{k=1}^N \sum_{i=1}^C [(u_{ki})^2/N]$	$1/C \leq F \leq 1$

of an empirical approach in combination with the indications obtained from the F and H parameters.

Fuzzy *c*-means clustering was chosen over other fuzzy techniques for the datasets at hand because the influence of various geochemical controls on the samples was sought. Related applications in geology of the fuzzy concept are those of GRANATH (1984), who uses the fuzzy-set theory in discriminant analysis, and of YU and XIE (1985), who apply a fuzzy hierarchical clustering to detect ore-element association patterns.

The NLM algorithm was first presented by SAMMON (1969, 1970) and has been applied to geochemical data by GARRETT (1973), HOWARTH (1973a,b), GLASBY *et al.* (1974), HOWARTH *et al.* (1977) and CHORK and GOVETT (1985). A great advantage of NLM and the reason for us to select this technique to evaluate the FCM results is that no presumptions about the number of clusters or even the existence of subgroups have to be made. The NLM basically determines a 2- or 3-dimensional image of a V -dimensional data cloud such that the interdata distances are minimally distorted. The distances displayed by NLM are therefore closer to reality than those displayed in the simple projection planes obtained with principal component analysis (see HOWARTH and SINDING-LARSEN, 1983, Fig. 6.18). Mapping is achieved by iteratively minimizing over all N samples the following criterion:

$$D = \frac{1}{\sum_{k=1}^N \sum_{k'=1}^{k-1} d_{kk'}} \sum_{k=1}^N \sum_{k'=1}^{k-1} \frac{(d_{kk'} - d_{kk'}^*)^2}{d_{kk'}}$$

$d_{kk'}$: distance in the original V -dim. variable space

$d_{kk'}^*$: distance in the 2 or 3-dim. mapping space.

using a so-called steepest descent method (SAMMON, 1969). The value of this mapping error D is normally unstable at the beginning of the iteration process, and then stabilizes while approaching asymptotically a minimum value.

NLM is, according to HOWARTH (1973a), particularly suited to the detection of outlying samples. Extreme outliers influence the scale of the NLM image and lead to insufficient resolution for the smaller distances. Therefore extreme outliers, which may also be identified by FCM or other statistical techniques, should preferentially be removed from the data.

The similarity measure used in both FCM and NLM is the squared distance. The simple Euclidean

distance of unstandardized data presents metric problems as a variable ranging from 0.01 to 0.05 wt.% would have less weight than a variable ranging from 100 to 500 ppm. The distance measure used in the present studies is the Diagonal Norm, equivalent to a division of each variable by its standard deviation (Table 1). This standardization, which provides the necessary scale invariance, is, given a certain dataset, independent of the number of clusters and can be applied in a straightforward manner in both FCM and NLM. Prior to applying this procedure, it is useful to transform the data, if necessary, to obtain unskewed frequency distributions (e.g. a log-transformation) and also to exclude the extreme outliers in order to obtain robust estimates of the standard deviations. Some alternative methods for the calculation of distances are discussed in the Appendix.

A great advantage of NLM is the simple but informative way in which the relation between samples is displayed. However, a graphical division in groups on the basis of NLM alone is often subjective. Through FCM a relatively unambiguous grouping of the data points is obtained, while the relation of samples to each of the clusters (and thus each other) is still maintained. Hardened clusters may eventually be derived from the fuzzy clustering by taking those samples together which have their highest membership on the same cluster. The signification of the fuzzy or hardened clustering is not always directly evident but a NLM plot may give weight to the obtained grouping. The combination of FCM with NLM provides a powerful method to detect meaningful groupings within a dataset.

CASE STUDIES

Two data sets were treated with FCM and NLM, in addition to the application of more conventional univariate statistical techniques. The samples of both datasets were collected in the drainage basin of the Rio Vouga, northern Portugal (Fig. 1). The first dataset (area I) was collected to evaluate the influence of the different geological formations present in the study area on the composition of natural waters. The second dataset (area II) was used to study the response of river waters and sediments to Pb, Zn and Cu mineral occurrences in a rather uniform geological hinterland. A value of 1.5 was chosen for the FCM q parameter. This agreed with the expected topologies of the datasets. Additionally, in previous applications values of 1.5 to 1.75 had provided satisfactory results (VAN GAANS *et al.*, 1986). For both studies repeated FCM runs gave virtually the same result.

Area I: the Rio Certima drainage basin

General. The river and stream waters of the drainage basin of the Rio Certima (Fig. 1), one of the main

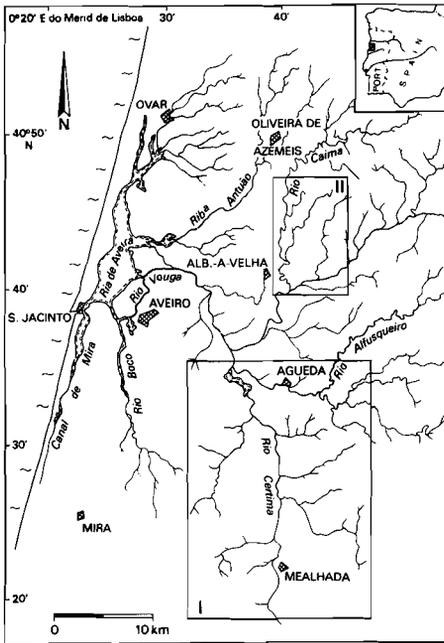


Fig. 1. Location map of the study areas.

tributaries of the Rio Vouga, were sampled. Important industries (potteries, brick works and wineries) are concentrated in the western part of the drainage basin and along the Rio Certima proper. A mineral water bottling plant is located near Luso (Fig. 2). The whole area is cultivated (grapes, corn, horticulture) except for the east, which is forested. Exposure of the geology is generally poor. Average temperatures are 19°C in summer and 9°C in winter. Rain falls mainly in winter and spring, totalling about 1000 mm/a (MUELLER, 1980). The countryside is relatively flat with an average altitude of 100 m above sealevel. In the east, upon entering the Beira schists, an escarpment rises to about 400 m.

Geology. No detailed geological map of the area is available. Information has been compiled from field observations and the 1:500,000 geological map of northern Portugal (Fig. 2). The eastern part of the area is underlain by low-grade regionally metamorphosed graywackes, schists and quartzites of the Infra-Cambrian Beira Formation. The middle part comprises Neogene silty sands with pebbles and Triassic sandstones. In the southwest Jurassic calcareous rocks crop out, which in the northwest are covered with Upper Cretaceous marine clays and sands with minor intercalations of calcareous strata. The rivers in the east are mainly fed by surficial water, while in the west, especially in the calcareous areas, the underground contribution through springs

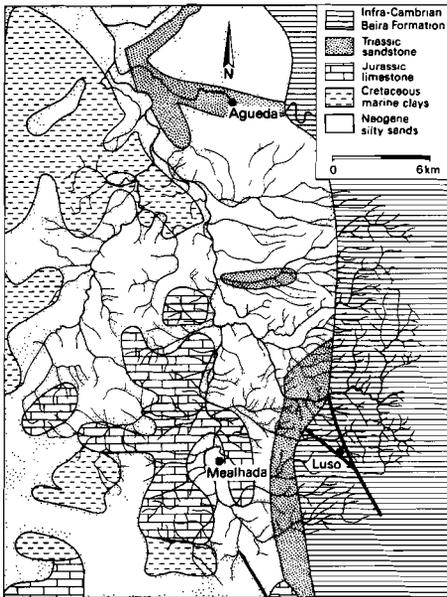


Fig. 2. Geological sketch map of the Rio Certima drainage basin.

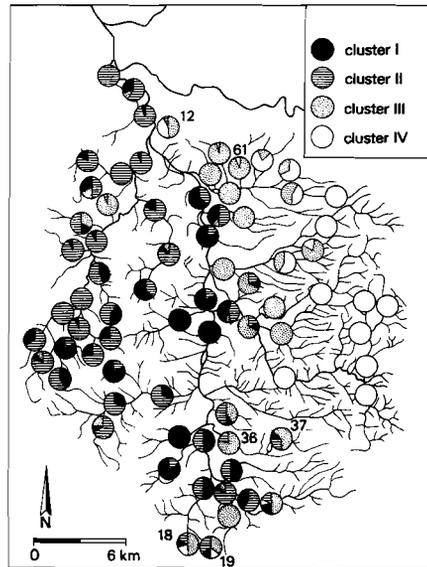


Fig. 3. Sample location map and areal FCM membership distribution in the Rio Certima basin. Memberships of <5% are not indicated. For the numbered samples see Fig. 6.

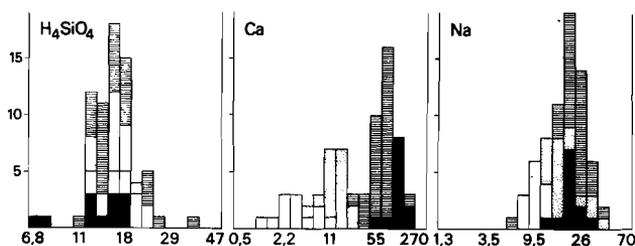


FIG. 4. Histograms of some selected variables for the Rio Certima dataset. The subdivision is made according to the so-called hardened clusters (for explanation see Table 4). For shadings see Fig. 3. Concentrations are in mg/l.

is of greater importance. This is reflected by the much denser pattern of the tributaries in the east. In the southeast the major mineral springs of Luso are related to SE–NW trending faults.

Sampling and analysis. In the summer of 1984 seventy-five water samples were collected (Fig. 3). The techniques used for sampling and analysis are described by TEN HAVEN *et al.* (1985). The waters were filtered through a 0.45 µm filter. The measured variables with values sufficiently above their analytical detection limits to be used in this study were the electroconductivity (*Ec*), pH, Na, K, Ca, Mg, Sr, Fe, H₄SiO₄, Cl, F, SO₄ and HCO₃.

Results and discussion. In this study most elements are lognormally distributed and the logarithmically transformed data were used throughout the data treatment. Multimodality (Fig. 4) is a common feature, as is to be expected for an area with widely varying geology and environment (Fig. 2). An unambiguous allocation of the samples to the different geological units is not possible on the basis of the histograms and cumulative frequency curves alone (SINCLAIR, 1976). Also, the geology is insufficiently well-known to allow an *a priori* grouping of all samples. The number of samples that can be unambiguously assigned to the different geological units is too small for DA (FOLEY, 1971). The application of FCM and NLM circumvented these problems.

The criteria for determining the number of FCM clusters (Table 3) indicated an initial best fit for two clusters. However, a four cluster model concurred better with the geological knowledge of the area. Cluster centers of the fuzzy clusters and geometric means of the hardened clusters are given in Table 4.

Table 3. The *F* and *H* cluster validity parameters for the Rio Certima dataset for various numbers of clusters

No. of clusters	<i>F</i>	<i>H</i>
2	0.889	0.189
3	0.793	0.370
4	0.673	0.582
5	0.635	0.696

The spatial distribution of the four clusters (Fig. 3), the NLM plot (Fig. 5) and the piper diagram (Fig. 6) all show the consistency of the partitioning. In the first two figures the values of the membership functions are visualized.

Initial inspection of the raw dataset had already revealed that for *Ec*, pH, Ca, Mg, Sr, SO₄, F and HCO₃ the presence or absence of calcareous rocks is an important control, while for all components except H₄SiO₄ the waters originating from the Beira schists have low concentrations with respect to the other geological units. The FCM clustering confirms, refines and appends these observations. The waters of cluster I mainly drain calcareous areas and belong to the Ca–HCO₃ watertype. Cluster II is intermediate between the Ca–HCO₃ and Ca–Cl types and is concentrated in the western part of the area. The shift towards the Cl apex in the piper diagram (Fig. 6) is caused by evapotranspiration and the leaching of salts from marine clays. Cluster III is strongly represented east of the Rio Certima outside the Beira schists and is of the Ca–Cl or of the Na–Cl watertype. Its composition is formed through mixing Beira schist-derived waters with those from the younger

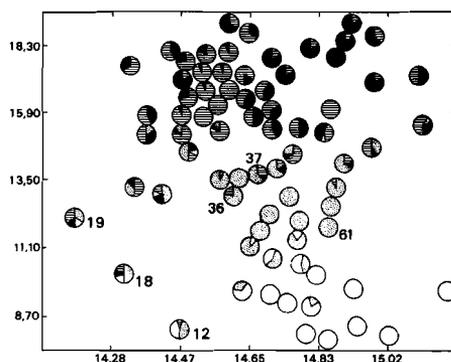


FIG. 5. FCM membership distribution represented in the NLM plot for the Rio Certima basin. For symbols see Fig. 3. For the numbered samples see Fig. 6.

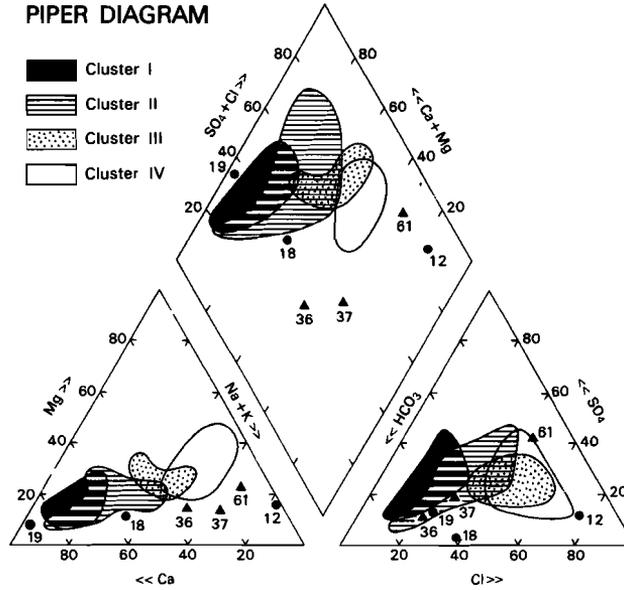


FIG. 6. Piper diagram of the water samples of the Rio Certima basin. Sample 12 is a spring. Samples 18 and 19 drain the Lower Cretaceous which has a higher porosity and permeability than the Upper Cretaceous (BARBOSA, 1983). Memberships for samples 36, 37 and 61 indicate their similarity to the third cluster. Sample 61 has a stronger Na-SO₄ characteristic. Samples 36 and 37 are from a stream in the southeast of the study area which drains the region where the important Luso mineral waters originate.

Table 4. Geometric mean (*CM*) and cluster center (*CC*) compositions for the Certima drainage basin. The *CM*'s are the geometric means of the so-called hardened clusters. Hardened clusters are derived from fuzzy clusters by taking those samples together which have their highest membership on the same cluster. Five samples belong equally to all four fuzzy clusters and are not allocated to one of the hardened clusters. Note that the *CC*'s are less extreme than the *CM*'s. This is in accordance with the notion, that when *q* nears infinity all cluster centers are identical. The geological units mentioned in parentheses indicate the units that are thought to have the greatest influence on the cluster composition. All variables are expressed in mg/l, except for Sr, Fe and F which are in µg/l and the *Ec* (µS/cm) and pH. Total number of samples is 75

Variable	Cluster I (Jurassic)		Cluster II (Cretaceous)		Cluster III (Triassic)		Cluster IV (Infra-Cambrian)	
	<i>CC</i>	<i>CM</i> (<i>n</i> = 12)	<i>CC</i>	<i>CM</i> (<i>n</i> = 29)	<i>CC</i>	<i>CM</i> (<i>n</i> = 17)	<i>CC</i>	<i>CM</i> (<i>n</i> = 12)
<i>Ec</i>	504	531	392	302	176	173	83	81
pH	7.70	7.85	7.25	7.20	6.80	6.90	6.40	6.35
Na	18.4	18.4	19.6	19.8	15.0	15.8	8.5	8.4
K	2.51	2.09	4.04	4.34	1.92	2.08	0.27	0.25
Ca	85.7	94.3	53.1	53.9	11.2	11.2	2.7	2.7
Mg	11.0	12.1	9.4	9.3	4.8	4.9	2.9	2.9
Sr	350	427	190	190	44	43	16	16
Fe	26	18	99	114	86	107	28	28
Cl	35.7	33.6	38.2	39.7	25.0	24.4	13.6	13.2
HCO ₃	188	206	116	111	28.6	28.6	13.3	12.5
SO ₄	63.9	78.1	47.8	50.1	17.7	18.5	9.4	9.3
H ₄ SiO ₄	13.5	12.5	14.7	14.9	15.1	14.6	17.6	17.1
F	155	163	124	119	51	50	30	29

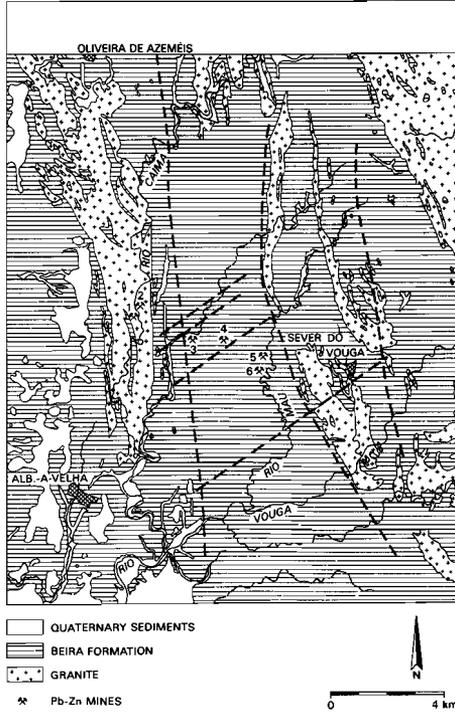


FIG. 7. Geological sketch map of the Rio Caima/Rio Mau drainage basin. The names of the mines are: Minas do Palhal (1), Minas de Telhadela (2), Minas de Bembe (3), Minas do Coval da Mo (4), Minas da Malhada (5) and minas do Bracal (6).

formations. Cluster IV is of the Na-Cl type; this waternature is also found in the Beira schists in case study II and by DEKKERS *et al.* (1986). It largely retains a rainwater signature (COMANS *et al.*, 1987).

The water composition in this study area is thus virtually completely controlled by the different geological formations that are present.

Area II: Pb-Zn mines in the Rio Caima/Rio Mau drainage basin

General. The second area comprises parts of the drainage basins of the Rio Mau and Rio Caima, both tributaries of the Rio Vouga (Fig. 1). Land use consists of agriculture (corn, rye, wheat and potatoes) and forestry (mainly eucalyptus). The climate is similar to that in the first study area, precipitation averages 1700 mm/a. Altitudes vary between 100 m and 800 m. The relief is relatively steep and has a NS-trending character caused by massive granite bodies and faults.

Geology. The main rock types in the study area are schists of the Infra-Cambrian Beira Formation and minor granite intrusions in the east and west (Fig. 7). Some major faults run roughly N-S while a minor fault system runs E-W. Several Pb, Zn and Cu mineral occurrences are related to the latter system (THADEU, 1977; GONCALVES 1974; SCHERMERHORN, 1981). The six occurrences present have slightly varying mineralogy. They all contain pyrite, galena, sphalerite and calcite, but at the Minas do Palhal (1) and Telhadela (2) also some Ni, Co, Cu, As, Sb and Ag minerals have been found (CABRAL, 1889). All the occurrences have been mined in the past, but activity ceased in 1974. Tailings are deposited in and along the rivers and streams.

Sampling and analysis. Some 50 water and sediment samples were collected in June 1984 (Figs 8 and 9). Sample density was somewhat increased near the old mine workings. Stream waters were collected and analyzed as described by TEN HAVEN *et al.* (1985). Arsenic was determined by flameless AAS. The sediments were collected from the active stream bed and wet-sieved through a 63 µm sieve. The fine fraction was dried and As, Sb, Ce, La, Eu, Yb, Lu, U, Th, Hf, Cs, Sc and Rb were determined by INAA (VAN DER SLOOT and ZONDERHUIS, 1979). Strontium, Pb, Co, Ba, Mn, S, Mg, Sn, Na, Ca, Zn, Cu, Li, Zr and Ni were analyzed by ICPES after an acid sample decomposition with a mixture of HF, HClO₄ and HNO₃.

Results and discussion. The histograms (Fig. 10) of the analyzed components in the waters and especially the sediments show multimodal tendencies. No *a priori* division on geological grounds can be made. All measured variables were logtransformed, because they more closely follow a lognormal distribution pattern than a normal one. The number of variables available for the sediment dataset is impractically large. Therefore, only one or two elements of each group of closely related elements (the REE, Zr-Hf, Rb-Cs etc.) were used in the data analysis. The values for the partition coefficient *F* and the classification entropy *H* in FCM (Table 5), favor a four clusters model for either dataset. The cluster centers are given in Tables 6 and 7. The spatial distribution of the clusters is shown in Figs 8 and 9. The NLM plots for the same datasets are given in Fig. 11. The coherence of the FCM derived clusters is evident in the NLM plots. The map patterns of the different clusters seem to be related to different drainages and areas. The membership functions are

Table 5. The *F* and *H* cluster validity parameters for the datasets of the Rio Caima/Rio Mau drainage basin for various numbers of clusters

No. of clusters	Water		Sediment	
	<i>F</i>	<i>H</i>	<i>F</i>	<i>H</i>
3	0.653	0.627	0.677	0.560
4	0.680	0.631	0.689	0.599
5	0.587	0.824	0.665	0.663
6	0.602	0.831	0.633	0.749

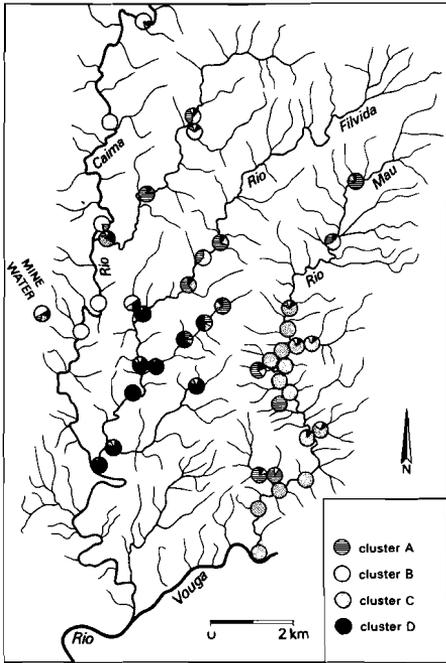


FIG. 8. Areal FCM membership distribution of the water samples of the Rio Caima/Rio Mau drainage basin. Memberships of <5% are not indicated.

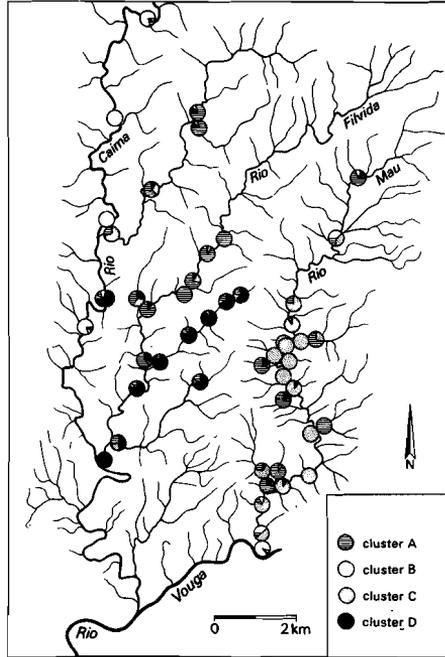


FIG. 9. Areal FCM membership distribution of the sediment samples of Rio Caima/Rio Mau drainage basin. Memberships of <5% are not indicated. For eight samples one or more analytical results are missing. In these cases the distance function is weighed according to the number of analytical results available (see also Table 7).

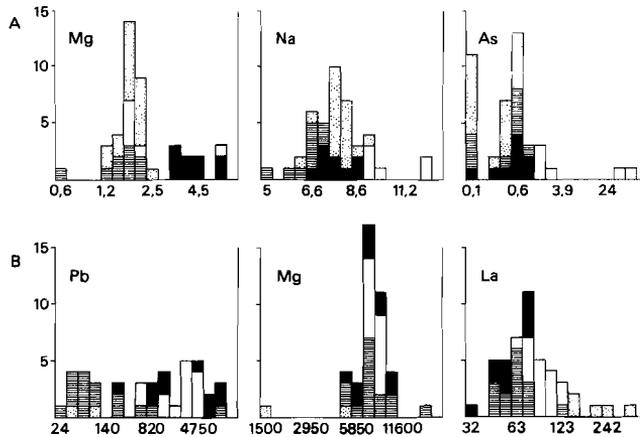


FIG. 10. Histograms of some selected variables of the Rio Caima/Rio Mau basin datasets. The subdivision is made according to the so-called hardened clusters (see Table 4). A: stream waters (concentrations in mg/l); three samples belong equally to all clusters and are not allocated to a specific hardened cluster. B: stream sediments (concentrations in ppm); three samples belong equally to all clusters and are not allocated to a specific hardened cluster; in addition, a varying number of values are missing for each element. For shadings see Fig. 8.

Fuzzy *c*-means cluster analysis and non-linear mapping

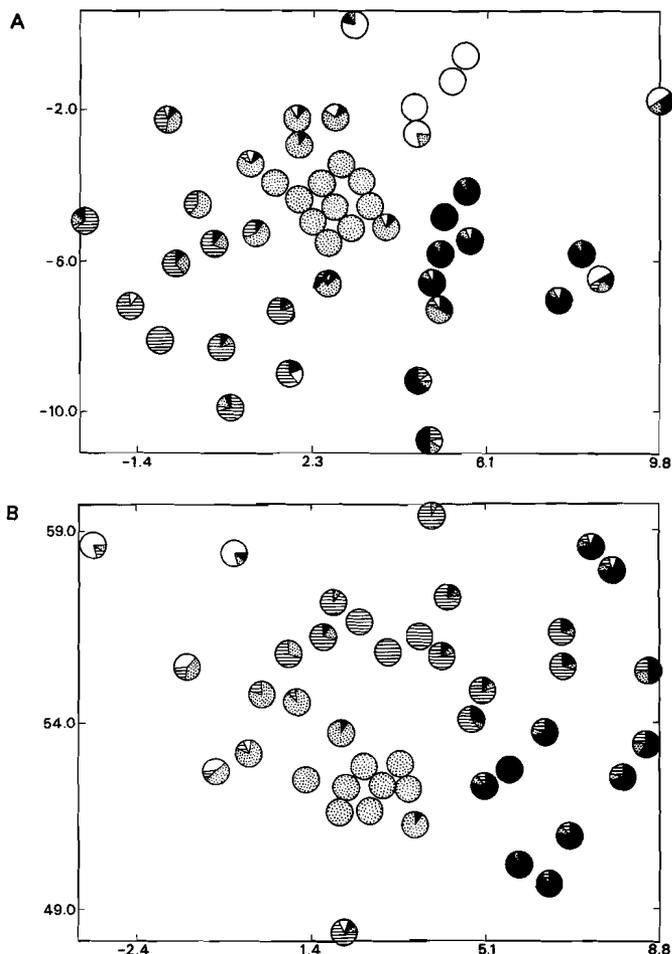


FIG. 11. FCM membership distribution represented in the NLM plot for the sediment (A) and water (B) samples of the Rio Caima/Rio Mau drainage basin. Memberships of <5% are not indicated. Eight sediment samples, owing to missing values, could not be included in the NLM calculations and are thus not mapped.

generally much closer to zero and one than in the first case study (compare Fig. 5).

The geographical distribution of the clusters for the two sample media is quite similar, they are therefore discussed together. The water compositions for this case study are, in general, close to the schist cluster of the first study area, especially to the waters originating in undisturbed schist areas (see cluster A below). The geochemical characteristics of the different clusters are as follows:

Cluster A. The area dominated by this cluster is in the north of the study area and in some small tributary catchment areas of the Rio Mau. The relief is steep, which precludes agriculture or any other human

activity except some forestry. There are no known mineral occurrences in these areas. The sediments are low in virtually all elements. Similarly, the waters are the most diluted of all the clusters, which is consistent with the above.

Cluster B. High membership samples of this cluster originate mostly from the Rio Caima proper. The sediment cluster is high in La, U, Th, Eu and Zr, pointing towards a granitic origin of these sediments, more specifically towards the heavy minerals that are released during granite weathering. The corresponding water group has high concentrations of Na, K, Cl, NO₃ and As. Along the river industrial and agricultural activities are the most intense for the

Table 6. The compositions of the cluster centers for the water samples of the Rio Caima/Rio Mau drainage basin. All variables are expressed in mg/l, except for Sr and Fe which are in $\mu\text{g/l}$ and pH. The number of samples equals 45

Variable	Cluster A	Cluster B	Cluster C	Cluster D
pH	6.21	6.55	6.59	6.65
Na	6.35	9.79	7.50	7.50
K	0.41	1.17	0.63	0.46
Ca	0.96	2.94	1.85	3.90
Mg	1.50	1.82	1.64	3.67
Sr	<10	20	10	10
Fe	30	60	30	40
As	0.28	4.19	0.20	0.41
Cl	8.74	14.56	10.76	10.06
HCO ₃	8.54	11.74	7.80	12.50
SO ₄	3.53	5.32	4.10	10.59
H ₂ SiO ₄	11.2	9.74	10.6	12.0
NO ₃	0.42	5.53	3.63	1.31

area, and apparently leave a distinct imprint on the water composition.

Cluster C. This cluster is concentrated in the Rio Mau. The sediments are high in Pb, Zn, S, Ca and Mg. The dispersion of the ore-related elements released by the weathering of the tailings of the Minas do Bracal (6) and Malhada (5) causes these highs. The waters are high in K, Cl and NO₃, indicating agricultural influence (fertilizers), which is indeed encountered along the Rio Mau.

Cluster D. The samples are mainly located along the lower stretches of the Rio Filvida, a tributary of the Rio Caima. High tenors for Pb, Zn and S but also for As, Sb, Co, Mn, Sn, Cu and Ni are found in the

sediments. This group of elements is also encountered in the mineralogy of the Minas do Palhal (1) and Coval da Mo (4). The waters contain high amounts of SO₄, HCO₃, H₂SiO₄, Mg, Ca and As. This composition is also largely the result of the weathering of tailings. The ore mineralogy effect in the waters of this cluster is far more explicit than in the former because the discharge is much lower than in the Rio Mau (VAN DER WEIJDEN *et al.*, 1984). Also, no agriculture is present in the drainage.

It is of interest to note that although the sediment and water clusters coincide, this is mostly the result of different factors. These factors can, of course, be interrelated through simple reasoning. A certain geology, for example, will be less favorable for agricultural activity than another. The geology will mainly determine the sediment composition, while the presence or absence of agricultural influence will set a group of waters apart from the others.

GENERAL DISCUSSION AND CONCLUSIONS

For smaller datasets the often used statistical methods based on correlation coefficients are less suitable than those proposed here. Used in combination the two alternative data treatment methods tested, FCM (fuzzy *c*-means clustering) and NLM (non-linear mapping), proved to be very powerful in dividing a dataset into interpretable clusters or groups. The application is easy, straightforward, and inexpensive. Only extreme outliers may be detrimental to FCM and NLM and are best removed from the dataset prior to treatment. Also, some simple transformation to remove skewness is useful.

Table 7. The compositions of the cluster centers for the sediment samples of the Rio Caima/Rio Mau drainage basin. *N* is the number of samples which varies for the different elements due to missing analytical values. In total eight samples had one or more values missing

Element	Unit	Cluster A	Cluster B	Cluster C	Cluster D	<i>N</i>
As	ppm	27.1	21.3	27.8	77.1	49
Sb	ppm	0.47	2.0	3.8	3.2	49
La	ppm	54.7	78.7	181	51.9	49
Eu	ppm	1.56	2.1	3.4	1.54	50
Th	ppm	20.9	33.3	86	20.0	50
U	ppm	8.65	9.87	30.8	10.1	49
Li	ppm	68	66	41	93	43
Na	%	0.37	0.48	0.49	0.40	43
Cs	ppm	7.3	6.8	1.2	9.9	50
Mg	%	0.65	0.71	0.33	0.69	43
Ca	%	0.13	0.23	0.14	0.12	43
Mn	ppm	484	517	240	725	43
Ni	ppm	51	40.7	20.6	76	43
Co	ppm	22.4	14.8	7.3	33	43
Cu	ppm	42	49	37.4	86	43
Pb	ppm	78	1720	84	1537	43
Zn	ppm	169	361	103	476	43
Zr	ppm	173	236	481	164	43
Sn	ppm	6.3	9.5	10.2	12.9	43
S	ppm	485	1940	534	1670	43

The application of FCM is preferred over conventional hard clustering techniques because the "fuzzy" concept fits better with what is normally encountered in nature. This observation is of course especially valid for stream sediment and water samples, which are often viewed as a composite sample of an area or volume created by nature.

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REFERENCES

- BEZDEK C. J. (1981) *Pattern Recognition with Fuzzy Objective Function Algorithms*. Plenum Press.
- BEZDEK C. J., EHRLICH R. and FULL W. (1984) FCM: the fuzzy c-means clustering algorithm. *Comput. Geosci.* **10**, 191–203.
- BARBOSA B. P. (1983) Roteiro da excursao no Cretacico da regio de Aveiro. (I congresso nacional de geologia). Unpublished excursion guide.
- CABRAL N. (1889) *Catalogica descritivo de seccas de Minas Associacas Industrial Portuguese*. Imprensa Nacional Lisboa.
- CHOK C. Y. and GOVETT G. J. S. (1985) Comparison of interpretations of geochemical soil data by some multivariate statistical methods, Key Anacon, N. B., Canada. *J. Geochem. Explor.* **23**, 213–242.
- COMANS R. N. J., VAN DER WEIJDEN C. H. and VRIEND S. P. (1987) Geochemical studies in the drainage basin of the Rio Vouga, Portugal. IV. Impact of land use on the hydrogeochemistry of natural waters in the Vouzela region. *Environ. Geol. Water Sci.* **9**, 119–128.
- DEKKERS M. J., VRIEND S. P., VAN DER WEIJDEN C. H. and VAN DIEST PH. (1986) The São Pedro do Sul granite, Portugal: Hydrogeochemistry related to the exploration of uranium. In: *Uranium Exploration: Results of European Communities Programme* (ed. L. VAN WAMBEKE). *Uranium* **2**, 261–277.
- DIXON W. J. (ed.) (1981) *BMDP Statistical Software*. University of California Press.
- ENGELMAN L. (1980) Annotated computer output for BMDPKM: K-means clustering. Tech. Rept 71. BMDP Statistical Software, Inc.
- FOLEY D. H. (1971) The probability of error on the design set as a function of the sample size and dimensionality. Rome Air Dev. Centre, Tech. Rept RADC-TR-71-171.
- VAN GAANS P. F. M., VRIEND S. P., VAN DER WAL J. and SCHUILING R. D. (1986) Integral Rock Analysis; a new approach to lithochemical exploration. Application: Carboniferous sediments of a coal exploration drilling, Limburg, The Netherlands. Report to the Commission of the European Communities, contract MSM-073-NL(N).
- GARRETT R. G. (1973) Regional geochemical study of Cretaceous acidic rocks in the northern Canadian Cordillera as a tool for broad mineral exploration. In *Geochemical Exploration 1972* (ed. M. J. JONES), pp. 203–219. Institution of Mining and Metallurgy, London.
- GLASBY G. P., TOOMS J. S. and HOWARTH R. J. (1974) Geochemistry of manganese concretions from the north-west Indian Ocean. *N.Z. J. Sci.* **17**, 387–407.
- GONCALVES L. S. M. (1974) *Geologie und Petrologie des Gebietes von Oliveira de Azemeis und Albergaria-A-Velha* (Portugal). Unpubl. Ph.D. Thesis, Free Univ., Berlin.
- GRANATH G. (1984) Application of Fuzzy Clustering and Fuzzy Classification to evaluate the provenance of glacial till. *Math. Geol.* **16**, 283–301.
- GUSTAFSON D. E. and KESSEL W. (1979) Fuzzy clustering with a fuzzy covariance matrix. In *Proc. IEEE-CDC*, Vol. 2 (ed. K. S. Fu) pp. 761–766, IEEE Press.
- TEN HAVEN H. L., KONINGS R., SCHOONEN M. A. A., JANSEN J. B. H., VRIEND S. P., VAN DER WEIJDEN C. H. and BUITENKAMP J. (1985) Geochemical studies in the drainage basin of the Rio Vouga, Portugal. II. A model for the origin of hydrothermal water in the Vouzela region. *Chem. Geol.* **51**, 225–238.
- HOWARTH R. J. (1973a) The pattern recognition problem in applied geochemistry. In *Geochemical Exploration 1972* (ed. M. J. JONES) pp. 259–273, Institution of Mining and Metallurgy, London.
- HOWARTH R. J. (1973b) Preliminary assessment of a non-linear mapping algorithm in a geological context. *Math. Geol.* **5**, 39–57.
- HOWARTH R. J., CRONAN D. S. and GLASBY G. P. (1977) Non-linear mapping of regional geochemical variability of manganese nodules in the Pacific Ocean. *Trans IMM London* **86**, B4–B16.
- HOWARTH R. J. and SINDING-LARSEN R. (1983) Multivariate analysis. In *Statistics and Data Analysis in Geochemical Prospecting* (ed. R. J. Howarth) Vol. 2, Chap. 6, pp. 207–283. Elsevier.
- JAIN A. K. (1986) Tutorial statistical pattern recognition, *8th Int. Conf. on Pattern Recognition*, Paris, pp. 3–75.
- LEFEBVRE J. D. and DAVID M. (1977) Dynamic clustering and strong pattern recognition: new tools in automatic classification. *Can. J. Earth Sci.* **14**, 2232–2245.
- MUELLER M. J. (1980) *Handbuch ausgewählter Klimastationen der Erde*. Forschungsstelle Bodenerosion der Universität Mertesdorf (Ruwertal). 2. verb. Auflage. Gerard Richter.
- SAMMON J. W. (1969) A non-linear mapping for data structure analysis. *IEEE Trans. Comput.* **C18**, 401–409.
- SAMMON J. W. (1970) An optimal discriminant plane. *IEEE Trans. Comput.* **C13**, 826–829.
- SCHERMERHORN L. J. G. (1981) Framework and evolution of Hercynian mineralization in the Iberian Meseta. *Leidsche Geol. Med.* **1**, 23–56.
- SINCLAIR A. J. (1976) Application of probability graphs in mineral exploration. *Ass. Explor. Geochem.*, Toronto Spec. Vol. 4.
- VAN DER SLOOT H. A. and ZONDERHUIS J. (1979) Instrumental neutron activation analysis of 37 geochemical reference samples. *Geostand. Newsl.* **3**, 185–193.
- THADEU D. (1977) Hercynian paragenetic units of the Portuguese part of the Hesperic massif. *Bol. Soc. Geol. Portugal* **20**, 247–276.
- VAN DER WEIJDEN C. H., TEN HAVEN H. L., BOER H. A., HOPSTAKEN C. F. A. M. and VRIEND S. P. (1984) Geochemical studies in the drainage basin of the Rio Vouga (Portugal). I. General hydrogeochemistry from its origin to the Ria de Aveiro. In *Hydrochemical Balances of Freshwater Systems (Proceedings of the Uppsala Symposium September 1984)*. Int. Ass. Hydro. Sci. Pub. No. 150, 263–276.
- YU BOCHANG and XIE XUEJING (1985) Fuzzy cluster analysis in geochemical exploration. *J. Geoch. Explor.* **23**, 281–291.
- ZADEH L. A. (1965) Fuzzy sets. *Inf. Control* **8**, 338–353.

APPENDIX

The choice of the distance or similarity measure is, next to the choice of clustering or mapping technique, of the utmost importance (HOWARTH and SINDING-LARSEN, 1983). In general, for the squared distance of two objects x_i and x_k in a V -dimensional space one can write:

$$(d_{kk})^2 = \sum_{j=1}^V \sum_{j'=1}^V (x_{kj} - x_{k'j'}) * A_{jj'} * (x_{kj} - x_{k'j'})$$

where A is a V by V norm inducing matrix.

In the most simple case A is the identity matrix and the distance measure then is the Euclidian Norm. For the Diagonal Norm, A is a diagonal matrix of the inverses of the variances, equivalent to a division of each variable by its standard deviation which is used in this study. To correct for statistical dependence between variables the Mahalanobis Norm, with for A the inverse of the covariance matrix, is theoretically appropriate (BEZDEK, 1981). As has been discussed in the text, proper steps have to be taken to deal with skewness and outlying values.

For multimodal distributions the overall (co)variance

over the total dataset is not necessarily a good estimate of the subgroup (co)variances. Use of especially the overall covariance matrix is only justified if the different clusters have directions and shapes more or less identical to the direction and shape of the total data cloud in the multi-dimensional space (see BEZDEK, 1981, Fig. 15.1). A pooled (fuzzy) covariance matrix of the various clusters could be used if directions and shapes of the clusters still more or less coincide with each other. The use of local fuzzy covariance matrices which induce a different norm for each cluster (GUSTAFSON and KESSEL, 1979; GRANATH, 1984) would be required in all other cases.

A disadvantage with the use of the Mahalanobis Norm is that for datasets with many variables relative to the number of samples, estimates of covariance matrices are notoriously poor (JAIN, 1986). This problem is therefore readily encountered in small datasets and even more so if pooled or local norms over clusters are introduced, owing to the loss of degrees of freedom. In addition, a pooled or local norm [see ENGELMAN (1980) and GRANATH (1984)] is very much dependent on the predetermined number of clusters and can therefore not be used in combination with NLM.

CHAPTER V

WELL SEDIMENTS: A MEDIUM FOR GEOCHEMICAL PROSPECTING, AN EXAMPLE FROM THE NISA REGION, PORTUGAL

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Abstract

The potential of well sediments for geochemical prospecting purposes is assessed in the Nisa region (Portugal). The semi-arid terrain is less suited for more conventional prospecting media. The composition of well sediments is dependant on local geology. Well sediments actively interact with emerging groundwater. These influences are identified and evaluated through statistical methods, including discriminant function analysis and factor analysis. Contamination, which may bias the geochemical landscape, appears to be of minor concern. Known mineralized areas (U, Pb, Zn, Ba) show up as strong anomalies. Additional anomalies of associations of several ore-related elements are attractive targets for follow-up study. Single element anomalies may be caused by local pollution. In general well sediments, if available, may offer an attractive alternative to more conventional prospecting media in arid and semi-arid regions.

Introduction

Geochemical prospecting for minerals is carried out through sampling of a wide variety of naturally occurring materials (Rose et al., 1979). For reconnaissance type surveys these include stream sediments, stream waters, ground waters, glacial debris, lake sediments and soils. These sample media are often less suited in arid or semi-arid regions. Ground water sampling has been shown to be successful in such areas especially for typically mobile elements like U and F and, more recently, even for Au (Bergeron and Choinière, 1989). However, this medium is not favorable for the lesser mobile metals. Their concentrations in solution generally are extremely low which complicates the analytical procedure. Moreover, effects of supersaturation with respect to many minerals - even at these low concentrations - bias the geochemical landscape.

Recently a ground water survey was carried out in the Nisa region, central Portugal (Dekkers et al., 1989) with the prime objective to study the manifestation of U deposits in these waters. The study area is located between Monte Claro and Povia e Meadas - an area rich in small mineralizations (cf. Fig.1). A genetic history was established for each water sample on basis of major element chemistry.

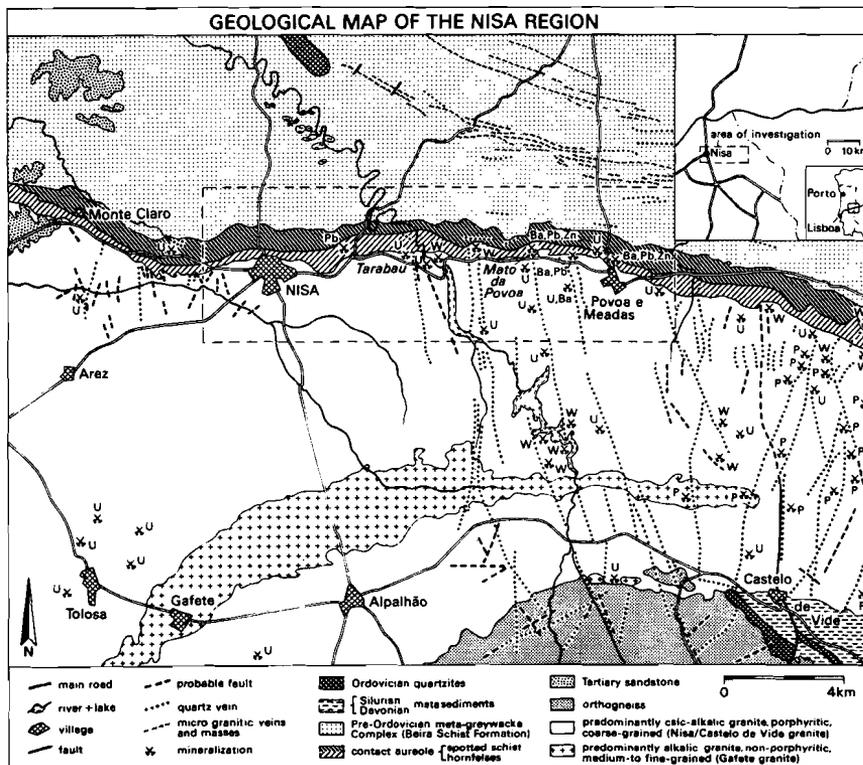


Fig. 1: Geological map of the Nisa region, east-central Portugal, after Ribeiro et al. (1965) and Fernandes et al. (1973).

Deep, surficial and polluted waters could be discriminated, thus greatly improving the interpretability of the anomaly pattern. However, mineral deposits other than U mineralizations appeared to be poorly reflected in the ground water composition. A possible alternative prospecting medium, not mentioned in current literature, is well sediment. The intimate interaction between emerging ground water and the well sediment may well prove suitable for mineral exploration, owing to a favorable element partitioning between the solution and scavenging sediments.

The present study in the same area between Nisa and Povoas e Meadas (Fig. 1) investigates this potential of well sediments in exploration geochemistry. The active interaction with passing groundwater is demonstrated through the impact of bedrock difference, major chemical processes and possible human influences. Statistical techniques are used as a major aid in visualizing geochemical differences

and processes. In a final test the anomaly pattern ensuing from the well sediment data is compared to the areal distribution of the known mineralizations.

Geological Setting

A multiple intrusive complex is located south of Nisa. A Caledonian intrusive body is bordered by two large intrusive bodies of the younger Hercynian granite series: the Nisa/Castelo de Vide (NCdV) and Gafete granites (Fig. 1; Fernandes, 1970, 1971). The Caledonian intrusive was altered into orthogneiss during the Hercynian orogeny. The northernmost coarse-grained, S-type, two-mica NCdV granite (age \pm 300 Ma) contains many vein-type mineralizations.

The probably infracambrian Beira Schist Formation (BSF, Thadeu, 1977) - with a large areal extent in the western Iberian Peninsula - forms the northern contact of the NCdV granite complex. In the Nisa region it has undergone low-grade regional metamorphism. Intrusion of the NCdV granite caused a contact-metamorphic overprint; an inner hornfels zone and an outer spotted schist zone are recognized (Fig. 1). Typical mineralogy of the spotted schist zone comprises quartz, feldspars, biotite, white mica, chlorite and cordierite, with accessory graphite and pyrite. The hornfels zone has a similar mineralogy; only chlorite is virtually absent. Garnet and (clino-)zoisite occur occasionally (Pilar, 1966a, 1966b).

Peneplanation was completed in Tertiary times. The present erosional level has reached the original roof zone of the NCdV granite (Pilar, 1966a).

Mineralizations

The Nisa region is known for its U deposits (Fig. 1). Quartzitic U-bearing veins occur in the NCdV granite, and disseminated U deposits in the contact zone. The disseminated deposits are thought to be extensions of the U-bearing vein-systems in the granite. Important ore-minerals in both mineralization types are uranyl-phosphates such as autunite, torbernite, Ba-autunite, bassetite, autunite-uranocircite.

Uranium occurrences in the study area are the Tarabau and Mato do Povoá veins (de Faria, 1966). To the west the well-known disseminated Nisa deposit occurs (Pilar, 1966a, 1966b) and to the south the formerly mined Tolosa vein (Ferreira, 1971).

Other mineralizations (Ba, Pb, Zn and marginally W) are also related to quartzitic veins in the granite with extensions into the granite/schist contact zone. The veins host (small) occurrences of wolframite, barite, apatite and galena-sphalerite (Fernandes et al., 1973; Ribeiro et al., 1965; Neiva et al., 1953). More comprehensive descriptions are given by Dekkers et al. (1984).

The mineralizations were formed under a widely differing hydrothermal regime. High temperature conditions are represented by wolframite deposits, intermediate temperature conditions by apatite deposits and low temperature conditions by barite, uranylphosphate and galena/sphalerite deposits. Age relations between these deposits are not definitely established; in the usually multiple metalliferous veins only relative ages are known (Neiva et al., 1953). However, it is possible that the deposits encompass a wide range of ages from late Hercynian for the high

temperature to late Alpine for the low temperature phases. Radiogenic heat could have driven mineralized fluids through vein-systems during rejuvenation of faults during geologic history (Fehn et al., 1978).

Hydrology and well description

The study area is characterized by a Mediterranean climate with hot summers and precipitation mainly in winter. The NCdV granite constitutes a virtually flat topographic high. Its contact metamorphic aureole slopes steeply to the north. The drainage system is poorly developed with very low discharge in summer. During summer water supply is chiefly maintained through artificial lakes. Most of the study area is dry and barren, almost without soil, or covered with forests (mainly eucalyptus). Horticulture and agriculture (cereals) are concentrated around small towns and villages.

In former times wells were commonly excavated for subsistence farming. Nowadays many are out of active use, thus diminishing the anthropogenic effect. Generally, the well diameter is some 2 m; well depths range from 2 to 20 m depending on the local water table. No masonry is used in their construction. Yields are low; in most cases water is manually extracted. More wells are located in the granite than in the schist.

Sampling and sample preparation

Sediment samples were collected from the bottom of the wells with a hand dredge. Wet sieving to a grain size of -1.0 mm was carried out in situ. The samples were sun-dried in Kraft paper bags. A small pilot study, comparing the $100-250$ μm and the -63 μm fractions, indicated that the -63 μm fraction gave generally a better anomaly-background contrast. Subsequently all samples were sieved to a grain size of -63 μm .

Analytical methods

Inductively Coupled Plasma (ICP) analysis for K, Ca, Mg, Fe, P, S, Li, Ti, Cr, Ba

Two hundred and fifty mg of each sample was leached overnight at 90°C with 12 N HCl and, after cooling, diluted to 250 ml with de-ionized water. These solutions were then directly analyzed by ICP.

X-ray fluorescence (XRF) analysis for Mn, Rb, Sr, Zr, Nb, Ta, Cu, Ni, Co, Pb, Zn, V, Y, U, W

Pressed powder tablets were prepared of 8 g sample with 0.75 g elvacite (Dupont-Nemours) as binder. The tablets were analyzed by XRF using a Philips PW1400 model. For calibration, pressed powder tablets of international natural rock standards were used.

Organic matter

An estimate of the organic content of the samples was obtained through determination of the weight loss at 950°C after drying the samples at 110°C. As a control on the quality of this rather crude approach, the organic content was also determined with the Kelsey method (Walkley, 1935; The method is based on the measurement of the pressure of CO₂ produced by heating the sample to 900°C. The evolved gasses are lead over hot CuO (900°C). H₂O is separated cryogenically. Interference of carbonate CO₂ is suppressed through prior treatment of the sample with HCl(1:1) in 18 samples. Agreement between the two methods was satisfactory.

Results and interpretation

If well sediments are indeed suited for prospecting, they must be geochemically active. This implies that geochemical parameters are reflected in their (varying) composition.

Bedrock differences - Discriminant Function Analysis

Bedrock differences are reflected in the composition of the well sediments. These show up particularly in the Cu, K, Cr, Fe, Mg, Ni, Co and V contents which are higher in the schist well sediments, and in the Y, Rb, U, Ta, Nb and Zr contents which are higher in the granite well sediments (Table 1). These differences (see Fig. 2 for some pronounced examples) are readily explained through the mafic character of the BSF and the acid character of the NCdV granite. The high Mg- and K-contents of the spotted schist may be related to ubiquitously occurring cordierite and K-micas.

To test the significance of the difference between well sediments of the granite and schist areas, a Discriminant Function Analysis (DFA) was carried out (SPSS, Nie et al., 1975). Sediments were assigned to either lithology on the basis of field observation. Field classification was impossible for some samples collected in the immediate vicinity of the contact. Prior to the DFA the constituents with lognormal characteristics were log-transformed. All constituents were entered into the analysis (direct method). The DFA classification concurs with the field observation for no less than 96 percent of the cases. Hence, differences between granite and schist sediment may be regarded as statistically significant. The few incorrectly classified samples are all close to the contact. For the samples with unknown provenance and these mis-classified samples the DFA classification is used throughout this study.

Geochemical processes - Factor Analysis

Important processes in the formation of well sediments within each lithology may be traced in their changing chemical composition. The ensuing correlation patterns are conveniently studied through Factor Analysis.

Factor analysis was carried out on the granite and schist data sets separately. The procedure to arrive at a final robust model (log-transformation if necessary,

TABLE 1: Geometric means (b) and geometric means plus and minus one standard deviation (s; based on the logarithmic values) for the analyzed compounds in granite and schist well sediments (respectively 46 schist and 61 granite samples). The arithmetic mean and arithmetic mean plus and minus one standard deviation are given for organic matter. All data are in parts per million unless otherwise indicated. Outliers were excluded.

Compound	SCHIST			GRANITE		
	b	b-s	b+s	b	b-s	b+s
K in %	0.41	0.26	0.64	0.24	0.16	0.34
Ca	1320	720	2420	1820	1020	3240
Mg	5180	3790	7080	2530	1730	3700
Fe in %	3.1	1.8	5.2	1.46	0.96	2.2
Mn	287	156	530	260	165	400
P	915	390	2180	800	470	1360
S	1590	455	5500	970	420	2220
Ti	555	315	980	365	210	645
ORG in %	3.7	1.9	5.4	4.8	2.6	7.0
Li	32	19	52	38	20	72
Rb	160	110	220	245	180	330
Sr	43	36	52	44	37	53
Ba	122	57	261	75	48	118
Zr	235	175	315	360	220	590
Nb	9	7	13	13	9	19
Ta	5.0	3.5	7.8	6.5	4.7	9
Cr	46	31	67	13	9	19
Ni	27	19	39	3.6	1.9	7.0
Co	20	13	30	7	3.5	14
V	117	87	157	34	25	48
Cu	40	21	74	18	7	42
Zn	225	115	445	130	80	215
Pb	49	26	93	38	25	58
U	19	6	58	55	32	92
Y	9.6	6.3	14	21	12	37

factoring procedure, removal of multivariate outliers) is described in some detail in Vriend et al. (1985) and Dekkers et al. (1986, 1989) and will not be re-iterated here. The SPSS (Nie et al., 1975) PA1 program for Principal Component Analysis combined with Kaiser Varimax rotation was used. Parallel factors in the schist (S) and granite (G) groups have been labelled by the same number. For clarity only the higher loadings are mentioned in the text. Full details are found in Table 2.

SCHIST

For the samples from the schist terrane a four-factor model was selected.

Factor S1: Clay mineral-mica factor, positive loadings for Cr, K, Mg, Ni, V, Ba, Sr and Ti.

This factor points towards weathering processes in the schist and reflects a clay mineral and mica association. The highly loading trace elements are common trace constituents in these minerals.

Factor S2: Fe-Mn coprecipitation factor, positive loadings for Fe, Mn, Co and negative ones for U and Y.

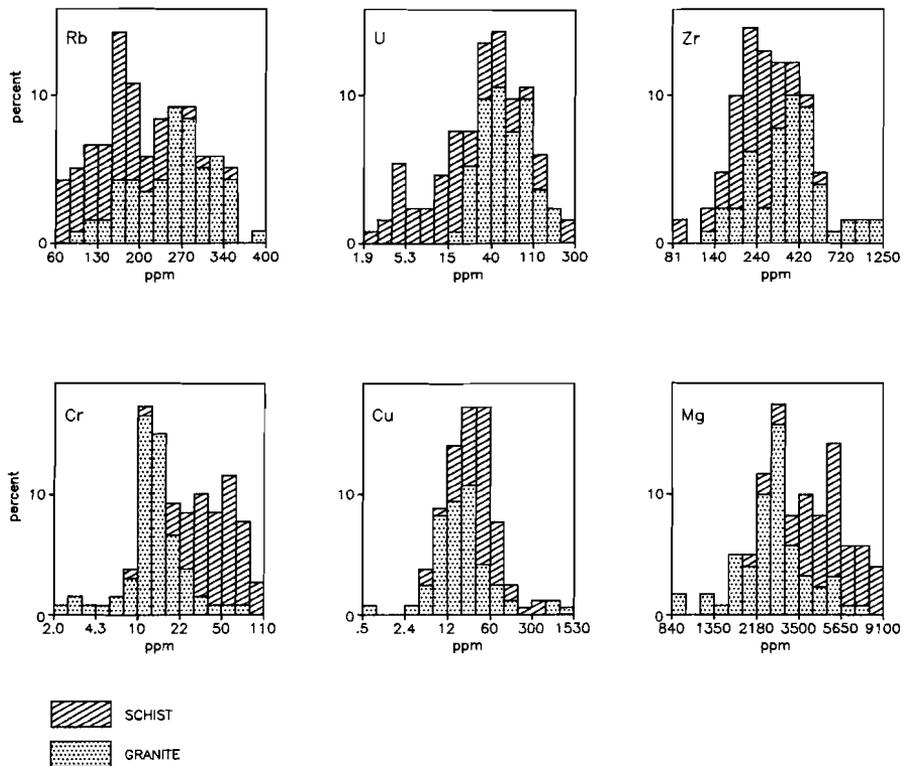


Fig. 2: Histograms of some elements, that show contrasting distributions for element concentrations in well sediments derived from different lithologies.

The element association expected on this factor would be elements coprecipitating and absorbing on Fe- and Mn-(oxy-hydr)oxides that form from waters that turn oxidic upon surfacing. These fresh (partly amorphous) hydroxides are very efficient in scavenging other ions (e.g. Whitney, 1975; Nowlan, 1976). An association with many metals would therefore be foreseen. However, only a relatively strong relation with Co is observed. Many trace elements load on the organic matter factor (S3). Organic matter also creates favorable conditions for complexing and immobilization of trace elements (e.g. Govett, 1960). It probably has a greater influence on the trace element behavior than Fe-Mn (hydr)oxides.

The negative loading of U and Y on this factor is somewhat enigmatic. This aberrant behavior may be explained by gradients generated by the granite: concentrations of U and Y fall with increasing distance to the granite (cf. Fig. 3). However a concurrent increase of Fe and Mn with decreasing metamorphic grade was not observed.

TABLE 2: Rotated Factor models for the granite and schist sediments.

Com- pound	SCHIST				GRANITE		
	FACTOR S1	FACTOR S2	FACTOR S3	FACTOR S4	FACTOR G1	FACTOR G2	FACTOR G3
ORGANIC			.65			.26	.76
Cu	.47	-.51	.32		.30	.31	.28
Pb	.25		.42			.56	
Zn	.27		.69			.64	
U		-.77				.62	.31
S	-.27		.71				.75
Li				.49	.87		
Rb		-.36	-.31	.74	.39		-.80
K	.80				.86		
P		.33	.44	.65	.29	.79	
Ca			.52	.51		.55	
Sr	.62			.46		.33	-.74
Ba	.64	-.26		.27	.42	.61	
Zr		-.42	-.43		-.27		-.66
Nb		-.40	-.60	.51			-.86
Ta			-.48				-.50
Mg	.77	.38			.57	.61	
Fe		.77	.36		.52	.70	
Mn		.77		.36		.65	-.42
Ti	.54				.86		
Cr	.83				.73	.34	
Ni	.75			-.29	.34	.62	
Co		.60	.40			.83	
V	.74	.34	-.30		.54	.43	-.36
Y		-.76				.51	.36

Only loadings and correlations outside the range of +0.25 and -0.25 are given. The Eigenvalues of the components prior to rotation are respectively for the granite sediments 7.4, 4.8, 2.8; for the schist 5.5, 4.3, 3.5 and 2.0. All compounds except organic matter were logtransformed in the factor analysis.

Factor S3: Organic matter factor, positive loadings for S, Zn and organic matter and a negative one for Nb.

The positive loading for organic matter, S and moderately to weakly for some chalcophile elements (Zn, Cu, Pb) versus the negative one for Nb and weakly negative for some other lithophile elements (Rb, Zr and Ta) is ascribed to the fact that high organic content precludes high contents of silicates and related elements and visa versa (an expression of the 'closure effect', see Aitchison, 1986). The chalcophile elements have a rather strong expression in the schist area, possibly related to minor pyrite.

Factor S4: Granitophile element factor, positive loadings for Rb and P.

Samples with high scores on this factor are confined to the immediate vicinity of the contact zone. The granite dips away under the schist and therefore these samples may reflect the proximity of the granite-schist contact.

GRANITE

A three-factor model was selected for the well sediments from the granite area (Table 2). As is to be expected, a factor expressing a concentration gradient

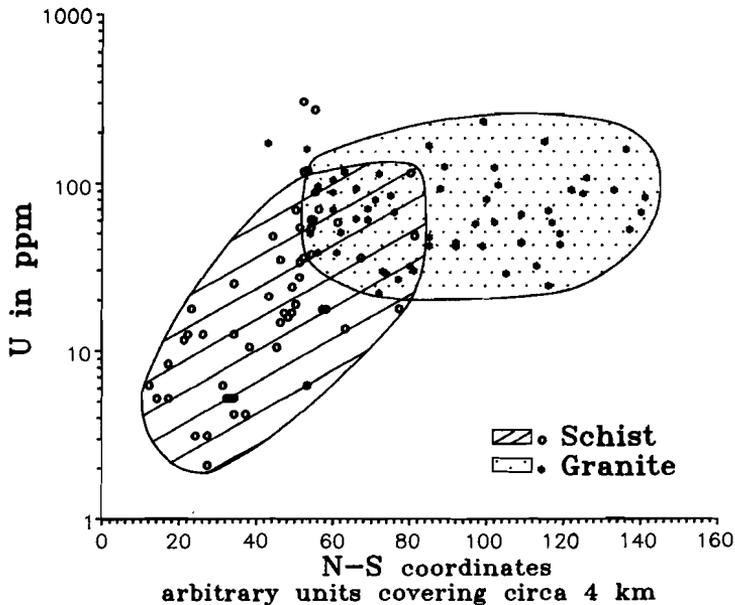


Fig. 3: Scattergram of U concentration vs the N-S coordinate. Note the strong increase in U in the schist well sediments with decreasing distance to the granite.

toward the granite like factor S4, does not show up in the granite sediments themselves.

Factor G1: Clay mineral-mica factor, high positive loadings for Li, K, Ti, Cr, Mg. This factor reflects very similar phenomena as factor S1 for the schist group. Obviously the different mica composition in the granite in comparison to the schist causes a different in element loadings.

Factor G2: Fe-Mn coprecipitation factor, high positive loadings for Co, P, Fe, Mn, Zn, Ni, U, Ba, Pb and Ca.

The trace elements coprecipitate with Fe- and Mn-(hydr)oxides upon oxygenating of the groundwater. While in the schist sediments this element association is mainly found under the organic matter factor, the balance has tipped over to the Fe-Mn coprecipitation factor in the granite sediments, perhaps due to diverse expression of oxidation phenomena in the different lithologies. In the granite sediments P has also a high loading on this factor. Like the trace elements phosphate is known to be adsorbed onto goethite-like phases (e.g. Atkinson et al., 1974).

Factor G3: Rock debris-organic matter dipole factor, high positive loadings for organic matter and S and negative ones for Nb, Rb, Sr and Zr.

This factor resembles factor S3 of the schist. Due to the lesser expression of the chalcophile elements the antipodal character of this factor is slightly enhanced with respect to that in the schist group.

The relations observed in the factors can be explained by common geochemical phenomena and processes. Moreover the soundness of the models is supported by the fact that both lithologies, although chemically quite distinct, broadly do yield similar factor models. Factors that should express distinct geographical trends, actually do yield such trends: schist samples with high scores on granite-related factors (S2 and S4) are indeed located close to the contact.

Two types of oxidation-reduction phenomena are thus discerned. Firstly, through a Fe (hydr)oxide precipitation upon oxygenation of emerging reducing water in oxic sediment. Fe^{2+} converts to Fe^{3+} which precipitates as Fe-(hydr)oxide. Such processes can presumably also occur in the absence of abundant organic matter, so that rock interaction plays a more important role. Secondly, in the presence of decomposing organic matter sediments readily use up their oxygen and reducing conditions result. In such environments sulphate, when present, is reduced to sulphide mediated through bacteria (odor of H_2S).

The strong association of Fe and P and the favorable geochemical environment (Nriagu and Dell, 1974) in the granite sediments led us to suspect the presence of vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) in those samples with high scores on the G2 factor. XRD examination of two of these high scoring well sediments did prove the presence of this mineral.

The behavior of U and Y in the well sediments is most interesting. They form a concentration plateau in the granite terrane while their concentration slopes down in the schist terrane with increasing distance to the granite (Fig. 3). If this present-day behavior may be linked to the ore-forming process, this could point to a metasomatic process whereby U (and Y) was transferred from the granite and trapped by changing chemical (redox?) conditions in the schist contact zone. This feature shows certain parallels with the observed vein-type U deposits in the granite and disseminated deposits in the schist contact zone.

Human impact

Factor models did not hint at any pollution-like process. Thus, it is reasonable to conclude that human impact, if present, is only marginal. This is corroborated by the fact that high values of pollution sensitive elements (like Pb and Zn) mostly coincide with high values for other common ore-paragenetic elements (Ba, Cu, U), favoring a natural origin. Nonetheless, since local pollution effects can not be totally excluded, single-element anomalies should be regarded with caution and assigned a low prospection priority. In the next section the value of anomalies is evaluated through its ore-element association.

Anomaly evaluation

In particular U, Pb, Zn, Ba mineralizations occur in the study area; therefore these elements are most interesting to evaluate the potential of well sediments for geochemical exploration. Study of the histograms of the ore-related elements already revealed the presence of anomalous values, and especially showed conspicuous highs for Pb.

In order to rectify the influence of differences in lithology on the background and threshold values, the following procedure was adopted, thereby avoiding the use of more than one threshold value per element and per map (Fig. 4):

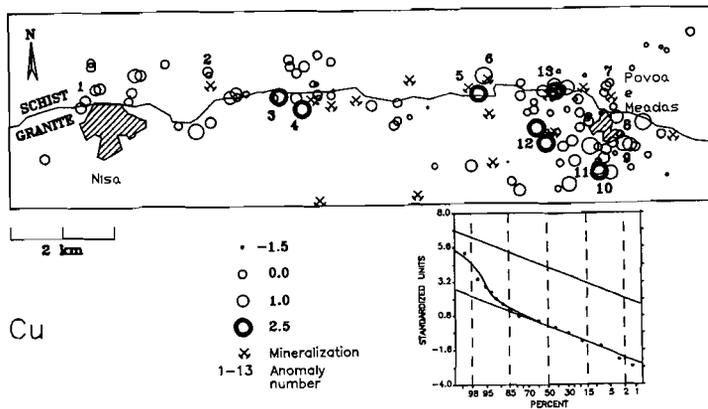
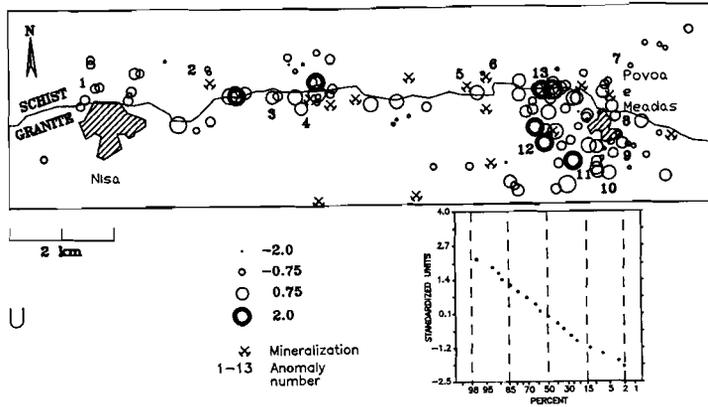
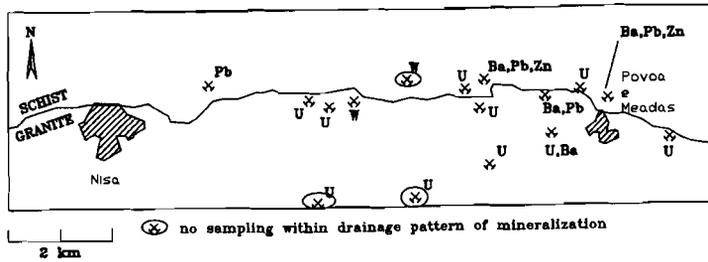
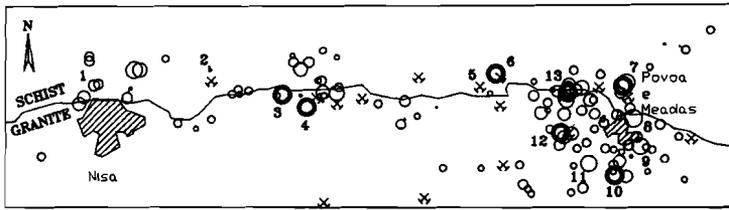


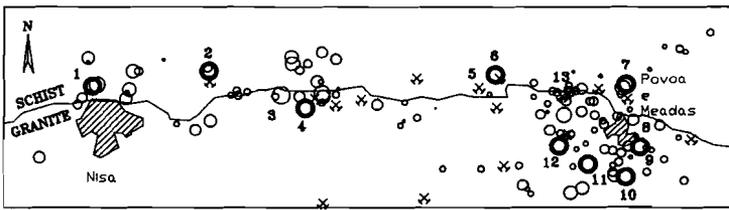
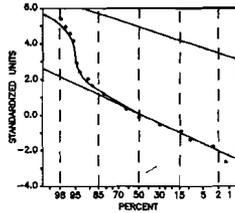
Fig. 4: Anomaly patterns and mineralizations for U, Cu, Ba, Pb and Zn. For each element the cumulative frequency curves are given that were used to determine the threshold value. Data for granite and schist well sediments were standardized separately and then joined for the construction of the curve. The diameter of the circle changes linearly with the standardized concentration in the maps; for reference purposes some circle sizes are labelled with their appropriate standardized units in the keys. The interpretation of each anomaly is listed in Table 3.



2 km

Ba

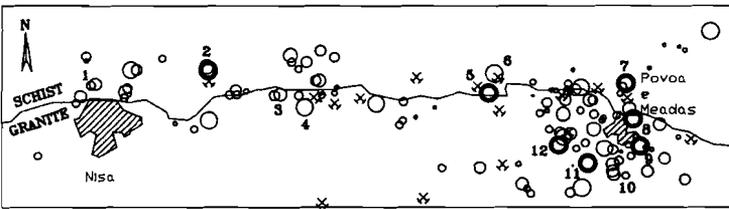
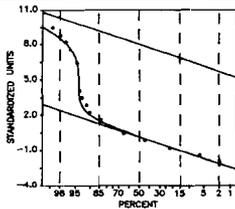
- -2.0
- -0.50
- 1.0
- 2.5
- ✕ Mineralization
- 1-13 Anomaly number



2 km

Pb

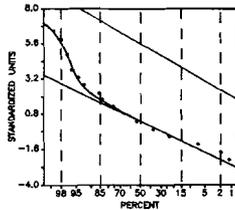
- 0.0
- 1.0
- 2.0
- 3.0
- ✕ Mineralization
- 1-13 Anomaly number



2 km

Zn

- 0.0
- 1.0
- 2.0
- 3.0
- ✕ Mineralization
- 1-13 Anomaly number



- Determination of the means and standard deviations in the distributions (logtransformation was applied if necessary) for the background populations of the separate lithologies with the help of cumulative frequency curves (Sinclair, 1976). Outlying parts of the distribution, expressed by breakpoints or inflection points in the cumulative frequency curve, were split off prior to the determination of these values.
- Standardization of the data per element and per lithology to a mean value of 0.0 and to a standard deviation of 1.0.
- Construction of cumulative frequency curves for the combined standardized data sets of both lithologies and determination of the threshold value for each element.

In the above procedure extensive use was made of the program PROBLOT (Stanley, 1987).

Only U did not show a clear inflection point in the cumulative frequency curve (Fig. 4). Therefore somewhat arbitrarily a (in these situations commonly used) value of the mean plus two standard deviations was defined as threshold (Hoffman, 1988). All U anomalies identified through the ground water survey (Dekkers et al., 1989) were also identified in the well sediments (Fig. 4), provided that sampling in the vicinity was possible (a number of water anomalies were found through spring sampling and thus no sediment could be collected in such cases).

All known Pb, Zn and Ba mineralizations are reflected in the anomaly pattern of the well sediments. This congruence demonstrates the merit of well sediment sampling for prospection purposes. A pollution explanation seems likely for some single-element Pb and Zn anomalies (cf. Table 3 and Fig. 4). The significance of the additional anomalies of associations of several ore-related elements may be evaluated in a follow-up study.

TABLE 3: Anomaly characterization for Pb, Zn, Cu and Ba

NUMBER	ELEMENT ASSOCIATION	(POSSIBLE) CAUSE
1	Pb	contamination
2	Pb, Zn	mineralization (Pb)
3	Ba, Cu, (Pb)	follow up
4	Pb, Ba, Cu, (Zn)	mineralization (U)
5	Cu, Zn	mineralization (U)
6	Pb, Ba, (Zn, Cu)	mineralization (Ba, Pb, Zn)
7	Pb, Zn, Ba	mineralization (Ba, Pb, Zn)
8	Zn, (Ba)	contamination?
9	Pb, Zn, (Ba, Cu)	follow up
10 (2 wells)	Pb, Zn, (Ba, Cu)	follow up
11	Pb, Zn, (Ba)	follow up
12 (3 wells)	Pb, Zn, Cu, (Ba)	mineralization (U, Ba)
13	Cu, Ba	mineralization (Ba, Pb)

Numbers correspond with those in Fig. 4. Elements between brackets have concentrations that fall very close to the threshold. Follow up implies an attractive element association warranting more detailed work.

The background-anomaly differences are rather large for all elements of interest, except for U which shows a more gradual background-anomaly pattern. This smoothing of the anomalous population may be due to the solubility of U in oxidizing water.

Only two W mineralizations of no economic interest occur in the study area. One has no well in its drainage. The other yielded a high W value. Tungsten was not considered in more detail.

Discussion and conclusions

An explanation for the strong response of ore deposits in the Nisa well sediment composition may well lie in the fact that places that are most favorable to find water close to the surface are also the most favorable to find mineralization. Water in semi-arid crystalline areas is most likely to be found in joint and fracture zones. Quartz veins are found frequently in these zones in the Nisa area. It is not uncommon to find springs originating in these veins. Quartz, a brittle mineral, poses in fractured veins little obstruction for water. Hydrothermal mineralizations are generally confined to these environments. These environments are also easiest for the rural population to excavate their wells in. In fact through this "natural selection" barren ground has for a large part already been eliminated from sampling. The well sediments contain clays, Fe-Mn (hydr)oxides and organic material, all phases that are very efficient in immobilizing solved or suspended trace elements. They thus have all characteristics required for an excellent prospecting medium.

Well sediments are an interesting alternative in regions where more conventional prospecting media are less successful. In the Nisa region virtually all known mineralizations are reflected in the well sediment samples, mostly as strong anomalies. Their zone of influence may reach deeper than stream waters and sediments or soils. Concentration levels are such that they can routinely be analyzed with presently available equipment. Factor analysis did not show the presence of any pollution-like process, thus anthropogenic influences are probably minor. Oxidation/reduction processes lead to precipitation of Fe-Mn hydroxides and phosphates which will scavenge trace elements, together with organic matter and clay minerals, from emerging ground water and thus greatly enhance the prospective potential of well sediments.

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References

- Aitchison J., 1986. *The statistical analysis of compositional data*: Chapman & Hall, London, 416pp.
Atkinson R.J., Parfitt R.L., Smart R.S.C., 1974, Infrared study of phosphate adsorption on goethite, *J.C.S. Faraday Trans. I*, 70, 1472-1479.

- Bergeron M., Choinière J., 1989. L'or dans les eaux souterraines: implications pour l'exploration. *J. Geochem. Explor.*, 31: 319-328.
- Dekkers M.J., Vriend S.P., van der Weijden C.H., van Gaans P.F.M., 1989. Uranium anomaly evaluation in groundwater: a hydrogeochemical study in the Nisa region, Portugal, *Applied Geochemistry* 4: 375-394.
- Dekkers M.J., Vriend S.P., Walen C.G., van der Weijden C.H., 1984. Geochemical controls of transport and deposition of uranium from solution, case study Nisa, Portugal, *Publ. Inst. Earth Sci., University of Utrecht*, contr. 007793 EXUNL, 90pp.
- Dekkers M.J., Vriend S.P., van der Weijden C.H., van Diest Ph., 1986. The Saõ Pedro do Sul granite, Portugal: hydrogeochemistry related to the prospection of uranium, *Uranium* 2: 261-277.
- de Faria F.L., 1966. Gites d'uranium portugais dans les formations metasedimentaires, *Port. Serv. Geol. Comun.* 50: 9-50
- Fehn U., Cathles L.M., Holland H.D., 1978. Hydrothermal convection and uranium deposits in abnormally radioactive plutons, *Econ. Geol.* 73: 1556-1566.
- Fernandes A.P., 1970. Contribucao para o estudo da regio dos granitos radioactivos de S. Pedro do Sul, *Junta de Energia Nuclear, Lisboa*, 45pp.
- Fernandes A.P., 1971. A geologia da provincia uranifera do Alto Alentejo, Contribution to the economic geological congress Hispano-Luso-Americano, Madrid and Lisbon sept. 19th-25th 1971: 13pp.
- Fernandes A.P., Perdigao J.C., de Carvalho H., Peres A.M., 1973. Carta geologica de Portugal escala 1:50.000; noticia explicativa da folha 28D: Castelo de Vide.
- Ferreira P.V., 1971. Jazigos uraniferos portugueses; jazigos de Au-Ag-sulfuretos do Norte de Portugal, excursion guide book Vol. 5, economic geological congress Hispano-Luso-Americano, Madrid and Lisbon sept. 19th-25th 1971.
- Govett G.J.S., 1960. Geochemical prospecting for Cu in Rhodesia, *Proc. 21st Int. Geol. Cong.*, Copenhagen 1960 Pt. II, 44-56.
- Hoffman S.J., 1988. Notes from the Editor. *Explore* 3: 2-3.
- Neiva J.M.C. de Queiroz N.M., de Faria F.L., 1953. Geologie et genese des gisements portugais d'apatite, *Int. Geol. Cong. 19th, Algeria C.R. sec 11, f 11*, 145-59.
- Nie N.H., Hull C.H., Jenking J.G., Steinbrenner K, Bent D.H., 1975. *Statistical Package for the Social Sciences*, 2nd ed., McGraw-Hill inc., 675pp.
- Nowlan, G.A., 1976. Concretionary Mn-Fe oxides in streams and their usefulness as a sample medium for geochemical prospecting. *J. Geochem. Explor.*, 6: 193-210.
- Nriagu J.O. and Dell C.I., 1974. Diagenetic formations of iron phosphates in recent lake sediments. *Am. Mineral.* 59: 934-946.
- Pilar L., 1966a. Condicoes de formacao do jazigo uranifero de Nisa, *Port. Serv. Geol. Comun.* 50: 51-83.
- Pilar L., 1966b. Petrografia das rochas metamorphicas e dos granitos de contacto da regio de Nisa, *Port. Serv. Geol. Comun.* 50: 85-107.
- Ribeiro O., Teixeira C., de Carvalho H., Peres A.M., Fernandes A.P., 1965. Carta geologica de Portugal escala 1:50.000; noticia explicativa sa folha 28B: Nisa.
- Rose A.W., Hawkes H.E., Webb J.S., 1979. *Geochemistry in mineral exploration*, Academic Press London, xvii + 657pp.
- Sinclair A.J., 1976. Applications of probability graphs in mineral exploration, *Assoc. Explor. Spec. Vol. 4*, Toronto, 35pp.
- Stanley, C.R., 1987. PROBLOT. An interactive computer program to fit mixtures of normal (or log-normal) distributions with maximum likelihood optimization procedures. *Assoc. of Explor. Geochem., Special Vol. # 14*, 40pp.
- Thadeu D.C., 1977. Hercynian paragenetic units of the Portuguese part of the Hesperic massif, *Bol. Soc. Geol. Port.* 20: 247-276.
- Vriend S.P., Oosterom M.G., Bussink R.W., Jansen J.B.H., 1985. Trace-element behavior in the W-Sn granite of Regoufe, Portugal. *J. Geochem. Explor.*, 23: 13-25.
- Walkley, A., 1935. An examination of methods for determination of organic carbon and nitrogen. *J. Agr. Sci.* 25: 598-609.
- Whitney, Ph.R., 1975. Relationship of manganese-iron oxides and associated heavy metals to grain size in stream sediments. *J. Geochem. Explor.*, 4: 251-263.

CHAPTER VI

THE SÃO PEDRO DO SUL GRANITE, PORTUGAL: HYDROGEOCHEMISTRY RELATED TO THE EXPLORATION OF URANIUM

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ABSTRACT

Dekkers, M.J., Vriend, S.P., Van der Weijden, C.H. and Van Diest, Ph., 1986. The São Pedro do Sul granite, Portugal: Hydrogeochemistry related to the exploration of uranium. In: L. van Wambeke (Guest-Editor), Uranium Exploration: Results of European Communities Programme. Uranium, 2: 261–277.

The São Pedro do Sul granite in the north-central part of Portugal is highly radioactive but is not affiliated with any known uranium mineralization. This setting therefore provided an interesting case study for the hydrogeochemistry of uranium. Spring, tap and stream water samples were collected and analysed for pH, Ec, Na, K, Ca, Mg, Cl, SO₄, HCO₃, H₄SiO₄, PO₄, NO₃, DOC, F, U, Sr and Ba.

Univariate and multivariate statistical techniques were applied to gain an understanding of the important factors that influence the water composition. Evaporation appeared to dominate the chemistry of the waters. Faults and the deeper weathering of the granite are also reflected in the water composition, especially in the behaviour of the pH, HCO₃, F and H₄SiO₄. The U concentrations are low and do not show any interesting groupings. The combined results concur with the absence of known outcropping mineralizations, and also indicate that the presence of hidden ore bodies is unlikely.

1. INTRODUCTION

Surface and groundwater compositions are determined by many different factors such as the initial rainwater composition, evapotranspiration, chemical, biological and mineralogical contents of bedrock and soil, anthropogenic contributions (agriculture) and depth of percolation. Water samples (stream, spring and tap) may thus contain indications of their genetic history, which is of interest in the search of (hidden) ore deposits.

The “radioactive” granite of São Pedro do Sul in north-central Portugal (Fig. 1) is an interesting target to test the potential of hydrogeochemistry in the prospection for uranium mineralizations: (1) to study the response of a granite not affiliated with any known U mineralizations but with high U and Th content, mainly enclosed in refractory minerals (Basham et al., 1982b);

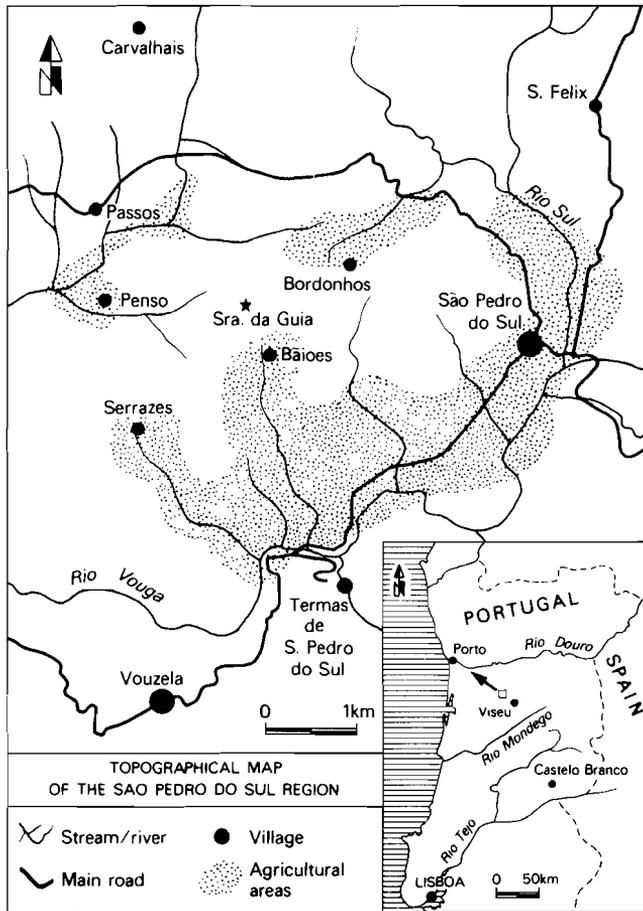


Fig. 1. Topographical map of the São Pedro do Sul area.

and (2) to investigate the likelihood of hidden ore deposits at shallow depth. Fernandes (1970) carried out an intensive radiometric survey of this area but found no outcropping mineralizations.

Granite and schist, the main rock types encountered in the study area, have a low porosity and permeability. Consequently, the waters of the São Pedro do Sul region display mainly characteristics of surficial water-rock interaction. In tectonically affected areas water may penetrate deeper and come into contact with fresh rock and vein material. The fault-related hot springs of São Pedro do Sul are extreme examples of this type of interaction (e.g., Lautensach, 1932; Basham et al., 1982b; Ten Haven et al., 1985).

The São Pedro do Sul granite is bordered in the south by the Rio Vouga, cut in the eastern part by the Rio Sul, and covers an area of $\sim 16 \text{ km}^2$. Farmlands (corn, potatoes) and vineyards are mostly assembled along riverbanks and around small villages (shaded areas in Fig. 1). The higher regions are covered with forests (pine tree, eucalyptus). Altitudes vary between 150 m in the Rio Vouga valley and 480 m of the Sra da Guia (Fig. 1).

2. GEOLOGY

The geology of the São Pedro do Sul area, as given by Fernandes (1970), is shown in Fig. 2. The main petrological units in the area are a complex of meta-graywackes, different granite types and, to a minor extent, (sub-)recent

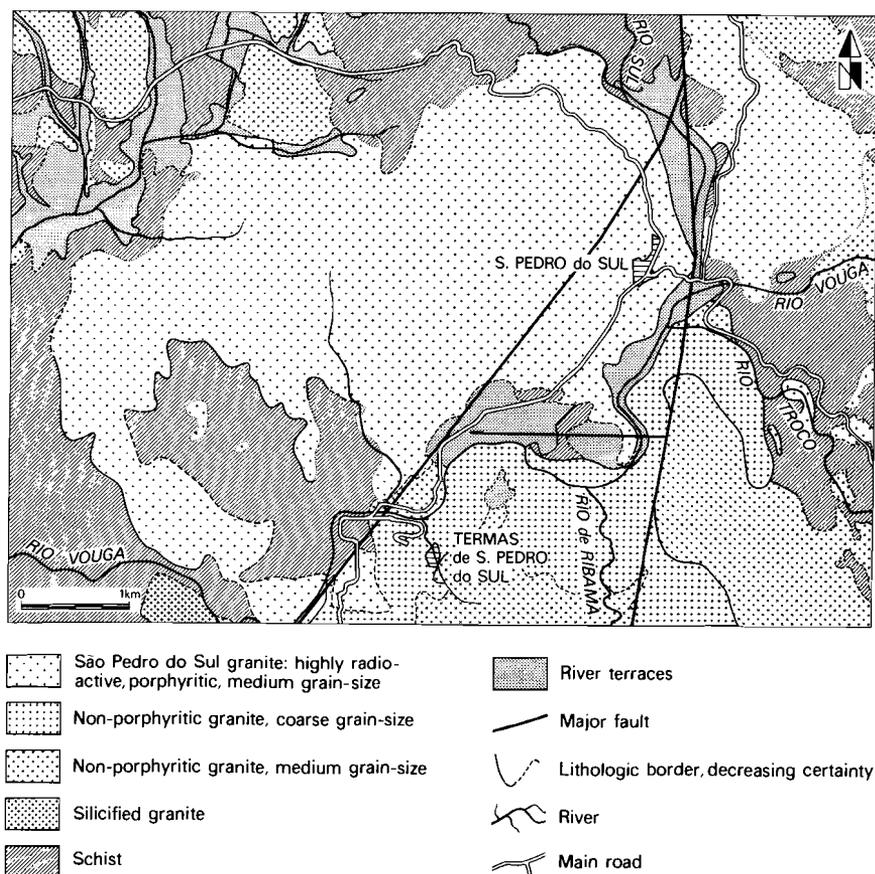


Fig. 2. Simplified geological map of the São Pedro do Sul granite (after Fernandes, 1970).

alluvial deposits. The meta-graywackes belong to the Beira Schist Formation which crops out in large parts of northern Portugal. The sedimentary age is Cambrian (Thadeu, 1977). During the Hercynian orogenic event the formation was regionally metamorphosed. Relatively low-pressure types of metamorphism are generally encountered. Hercynian granites caused contact metamorphic overprints. In the São Pedro do Sul area the formation was metamorphosed into the staurolite + andalusite and biotite zones along the contacts of the São Pedro do Sul granite (Oen, 1958, 1970).

Older and Younger Hercynian granites can be distinguished (Oen, 1958, 1970; Schermerhorn, 1959). The Older granites have concordant contacts and radiometric ages of 330–320 Myr. The Younger ones are porphyritic, intruding into the Beira schists or the Older granites and having discordant contacts. Their radiometric ages vary between 310 and 280 Myr.

Various subtypes are recognized on the basis of petrographic and chemical criteria. Age relations are somewhat ambiguous, e.g. Pinto (1979) distinguishes five Hercynian granite generations in northern Portugal.

2.1. São Pedro do Sul granite

The São Pedro do Sul granite has a blue appearance and is porphyritic and medium-grained. In the border-zones the grain size decreases. Schlieren and interfingering schist fragments are common (especially close to their wall rocks). The major mineralogical constituents of the granite are quartz, plagioclase and K-feldspar, minor components are biotite and white mica while accessory sillimanite also occurs. The chemical composition of the granite is given by Fernandes (1970). In terms of chemical classifications of granites the São Pedro do Sul granite is peraluminous. Very important is its anomalous radioactivity — 40–60 c.p.s. (Geiger–Müller A.V.P.), sometimes up to 300 c.p.s. Normal c.p.s. values for the neighbouring rocks are in the range of 20–25 c.p.s. (Fernandes, 1970).

The age determination of Mendes (1961) (316 ± 11 Myr.) is in accordance with a later age determination of Priem et al. (1984) (315 ± 3 Myr.). Neighbouring rock units are the Beira Schist Formation north- and westwards and an Older granite southwards.

Two major faults run N–S and NE–SW through the eastern part of the São Pedro do Sul granite.

3. SAMPLING AND ANALYTICAL TECHNIQUES

Eighty-three water samples were collected in the period of June 18–27, 1981. At the sample site two separate samples were filtered through a 0.45- μ m membrane filter; one was acidified with 1 ml 6 N HCl per 250-ml sample to prevent adsorption onto the container walls. The alkalinity and Cl were measured in the unacidified sample, the other constituents in the

During the interpretation of the results extensive use was made of the computer packages SPSS (Nie et al., 1975) and BMDP (Dixon, 1981). The variables Ec, pH, Na, K, Ca, Mg, U, HCO₃, Cl, F, NO₃, PO₄, SO₄, DOC, Sr, Ba and H₄SiO₄ were used in the statistical analysis. In Table I means, standard deviations, minima and maxima for each variable are listed. In general, the waters from the São Pedro do Sul area are dilute.

TABLE I

Levels of chemical constituents in the São Pedro do Sul waters

	Mean	Geometric mean, <i>b</i>	$b - s_L$	$b + s_L$	Min.	Max.	Unit
pH	6.01	5.99	5.49	6.54	4.95	7.47	
Ec	86.3	74.9	44.7	125	29.4	250	μS
Na	11.2	10.1	6.5	15.7	4.0	34.7	mg l ⁻¹
K	2.23	1.40	0.57	3.42	0.45	13.7	mg l ⁻¹
Ca	2.41	1.99	1.06	3.74	0.23	9.2	mg l ⁻¹
Mg	1.54	1.26	0.67	2.37	0.37	4.4	mg l ⁻¹
Cl	16.3	14.4	9.1	22.8	7.0	52	mg l ⁻¹
HCO ₃	11.5	9.0	3.5	23.2	0.1	29.6	mg l ⁻¹
H ₄ SiO ₄	30.2	28.0	18.9	41.4	10.1	67	mg l ⁻¹
SO ₄	5.1	4.0	1.90	8.4	0.38	16.5	mg l ⁻¹
NO ₃	1.38	0.15	0.013	1.67	0.01	13.7	mg l ⁻¹
PO ₄	0.223	0.080	0.187	0.343	0.020	2.56	mg l ⁻¹
DOC	1.56	1.54	1.25	1.90	1.0	2.7	mg l ⁻¹
F	0.10	0.087	0.055	0.14	0.035	0.32	mg l ⁻¹
U	0.22	0.15	0.06	0.38	0.04	1.0	μg l ⁻¹
Sr	17	13	6	28	2	49	μg l ⁻¹
Ba	26	11	3	34	2	305	μg l ⁻¹

$b \pm s_L$ indicates the antilogs of arithmetic means \pm one standard deviation of the logarithmic transforms of the constituents. Data are based on 83 samples.

4.1. Histograms and cumulative frequency distributions

Apart from the pH and H₄SiO₄, which are unimodally and normally distributed, all variables have unimodal distributions of lognormal character. Only the nature of the distributions of NO₃ and PO₄ is difficult to judge, because a large percentage of these constituents was below the limit of detection. Stream waters show the smallest variations (Dekkers et al., 1983a), which are caused by their composite nature. Taps are fed by captured local springs, selected for their constant flow even after long periods of dry weather. Sometimes small storage reservoirs were built to improve their effectiveness. The chemistry of the taps is therefore comparable with that of the uncaptured springs and no obvious differences between these two are noticeable in the histograms.

4.2. Piper diagrams

Relative amounts in meq% of the major cations and anions are expressed in Piper (1944) diagrams as shown in Fig. 4. All waters belong to one group and can be classified as Na-Cl type. Spring, stream and tap waters do not show any systematic differences. Waters with higher Ec's are generally shifted towards the SO_4 and (Ca + Mg) apices, probably due to agricultural activities (Dekkers et al., 1983a). The waters with a low Ec represent best the original São Pedro do Sul granite waters, because those are the least (or not at all) polluted.

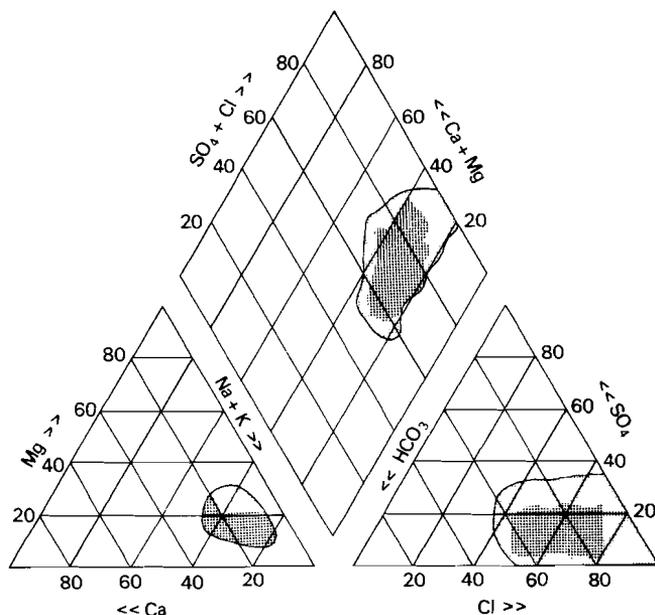


Fig. 4. Piper diagram of the São Pedro do Sul water samples. The darkly shaded areas contain 70% and the contoured areas 95% of the samples.

4.3. Scattergrams

In the Na vs. Cl plot (Fig. 5a) the seawater dilution line ($\text{Na}/\text{Cl} = 0.85$) is drawn. Compared to the seawater ratio a slight excess of Na over Cl exists. Obviously evapotranspiration is an important process in the area. The excess Na is added by the chemical weathering of rocks.

The seawater dilution line in the SO_4 vs. Cl plot (Fig. 5b) shows that SO_4 must have been added to the water. The application of fertilizers and the combustion of fossil fuels are explanations for the relatively increased SO_4 amounts. The extent of either source is difficult to estimate.

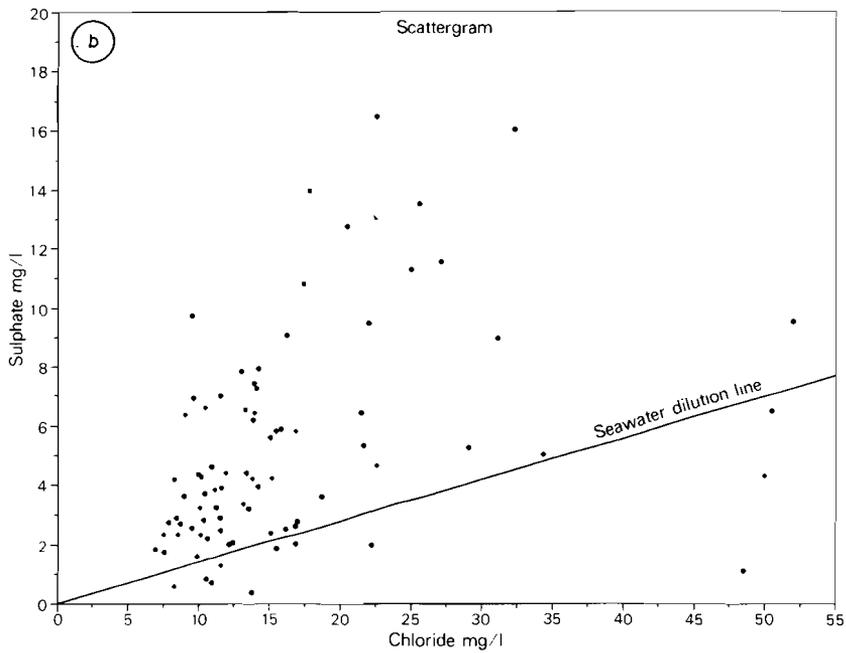
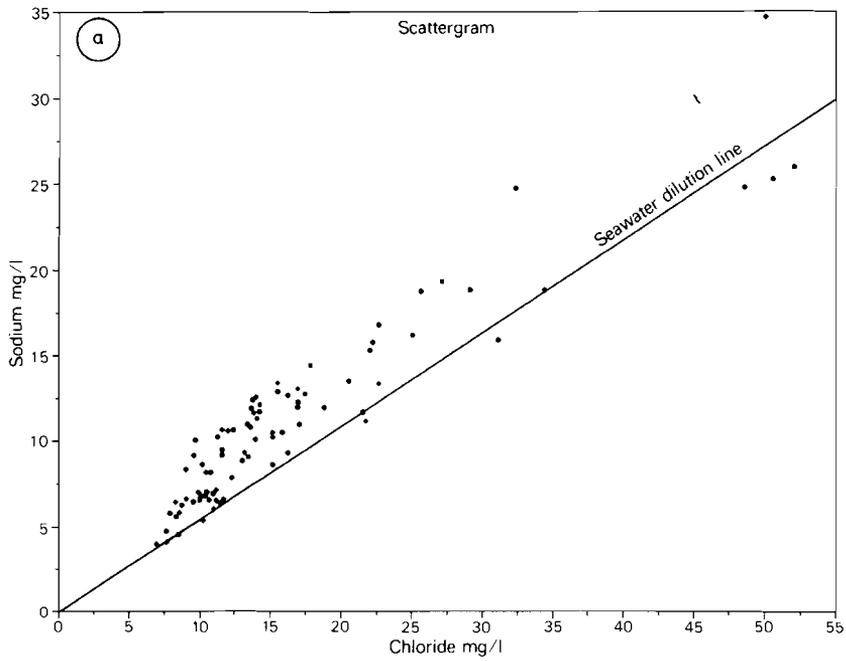


Fig. 5. Scattergrams of (a) Na vs. Cl and (b) SO_4 vs. Cl for the São Pedro do Sul water samples. Symbols have the same meaning as in Fig. 3.

4.4. Component analysis

In order to obtain interpretable results, it must be established prior to component analysis (CA) that the variables are unimodal, normally distributed and free of outliers. The histograms and cumulative frequency curves showed no significant outliers nor deviations from unimodality. A transformation to skewness zero (Miesch, 1981; Selinus, 1981) resulting in symmetrically distributed variables was applied. The transformation has the form $\ln(x - \alpha)$ or $\ln(\alpha - x)$, whereby α was chosen through an iterative procedure.

Although in the histograms stream, spring and tap waters show no significant differences, this unimodality may not exist for the multivariate data set. Discriminant function analysis (DFA) is an appropriate technique to test for differences between groups of samples. In this case DFA did not indicate any significant difference and hence it is justified to treat all samples as one group.

Component analysis with Kaiser varimax rotation was applied. Variables with more than 30% of their concentrations below the limit of detection and samples of which the charge balance deviated more than 10% from electro-neutrality were excluded from the calculations to avoid possible spurious

TABLE II

Component loading matrix of the São Pedro do Sul water data .

	Evaporation component	Fault/depth component
pH		0.75
Ec	0.92	0.29
Na	0.85	0.40
K	0.87	
Ca	0.82	
Mg	0.95	
Cl	0.86	0.29
HCO ₃	0.26	0.81
H ₄ SiO ₄		0.87
SO ₄	0.73	
NO ₃	0.77	-0.26
F		0.56
-----		-----
PO ₄		0.72
DOC		
U		
Sr	0.86	
Ba	0.55	-0.42

The constituents below the dashed line were not included in the component model. Figures indicate their correlations with the component scores. Coefficients with an absolute value below 0.25 are not given. The first three eigenvalues of the corresponding principle component solution were respectively: 6.37, 2.39 and 0.84.

influences they might have on the outcome of the CA. The program (PA1 in the SPSS manual; Nie et al., 1975) allowed the scores of these samples in the component model to be calculated. The Gutman criterion was applied as a rough guideline for the number of components (extracting only those factors that have eigenvalues > 1.0). Other possibilities close to this criterion were also tested, since there is no precise method to determine the number of components (Jöreskog et al., 1976). All results were checked for their hydrogeochemical interpretability. A two-component model was chosen in this study, whereby only those variables were retained that had significant loadings on at least one of the components. This model satisfied the hydrogeochemical and statistical criteria best.

Table II presents the adopted two-component model. The remaining variables were correlated with the derived components. The correlation coefficients of constituents which were excluded from the computation of the component model, are also presented in Table II. U and DOC have no relation with either one of the components.

5. HYDROGEOCHEMICAL INTERPRETATION

The two components given in Table II are termed evaporation component and fault/depth component respectively.

5.1. *Evaporation component*

Variables with a high loading on this component are Ec, Cl, NO_3 , Ca, Mg, Na and K; SO_4 has a slightly lower loading. Cl, NO_3 , K and also SO_4 are related to the combination of surficial and anthropogenic influences. In agricultural areas high evaporation is due to relatively intense soil use, irrigation and high moisture retention of the agricultural soil. These factors and the application of fertilizers contribute to high scores on the evaporation component. In forests no fertilizers are applied; shade keeps the temperature lower and the rate of evaporation is consequently somewhat lower. Due to a relatively "loose" soil structure, the rate of infiltration of rainwater in forest soils is higher than in agricultural areas. This implies that water which enters the groundwater system is more concentrated in agricultural areas.

The distribution of the scores of the evaporation component are presented in Fig. 6a. The areas with high values are indeed farmlands and villages.

5.2. *Fault/depth component*

Variables with a high loading on this component are pH, HCO_3 , F and H_4SiO_4 . HCO_3 and pH are related to each other in the carbonate system. Higher values of F and H_4SiO_4 generally indicate a somewhat deeper percolation level. The interpretation of this component is that fault and fracture

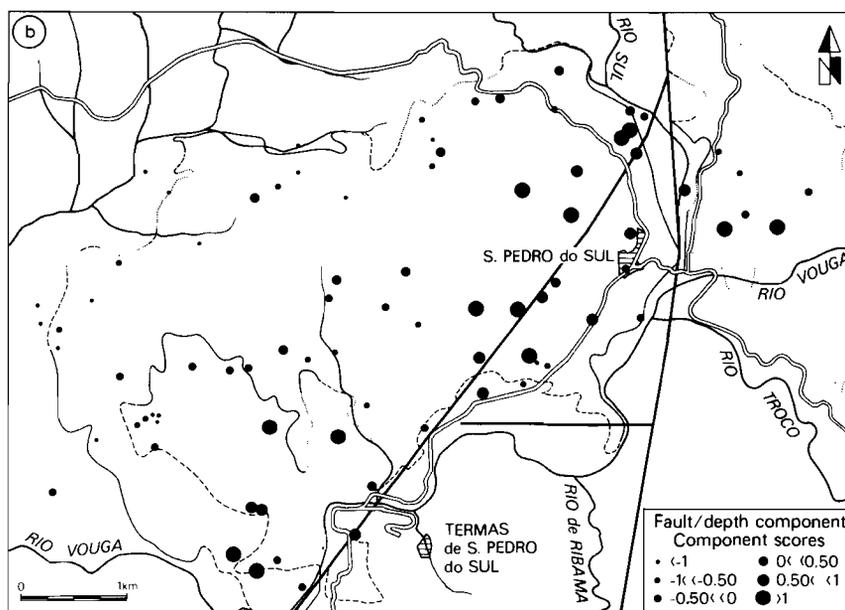
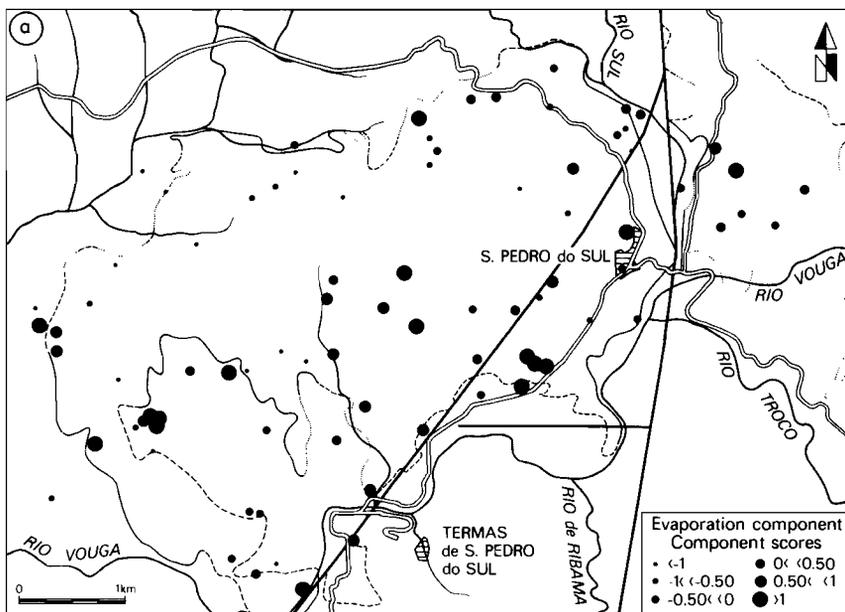


Fig. 6. Distribution maps of the component scores in the São Pedro do Sul granite.

zones permit a percolation of meteoric water through deeper zones, thus acquiring a composition more or less in equilibrium with “fresh” rock. The geographical distribution of the scores (Fig. 6b) on the fault/depth component reveals that the scores are high in tectonized areas.

5.3. Component scores plot: genetic implications

A plot of scores of the evaporation component vs. the fault/depth component is given in Fig. 7. The estimated areas of the streams, springs and taps are contoured. The following trends are depicted in the plot:

(I) Stream waters are found in the center, indicating their “average” character.

(II) Arrows which express the “vectorial relation” between the following phenomena are indicated:

- (1) evaporized surficial: agriculture and/or villages;
- (2) non-evaporized surficial: forests;
- (3) evaporized deep; and
- (4) non-evaporized deep.

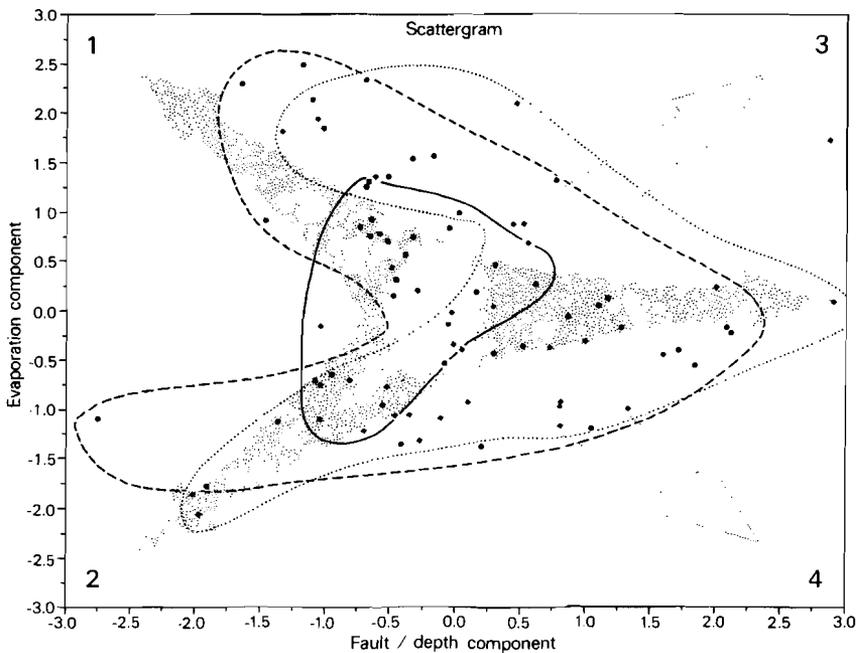


Fig. 7. Scattergram of the evaporation component scores vs. the fault/depth component scores. Symbols have the same meaning as in Fig. 3. The solid line outlines the stream water samples, the dashed line the spring water samples and the dotted line the tap water samples. Arrows are explained in the text.

Phenomena (1) and (2) are portrayed by shaded arrows while (3) and (4) are indicated by dotted ones in Fig. 7.

(III) Tap waters have a deeper origin than spring waters.

The evaporized deep type waters do not exist: it is unlikely in this area for one and the same water sample to show both surficial and depth characteristics. A similar reasoning applies to non-evaporized deep type waters: the deeper a water percolates, the longer it remains in contact with rock components and thus its solute content will increase. A more realistic presentation (shaded arrow in Fig. 7) will be a kind of vectorial sum of these two, displaying (almost) no influence of the evaporation component. There is evidence for the existence of such an arrow in Fig. 7.

The component model presented is relatively simple and internally consistent. The influence of evaporation on the water composition is considerable, a result supported by the fact that many springs dry out during summer, indicating that spring water remains underground for relatively short periods.

An attempt was made to correct for the influence of the evaporation, expressed by the E_c , as a method to "standardize" the water compositions. The partial correlations, remaining after the removal of the correlation attributable to the E_c , have been computed and on the residuals CA was performed again. Unfortunately the results had no hydrogeochemical meaning, because evaporation dominates the total variance within the samples to such an extent that, after correction, the remaining variance is influenced for an important part by sampling and analytical errors. It is obvious that in such cases a reasonable interpretation of the residuals is virtually impossible. It is to be expected that in areas with high evaporation this process will obscure other phenomena that may be apparent in areas not characterized by high evaporation (e.g., Van Diest et al., 1982).

6. DISTRIBUTION OF URANIUM IN THE WATER SAMPLES

The uranium distribution in the waters of the study area is shown in Fig. 3. The U concentrations are low (the highest concentration is $1 \mu\text{g l}^{-1}$) compared with other granitic regions with known U mineralizations, e.g. Nisa, Portugal: 43 out of 116 samples above $1 \mu\text{g l}^{-1}$, up to $25.5 \mu\text{g l}^{-1}$ (Dekkers et al., 1983b), Sortelha, Portugal: 34 out of 92 samples above $1 \mu\text{g l}^{-1}$, up to $9.5 \mu\text{g l}^{-1}$ (Walen et al., in prep.) and Lachaux, France: 26 out of 70 samples above $1 \mu\text{g l}^{-1}$, up to $6.3 \mu\text{g l}^{-1}$ (Van Diest et al., 1982). No significant correlation of U with either of the components exists (Table II). This is in contrast with the Vouzela region, south of the study area, where U scores highly on a fault/depth-related component (Ten Haven et al., 1985). In this area small uranium mineralizations are known (Cerveira, 1951). The low U values — the bulk of the samples has concentrations close to or below the detection limit of the analytical method — and the absence

of correlations of U with either of the components leads to the conclusion that uranium has not undergone any concentration process. The absence of any correlation with the fault/depth component may imply that the uranium is not mobilized. The occurrence of (hidden) U mineralizations in the São Pedro do Sul granite itself seems therefore unlikely.

7. DISCUSSION

The high U (8–58 ppm) and Th contents (39–621 ppm) are responsible for the high radioactivity of the granite. Basham et al. (1982b) reported uraninite as a common accessory mineral and they suggested that a considerable part of U is built in refractory and non-leachable minerals, such as monazite, apatite, zircon and rutile. A mineralogical assessment for U is given, but unfortunately not for Th.

Uraninite is a leachable U mineral when its Th content is low (Grandstaff, 1976). In the São Pedro do Sul granite the Th contents are in the range of 3–7% ThO₂, implying that this uraninite is not easily leachable (Basham et al., 1982a). This is supported by the concordance of the uraninite chemical age (321 ± 31 Myr.; Basham et al., 1982b) with the age of the granite determined by other methods.

The granite intrusion did not reach high crustal levels indicated by the paucity of veins and by the occurrence of sillimanite. In the Nisa–Monte Claro region, central Portugal, andalusite is found in the granite (Pilar, 1966; Dekkers et al., 1983b), indicating that the Nisa granite was a so-called high-level intrusion. In this granite many mineralized veins are present and in the contact zone mineralizations of U, W, Ba, Pb and Zn occur. It could well be that a relation exists between the depth of intrusion and the occurrence of (mineralized) veins; in other words, a relatively shallow intrusion depth is a favourable factor for vein development which may lead to mineralizations when other circumstances are also favourable [e.g., in the (granitic) intrusion there should be a fluid with mineralizing power (Simpson et al. (1979)]. A similar conclusion was derived by Plant et al. (1983) in a study of the granites in the Scottish highlands, U.K.

The conclusion must be drawn that the granite of São Pedro do Sul, despite its high radioactivity, is not a favourable site for the development of U mineralizations. The granite is only slightly altered (an early alteration stage may have generated part of the muscovite): the uraninite (Th-bearing) was not remobilized during the cooling history of the granite. Tectonic activity caused faulting and fracturing which allows for a deeper penetration of surface water. However, fluids which may have acted upon the granite were unable to liberate uranium from the rock.

In the neighbouring southern granite greisenization phenomena are well developed (Oen, 1958; Ten Haven et al., 1985); along the N–S-directed fault vein type uranium mineralizations developed (Cerveira, 1951). Genetically the probability of occurrence of U mineralizations in the São Pedro do Sul

granite itself seems very low. This is confirmed by the low U concentrations of the waters. There is no indication for a geochemical anomaly which could lead to the discovery of an U mineralization.

8. CONCLUSIONS

(1) The statistical methods adopted lead to a consistent interpretation of the water chemistry. A two-component model comprising an "evaporation" component and a "fault/depth" component was derived.

(2) Evaporation is an important process in areas characterized by low rainfall and/or relatively dry seasons. The time period between infiltration and discharge of spring waters in the São Pedro do Sul granite is relatively short.

(3) Stream water samples represent more or less an average of the waters in a (restricted) geographic area, eliminating outlying effects and obscuring local trends. Therefore springs and taps are more suitable for the investigation of water-rock relationships.

(4) Tap (perennial spring) water usually originates from greater depth than (seasonal) spring water and therefore has more prospective value for hidden ores than stream and (seasonal) spring water.

(5) It is unlikely that hidden U mineralizations are present in the São Pedro do Sul granite.

(6) The attempt to "standardize" water compositions by correcting for the influence of the Ec failed because evaporation dominates the total variance amongst the samples to such extent, that the remaining variance is for a major part determined by sampling and analytical errors.

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REFERENCES

- Basham, I.R., Ball, T.K., Beddoe-Stephens, B. and Michie, U. McL., 1982a. Uranium-bearing accessory minerals and granite fertility, II. Studies of granites from the British Isles. Proc. Symp. on Uranium Exploration Methods, Review of the NEA/IAEA R & D Programme. Paris 1982. Nucl. Energy Agency, Paris, pp. 398–411.
- Basham, I.R., Vairinho, M.M.B. and Bowles, J.F.W., 1982b. Uranium-bearing accessory minerals in the São Pedro do Sul granite, Portugal. In: Vein-type and Similar Uranium Deposits in Rock Younger than Proterozoic. Proc. Tech. Comm. Meet., Lisbon, IAEA (Int. At. Energy Agency), Vienna, pp. 279–298.
- Cerveira, A.C., 1951. Sobre a metallogenia do uranio em Portugal. Bol. Soc. Geol. Port., 8: 142–182.
- Dekkers, M.J., Vriend, S.P., Van Diest, Ph., Van der Weijden, C.H. and Oosterom, M.G., 1983a. Geochemical controls of transport and deposition of uranium from solution. Case study: São Pedro do Sul (Portugal). Extern. Rep., Inst. Earth Sci., State Univ. of Utrecht, Utrecht, 54 pp.
- Dekkers, M.J., Vriend, S.P., Walen, C.G. and Van der Weijden, C.H., 1983b. Geochemical controls of transport and deposition of uranium from solution. Case study: Nisa (Portugal). Extern. Rep., Inst. Earth Sci., State Univ. of Utrecht, Utrecht, 87 pp.
- Dixon, W.J. (Chief-Editor), 1981. BMDP Statistical Software 1981. University of California Press, Berkeley, Calif., 725 pp.
- Fernandes, A.P., 1970. Contribuição para o estudo da região dos granitos radioactivos de S. Pedro do Sul. Junta de Energia Nuclear, Lisbon.
- Grandstaff, D.E., 1976. A kinetic study of the dissolution of uraninite. Econ. Geol., 71: 1493–1506.
- Jöreskog, K.G., Klován, J.E. and Reymont, R.A., 1976. Geological Factor Analysis. Methods in Geomathematics 1. Elsevier, Amsterdam, 178 pp.
- Korkisch, J. and Hecht, F., 1972. Elemente der sechsten Nebengruppe. Springer, Berlin, 524 pp. (see especially pp. 203–211).
- Lautensach, H., 1932. Portugal I. Ergänzt. Heft No. 213, Petermanns Mitt., 187 pp.
- Mendes, F.J., 1961. Determinação pelo método do estrôncio, da idade absoluta de algumas rochas e minerais de Portugal Continental e Ultramarino, Lisboa. Junta de Energia Nuclear, Lisbon.
- Miesch, A.T., 1981. Estimation of the geochemical threshold and its statistical significance. J. Geochem. Explor., 16: 49–76.
- Nie, N.H., Hull, C.H., Jenking, J.G., Steinbrenner, K. and Bent, D.H., 1975. Statistical Package for the Social Sciences. McGraw-Hill, New York, N.Y., 2nd ed., 675 pp.
- Oen, I.S., 1958. The geology, petrology and ore deposits of the Viseu region, northern Portugal. Ph.D. Thesis, University of Amsterdam, Amsterdam, 179 pp.
- Oen, I.S., 1970. Granite intrusion, folding and metamorphism in central northern Portugal. Bol. Geol. Min., 81(2–3): 271–298.
- Pilar, L., 1966. Petrografia das rochas metamórficas e dos granitos de contacto da região de Nisa. Port. Serv. Geol. Comun., 50: 51–83.
- Pinto, M.C.S., 1979. Geochemistry and geochronology of granitic rocks from the Aveiro and Viseu districts (northern Portugal). Ph.D. Thesis, University of Leeds, Leeds, 196 pp.
- Piper, A.M., 1944. A graphic procedure in the geochemical interpretation of water-analyses. Am. Geophys. Union Trans., 25: 914–923.
- Plant, J.A., Simpson, P.R., Green, P.M., Watson, J.V. and Fowler, M.B., 1983. Metalliferous and mineralized granites in relation to regional metamorphism and fracture systems in Northern Scotland. Inst. Min. Metall., Trans., Sect. B, pp. 33–42.
- Priem, H.N.A., Schermerhorn, L.J.G., Boelrijk, N.A.I.M. and Hebeda, E.H., 1984. Rb–Sr geochronology of Variscan granitoids in the tin–tungsten province of northern Portugal: a progress report. Terra Cognita, pp. 212–213.

- Schermerhorn, L.J.G., 1959. Igneous, metamorphic and ore geology of the Castro Daire—São Pedro do Sul region (northern Portugal). Ph.D. Thesis, University of Amsterdam, Amsterdam, 617 pp.
- Selinus, O., 1981. Litho-geochemical exploration data in sulphide prospecting in northern Sweden. In: A.W. Rose and H. Gundlach (Editors), *Geochemical Exploration 1980*. *J. Geochem. Explor.*, 15: 181—201.
- Simpson, P.R., Brown, G.C., Plant, J.A. and Ostle, D., 1979. Uranium mineralization and granite magmatism in the British Isles. *Philos. Trans. R. Soc. London, Ser. A*, 291: 385—412.
- Ten Haven, H.L., Konings, R., Schoonen, M.A.A., Jansen, J.B.H., Vriend, S.P., Van der Weijden, C.H. and Buitenkamp, J., 1985. Geochemical studies in the drainage basin of the Rio Vouga (Portugal), II. A model for the origin of hydrothermal water in the Vouzela region. *Chem. Geol.*, 51: 225—238.
- Thadeu, D.C., 1977. Hercynian paragenetic units of the Portuguese part of the Hesperic massif. *Bol. Soc. Geol. Port.*, 20: 247—276.
- Van Diest, Ph., Vriend, S.P., Van der Weijden, C.H., Zuurdeeg, B.W., Oosterom, M.G. and Keuken, M.P., 1982. Geochemical controls of transport and deposition of uranium from solution. Case study: Lachaux (France). *Extern. Rep. Inst. Earth Sci., State Univ. of Utrecht, Utrecht*, 57 pp.
- Walen, C.G., Van der Weijden, C.H., Vriend, S.P. and Oosterom, M.G., in press. Geochemical controls of transport and deposition of uranium from solution. Case study: Sortelha (Portugal).

CHAPTER VII

Uranium anomaly evaluation in groundwaters: a hydrogeochemical study in the Nisa region, Portugal

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Abstract—The hydrogeochemistry of the Nisa region, central Portugal, an area of known U mineralization, was studied. The geology of the region comprises an S-type high-level granite intrusion with vein-type U-mineralization, its contact-metamorphic aureole developed in a schist host rock containing disseminated U-mineralization. An integrated multi-variate statistical, hydrogeochemical and thermodynamic approach was adopted for the interpretation of groundwater data from the granite and its contact aureole. The U groundwater anomalies are evaluated within the local hydrogeochemical context. One-hundred-and-fifteen water samples were collected and analyzed for pH, Ec, Eh, Na, K, Ca, Mg, Fe, Mn, Al, U, Li, Ba, Sr, Cl, HCO₃, SO₄, NO₃, PO₄, F, DOC and H₂SiO₄. Uni- and bi-variate statistical studies of these dilute waters indicate that mainly surface and land-use characteristics control the dominant chemical processes, with water-rock interaction playing a lesser role. Granite/schist compositional differences show up especially in the Mg and HCO₃ content of the waters. Multi-variate statistical analyses (Principal Component Analysis and Q-mode Cluster Analysis) were carried out separately on the granite and schist water groups. Evapotranspiration is an important process both in the schist and granite environment. The impact of fault/fracture zones, land-use, oxidation/reduction reactions and water-rock interaction is different for the waters from each bedrock type. For both rock types, the waters can be classified into genetic groups or clusters ranging from surface runoff/shallow interflow, through surface, agriculture, and infiltrated, to village-pollution type water. The distribution pattern of these groundwater types is not disrupted by the granite-schist contact, allowing for an interpretation of the U distribution in the entire study area. Thermodynamic calculations indicate that the predominant U species in solution is UO₂(HPO₄)₂⁻. Virtually all waters are undersaturated with respect to U minerals. The distribution of U in the waters is thus not influenced by precipitation of U-bearing minerals. The distribution of U in the water samples as well as that for U/Ec (in an attempt to correct for evapotranspiration) are evaluated. The U- and U/Ec-anomaly patterns are considerably biased by bedrock differences and varying genetic history. Interpretability is greatly improved if these differences are taken into account by defining U-threshold values for each genetic water cluster. All known radiometric anomalies are reflected in the hydrogeochemical U-anomaly pattern. The general hydrogeochemical features allow for a refined evaluation of the known radiometric anomalies and of the additional anomalies found in the present study. Additional hydrogeochemical anomalies from waters reflecting depth characteristics are attractive exploration targets.

INTRODUCTION

THE MERIT of multi-variate statistics in distinguishing groundwater types and in unravelling factors and processes which determine the composition of groundwater samples, has recently been demonstrated in several hydrogeochemical studies (e.g. VAN DIEST *et al.*, 1982; TEN HAVEN *et al.*, 1985; DEKKERS *et al.*, 1983, 1986; COMANS *et al.*, 1986; ZIELINSKI *et al.*, 1987). Multi-element analyses are used to gain information on the origin and evolution of the water samples. Important factors and processes influencing the chemical composition of groundwaters are the following:

- (1) Distance to the ocean, i.e. rainwater composition.
- (2) Climatological influences.
- (3) Redox processes in the surficial environment.
- (4) Thickness of the soil.
- (5) Depth of percolation of meteoric water, determined by the porosity and permeability of the bed-

rock, by topography and by fault- and fracture-zones.

(6) Bedrock chemistry.

(7) Anthropogenic contributions (agriculture and pollution).

The hydrogeochemical response of U deposits in a granite-schist contact zone is the subject of this investigation. The U-anomaly pattern in water samples in the Nisa region, central Portugal (Fig. 1), was studied in the context of the above mentioned hydrogeochemical features. A groundwater survey was adopted for its potential to locate hidden U deposits in addition to outcropping mineralization.

Geological setting

The Nisa region (Fig. 1) consists of three main geological units:

- (1) the Hercynian Nisa/Castelo de Vide (NCdV) and Gafete granites;
- (2) the pre-Ordovician Beira Schist Formation (BSF);

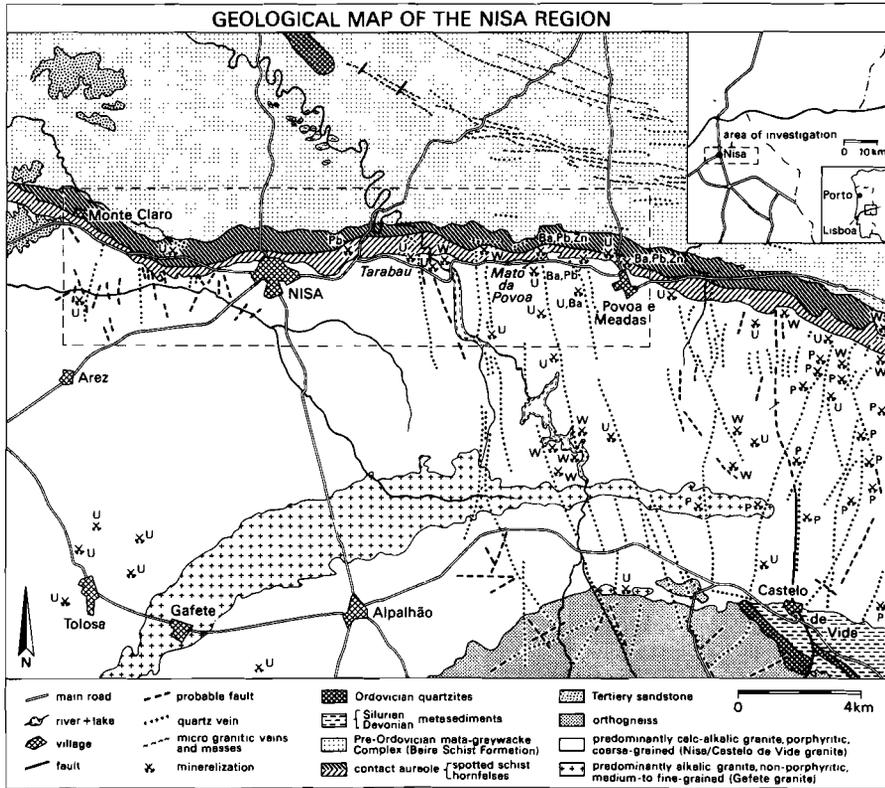


FIG. 1. Geological map of the Nisa region, east-central Portugal, after RIBEIRO *et al.* (1965) and FERNANDES *et al.* (1973).

(3) the contact metamorphic aureole around the granite.

The Hercynian granites belong to a complex of intrusive bodies south of the Tejo River. The oldest bodies are of Caledonian age (FERNANDES, 1970, 1971; PINTO, pers. comm.) and these were altered into orthogneiss during the Hercynian orogeny. Two younger granites were intruded during the Hercynian orogeny (some 300 Ma ago) on the northern flank of the complex: the NCdV granite and the smaller Gafete granite (FERNANDES, 1970, 1971). The NCdV granite is a coarse-grained, porphyritic, calc-alkalic, high level S-type two-mica granite. Andalusite is a common accessory mineral (PILAR, 1966a). The Gafete granite is a medium- to fine-grained alkalic non-porphyritic biotite granite.

The BSF crops out over large parts of the western part of the Iberian Peninsula. Phyllites and quartz-phyllites with minor intercalations of more Ca-rich rocks are typical. These have been regionally metamorphosed (low-grade) in the Nisa region. The sedimentary age of the BSF is probably Infracambrian (THADEU, 1977).

The intrusion of the NCdV granite caused a contact-metamorphic overprint on the BSF forming a hornfels and a spotted schist zone. Typical mineralogy of the spotted schist zone (besides quartz and feldspars) comprises biotite, white mica, chlorite and cordierite, with accessory graphite and pyrite. Close to the NCdV granite, the spotted schist grades into hornfels with similar mineralogy; only chlorite is virtually absent. Garnet and (clino-)zoisite occur occasionally.

The area was uplifted and eroded after the Hercynian orogeny. Alpine movements created or rejuvenated an approximately N-S directed vein- and fracture-system in the northern part of the NCdV granite. Peneplanation was completed in Tertiary times; continental sands were deposited up until the Pleistocene. The present erosional level has reached the original roof zone of the granite (PILAR, 1966a).

Mineralization

The Nisa region is known for U deposits (Fig. 1). Quartzitic U-bearing veins occur in the NCdV

granite, and in the contact zone disseminated U deposits, thought to be extensions of vein-systems in the granite, occur. The important ore-minerals are uranyl-phosphates (autunite, torbernite, Ba-autunite, bassetite, autunite-uranocircite). The disseminated Nisa deposit, located between Nisa and Monte Claro, is the largest in the study area. The phosphuranylite variety nisaite predominates in certain parts of this deposit (LENCASTER and VAIRINHO, 1970). PILAR (1966a, 1966b) favors a hydrothermal origin, postulating that the U-phosphates are the result of (sub-recent) oxidation in the superegene zone.

Other important U occurrences in the study area are the Tarabau and Mato do Povoá veins (DE FARIA, 1966). The Tolosa vein is located farther to the south, and is the only vein mined in the past (FERREIRA, 1971).

In addition small occurrences of wolframite, barite, apatite and galena-sphalerite are found in quartz veins (FERNANDES *et al.*, 1973; RIBEIRO *et al.*, 1965; NEIVA *et al.*, 1953). A more detailed overview is given in DEKKERS *et al.* (1984).

Hydrology

A Mediterranean climate with hot summers prevails in the study area. Precipitation falls predominantly in winter; evapotranspiration exceeds precipitation in summer. The granite forms a nearly flat topographic high and drains into a relatively steeply dipping north-sloping schist zone. Dry granite and schist areas are either barren, virtually without soil, or covered with forests (mainly eucalyptus). Sparsely occurring springs in both the granite and the schist have low yields (1–5 l/min) and are confined to fault- and fracture-zones which occasionally have (quartz) vein development.

Because water is scarce in the region, wells are excavated out of the bedrock for domestic and agricultural purposes. Their diameter is typically about 2 m and their depths range from 2 to 20 m depending on the local water table. Well-walls are not cemented, nor is any masonry used. Yields are generally low; in most cases water is manually extracted. The crops grown are strongly dependent on water availability: horticulture and corn fields are found in the direct vicinity of wells, whereas cereals, which consume less water, are cultivated at greater distances.

More wells are located in the granite than in the schist. Therefore, agriculture is predominantly located in granitic areas. However, between Nisa and Monte Claro the schist zone dips more gently, which results in increased water availability, making this schist area partly suitable for agriculture.

Sampling and analytical techniques

Twenty spring water samples (12 in the granite, eight in

the schist) and 95 well water samples (54 and 41 in the granite and schist, respectively) were collected in the early summer of 1982. All springs in the study area were sampled. Only wells showing no visual signs of contamination and without excessive growth of water plants and algae were selected.

Each water sample was filtered through a 0.45 μm membrane filter at the sample site. A portion of the filtrate was acidified with analytical grade 6 N HCl (1 ml/250 ml filtrate) to prevent adsorption by the container walls. The remainder was kept for anion analysis. *In situ* measurements of the pH, electroconductivity (Ec), redox-potential (Eh) and water temperature were carried out. Bicarbonate was determined titrimetrically (Gran-plot method for endpoint indication) at a field laboratory.

Fluoride, Cl and NO_3 were determined in the unacidified portions by ion selective potentiometry and spectrophotometry (NO_3^-). The other components were determined in the acidified portions. Aluminium, Fe and Mn were determined by graphite furnace atomic absorption spectrometry and Ca, Mg, Na, K, Sr, Ba, S, Si, Li and P by inductively coupled plasma emission spectrometry. Dissolved organic carbon (DOC) was analyzed with a Coleman Carbon Analyzer. Uranium was preconcentrated by evaporation and solvent extraction with ethyl acetate, then measured in a 98% NaF, 2% LiF fusion flux by fluorimetry using a Galvanek/Morrison fluorometer (KORKISCH and HECHT, 1972). All samples were checked with respect to their charge balance, and if necessary they were re-analyzed.

GENERAL HYDROGEOCHEMICAL INTERPRETATION OF THE RESULTS

The U distribution is, apart from proximity to mineralization, influenced by many factors. A meaningful interpretation of the U contents is therefore only attained after a good understanding of the water chemistry in the area has been acquired. For this purpose univariate and multivariate statistical as well as thermodynamic considerations were taken into account.

Discriminant function analysis

Because water samples were collected from two distinct geological domains the samples may be grouped accordingly. Discriminant function analysis (DFA) (SPSS; NIE *et al.*, 1975), which assumes *a priori* knowledge about the grouping, is a common technique to test whether this grouping is statistically significant. Additionally, if a grouping is significant, DFA can assign samples of unknown origin to a specific group.

The water samples were divided into a granite and a schist group, based on field observation; in a few dubious cases from close to the contact zone no grouping was pre-assigned. The direct method (NIE *et al.*, 1975), in which all the independent variables are entered concurrently, was applied with the variables: pH, Eh, Na, K, Ca, Mg, HCO_3^- , SO_4^{2-} , H_4SiO_4 , PO_4^{3-} and F. Trace elements were excluded, because their analytical precision is somewhat poorer, owing to concentration levels being close to their respective

detection limits. Chloride and NO_3 were excluded because their relation to surficial and anthropogenic processes makes them less suitable for discrimination between rock types. Because the statistical tests of DFA are based on normal distributions, the actual distributions were transformed to distributions with skewness zero by means of adjusting the α -parameter in the transformation of the type $\ln|x - \alpha|$ (MIESCH, 1981; SELINUS, 1981).

The classification that emerged from the DFA scores is consistent with the pre-assigned grouping except for a few samples collected in the vicinity of the contact zone. Reconsideration of geomorphological and hydrological arguments regarding the catchment area of those sampling sites leads to the conclusion that the DFA scores rectified some ambiguous field classifications. The outcome of the DFA, which is a classification on geochemical grounds, is used in the following statistical data interpretation.

Histograms

Histograms of the constituents are presented in Fig. 2. The low E_c of the waters indicates their dilute nature. The waters from the schist contain more dissolved mineral matter, e.g. Mg and HCO_3 , than the waters from the granite. Many constituents show a tendency towards bimodality due to geochemical differences between the two lithologies. Except for the pH, Eh (both intrinsically logarithmic) and H_4SiO_4 , all constituents show lognormal characteristics. The normal distribution of H_4SiO_4 , also observed in many other data sets (e.g. VAN DIEST *et al.*, 1982; VAN DER WEIJDEN *et al.*, 1984; DEKKERS *et al.*, 1983, 1986), is explained by the equilibrium between dissolved silica and amorphous silica, as is indicated by thermodynamic calculations, thus limiting the upper tail of the distribution.

Piperdiagrams

The relative amounts of the major constituents are plotted (Fig. 3a and b) in a Piperdiagram (PIPER, 1944). The Ca/Mg ratio differs between waters from the granite and the schist areas, the relative Mg and HCO_3 contents being higher in the schist waters. In the granite as well as in the schist, the Ca/Mg ratio of the waters remains almost invariant with increasing Na + K contents. Samples with the highest E_c values contain relatively more Ca and Mg in both water groups. This is an indication that apart from mere evapotranspiration other processes (water-rock interaction, fertilizer application) are of importance.

Scattergrams

Scattergrams of some selected species in the water samples are presented in Fig. 4a–d. The Na/Cl ratios

(Fig. 4a) deviate only slightly from the seawater ratio, indicating that the samples display dominantly surface water characteristics. Apparently, the waters from the schist areas are more influenced by evapotranspiration and thus circulate at shallower depths than the waters from the granite areas. The large excess of SO_4 over Cl compared to the seawater ratio (Fig. 4b) is caused by acid rain and leached fertilizer. The observed correlation indicates the conservative behavior of SO_4 in this region. Although this part of Portugal is neither intensively cultivated nor heavily industrialized, a relatively small amount of sulfate has already made a noticeable impact on these dilute waters with little buffering capacity. Chloride is plotted vs NO_3 in Fig. 4c together with the 1:1 ratio line. Generally, the Cl content is considerably higher than the NO_3 content with no evident correlation. This implies different origins for the constituents. An excess HCO_3 over Ca exists compared to the calcite dissolution line (Fig. 4d), demonstrating that the use of CaCO_3 for agricultural purposes has not affected the water composition.

Eh/pH diagram

The waters display the common Eh/pH features (cf. Fig. 5) of natural surface water samples in granitic terrains (slightly acid and oxidizing). The waters from the schist are slightly less oxidizing than the waters from the granite, which is in accord with the lithological characteristics of their catchment areas. The schist, in contrast to the granite, contains organic matter. Of course the pH values of the samples of the present study are somewhat lower than those measured by HENRY *et al.* (1982) in U-bearing sandstones deposited in a fluvialite to deltaic sedimentary environment.

DOMINANT PROCESSES: PRINCIPAL COMPONENT ANALYSIS

Principal component analysis (PCA) was applied to study the correlation patterns in either data set and to evaluate the relative importance of the processes determining the water composition. PCA (principal component analysis, number of components selection and Kaiser Varimax rotation) was carried out on the granite and schist water data sets, using the SPSS PA1 software (NIE *et al.*, 1975). Any statistical model increases in reliability with an increasing number of samples. Statistical criteria and experience with these types of data sets (e.g. VAN DIEST *et al.*, 1982; TEN HAVEN *et al.*, 1985; DEKKERS *et al.*, 1983, 1986) indicate that for a reliable model 50 samples is an absolute minimum for a sound interpretation. The rule "number of samples > three times the number of variables", recommended by HOWARTH and SINDING-LARSEN (1983), leads to similar minimum sizes for data sets.

U anomaly evaluation in groundwater, Nisa, Portugal

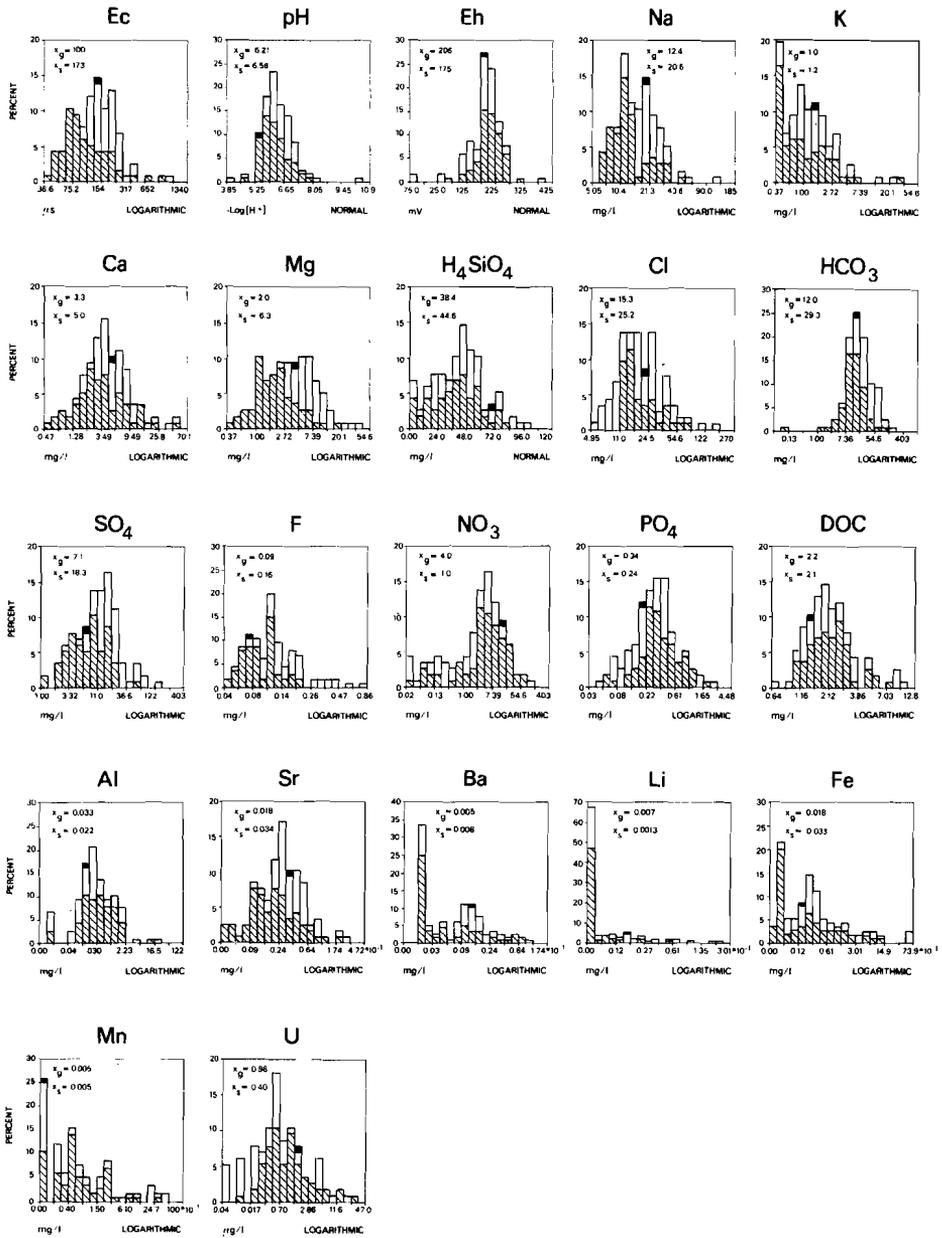


FIG. 2. Histograms of the dissolved chemical species in 66 granite and 49 schist waters. Granite waters are indicated with the hatched parts of the bars and schist waters with the open parts. For one sample (black) the origin is unknown. X_g and X_s denote either the geometric or arithmetic means depending on the nature of the distribution.

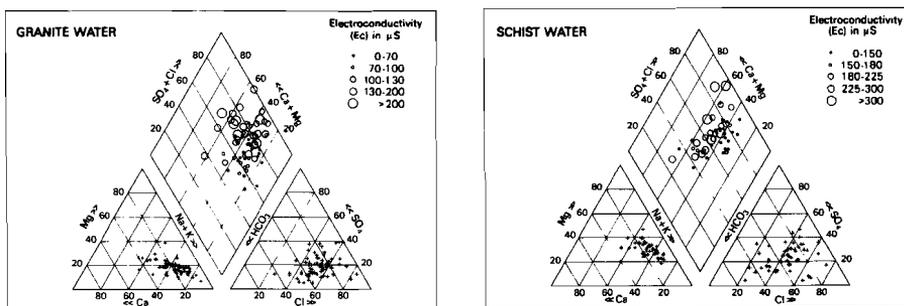


Fig. 3. Piperdiagrams for the granite and schist water samples. The relative contents in milli-equivalents are plotted for the cations Ca^{2+} , Mg^{2+} and $(\text{Na}^+ + \text{K}^+)$ and the anions Cl^- , HCO_3^- and SO_4^{2-} . In the central diamonds, the circle size increases with the Ec.

The variables used in a PCA must have normal distributions in order to obtain a reliable interpretation. The data sets were transformed with the same procedure as was used in the DFA. Samples with highly deviating values for its variables, i.e. values outside the range of the mean plus or minus two standard deviations, were removed from the data set. The coefficient α was then redetermined.

With this transformed data set, a first PCA model with corresponding component scores was calculated, using only those variables for which the values

were not close to the analytical limit of detection. Samples with multivariate outliers, i.e. highly deviating component scores (three granite and four schist water samples), and variables showing no significant correlations with other variables were removed from the data set. With this data set, which was again transformed with newly determined α s, the final robust PCA model was calculated. For this robust model, the component scores for the removed samples were calculated as well as the correlation coefficients between the components and the

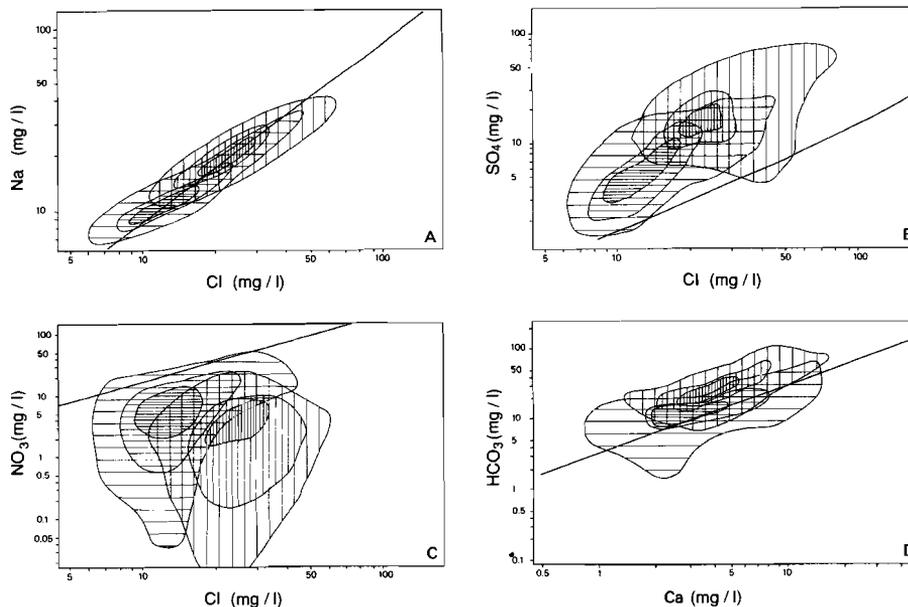


Fig. 4. Scattergrams of Na vs Cl (A), of SO_4 vs Cl (B), of NO_3 vs Cl (C) and of HCO_3 vs Ca (D). The areas encompassing 30, 50 and 90% of the samples are contoured with increasingly wider hatching. Granite waters are represented by horizontal hatching and schist waters by vertical hatching. Concentrations are in mg/l. For reference purposes, in the Na vs Cl and the SO_4 vs Cl plots, the seawater dilution line is drawn. In the NO_3 vs Cl plot the 1:1 ratio line and in the HCO_3 vs Ca plot the calcite dissolution line is drawn.

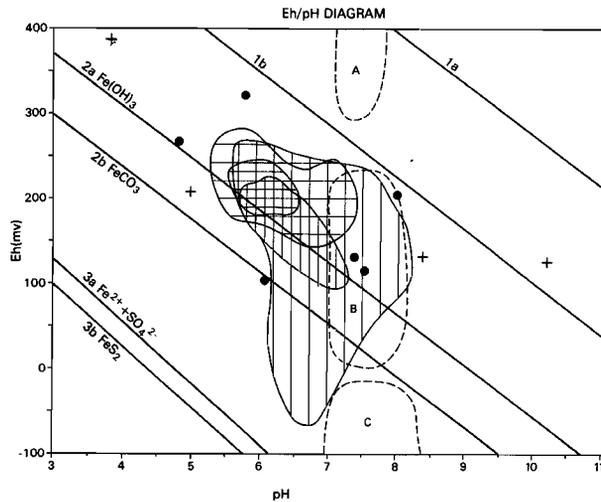


Fig. 5. Eh/pH diagram with 50 and 90% sample contours (close and wide hatching, respectively). Granite waters have horizontal hatching and schist waters vertical hatching. Samples which are outside the contoured areas are represented by ● for granite waters and + for schist waters. The fields of HENRY *et al.* (1982) are drawn for comparison for their oxidized, intermediate and reduced water, indicated with the contoured A, B and C areas, respectively.

The reactions, shown in the diagram, are:

- 1: $\text{H}_2\text{O}_2 = \text{O}_2 + 2\text{H}^+ + 2\text{e}$
 $\text{Eh} = 0.682 - 0.059\text{pH} + 0.0291(\text{pO}_2/[\text{H}_2\text{O}_2])$
 1a: $\log(\text{pO}_2/[\text{H}_2\text{O}_2]) = 10^6$
 1b: $\log(\text{pO}_2/[\text{H}_2\text{O}_2]) = 1$
- 2: $\text{FeCO}_3 + 2\text{H}_2\text{O} = \text{Fe}(\text{OH})_3 + \text{CO}_2 + \text{H}^+ + \text{e}$
 $\text{Eh} = 0.614 - 0.059\text{pH} + 0.0591 \log(\text{pCO}_2)$
 2a: $\log(\text{pCO}_2) = -1.4$
 2b: $\log(\text{pCO}_2) = -2.4$
- 3: $\text{FeS}_2 + 8\text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 14\text{e}$
 $\text{Eh} = 0.345 - 0.067\text{pH} + 0.0084 \log[\text{SO}_4^{2-}]$
 $+ 0.00421 \log[\text{Fe}^{2+}]$
 3a: $\log[\text{Fe}^{2+}] = -5.5, \log[\text{SO}_4^{2-}] = -3$
 3b: $\log[\text{Fe}^{2+}] = -5.5, \log[\text{SO}_4^{2-}] = -4$

excluded variables. A comparable procedure was followed by OLESEN and ARMOUR-BROWN (1984) by their deduction of robust factor models.

No unambiguous procedures are available to determine the "correct" number of components (JÖRESKOG *et al.*, 1976). Therefore, geochemical criteria in combination with the scree test (CAITTELL, 1966) and the Guttman criterion (GUTTMAN, 1954)—extracting only components with eigenvalues greater than one—were used for this determination.

A four component model was selected for the granite waters and a three component model for the schist waters. The component loading matrices are presented in Table 1.

Geochemical interpretation

In the interpretation of the component models it must be kept in mind that components are indepen-

dent of each other, i.e. their intercorrelations are zero. However, they are used to trace processes in nature which are often intercorrelated to some extent. The waters from the granite and schist result in different PCA models due to differences in bedrock chemistry, hydrological regimes and anthropogenic contributions to either sample group. For example, the schist contains organic material and minerals that weather relatively easily. The granite is highly fractured compared to the schist. Agriculture is by and large restricted to the relatively water-rich granitic part of the study area.

Granite

Component 1. Evapotranspiration component. Component 1 is termed the evapotranspiration component because of the high loadings (>0.70) of the Ec, Na, Ca, Mg, Cl and SO₄, and the intermediate

loadings of K and HCO_3 . As in other studies (e.g. COMANS *et al.*, 1986; TEN HAVEN *et al.*, 1985; DEKKERS *et al.*, 1986) samples with high scores on this component are confined to the agricultural areas where irrigation cycles the groundwater through additional evapotranspiration stages. Generally, evapotranspiration components are characterized by high loadings of the Ec and the major species in water. The high loading of the relatively conservative Cl, originating from rainwater and inferior fertilizers, is typical.

With respect to the additional correlations it can be noted that more mineral-rich, re-cycled waters for agricultural purposes, contain more DOC. The alkaline earth metals Ca, Ba and Sr behave isochemically. The negative correlations of PO_4 and H_4SiO_4 indicate that their behavior is not influenced by merely evapotranspirative processes (cf. TEN HAVEN *et al.*, 1985; DEKKERS *et al.*, 1986).

Component 2. Fault/depth component. Component 2 is labelled the fault/depth component because of the high loading of F, released through weathering of F-bearing minerals, such as apatite, biotite and muscovite. The high HCO_3 loading is explained by water-rock interaction processes. Water, when penetrating through the soil increases in reactivity through the uptake of CO_2 formed through the decay of organic matter. The resulting circulating groundwaters of low pH are (partly) neutralized through cation release from the surrounding rock. Evidence for this is seen in the moderate loadings of Na and Ca, released through the weathering of feldspars.

Component 3. Fertilizer component. Component 3 is characterized by high loadings for K and NO_3 and moderate ones for F, Na and Ec. High loadings of K and especially NO_3 are related to fertilizer application. The slight association of the other variables is possibly due to the fact that water in relatively arid regions is mostly confined to fault and fracture zones. This is reflected in the moderate loading of F and related variables. The weak correlation of U to this component suggests that fertilizer application may contribute to the U concentration in the granite waters. However, DURRANCE (1986) demonstrated for an area of intensive agriculture in East Devon, England, that a significant contribution of U from fertilizers to the U concentration in surface waters is unlikely.

Component 4. Eh/pH component. High and opposite loadings of the pH and Eh characterize component 4. The opposite loadings are expected from general Eh/pH relations. The contribution of HCO_3 to component 4 is explained by the carbonate system in natural waters (GARRELS and CHRIST, 1965). The measured Eh is a fair indicator of the "real" Eh determined by various redox couples acting together resulting in an "intermediate" Eh as will be discussed elsewhere in this paper. The fact that the Eh/pH

component is defined separately from the components that express or contain depth influences, indicates that Eh and pH are not governed by depth of penetration. This agrees with GERMANOV *et al.* (1958), who argue that in a granitic environment waters may remain oxidizing up to several hundred meters depth.

Schist

Component 1. Evapotranspiration component. Component 1 is characterized—as in the granite waters—by high loadings of the variables: Ec, Na, Mg, Cl and SO_4 . It is, therefore, also termed the evapotranspiration component. Calcium, HCO_3 and F have moderate loadings. Samples with high scores on component 1 are mostly encountered in agricultural areas just as in the granitic environment.

The additional correlations of Sr and PO_4 are caused by similar processes as in the granite waters. The Li correlation may be related to the moderate loading of F on component 1; anyway Li is a very conservative element in dilute waters. The schist waters in the study area contain relatively high contents of F and Li.

Component 2. Water-rock interaction component. The variables with high loadings on this component are: Ca, HCO_3 , K and Eh (negatively). Both Ec and Mg have moderate loadings. The high loadings of HCO_3 and Ca point to waters which have used their CO_2 to react with surrounding rock (see component 2 of the granite waters). The loading of K may have its origin in weathering or in fertilizer application. In this case, the latter is less likely as NO_3 has an insignificant loading on this component. The behavior of NO_3 in the schist contrasts that of most other elements, which have higher contents in the schist, whilst NO_3 is four times lower than in the granite (cf. Fig. 2). This implies that fertilizer application is of minor importance in the schist areas, which explains the differing behavior of K, which is in granite areas predominantly fertilizer-related and in schist areas predominantly weathering-related.

The additional correlation of Sr is caused by its isochemical behavior to Ca. Manganese is related to the Eh, i.e. related to oxidation/reduction phenomena (this applies also for component 3).

Component 3. Surface/depth dipole component. Component 3 is characterized by high loadings of F, pH, and NO_3 (negatively). Moderate loadings are found for HCO_3 , and Eh (negatively). Because NO_3 is derived from fertilizers, the negative loading combined by the positive loading of F implies that waters with high scores on component 3 are unpolluted and may have their origin from somewhat deeper levels (faulting and fracturing). However, because no direct relation exists with the bigger (mapped) faults, this reasoning is difficult to substantiate. The pH, HCO_3

and Eh relations are similar to those in the granite areas (cf. component 4). If waters penetrate to similar depths in schistose and granitic environments, the relatively reduced and organic matter-rich character of the schist will have more influence on the Eh and pH of the penetrating waters than a granite. Therefore, an Eh/pH component is not separately defined in the schist waters, but related to both weathering and fracture zones.

Comparison of the component models of the granite and schist waters

The evapotranspiration components in both sample groups are similar. The geographical patterns of the component scores in both lithological units also link up over the contact. The equivalent of the water-rock interaction component (component 2) of the schist waters is the fault/depth component (component 2) of the granite waters. However, due to chemical differences between the two lithologies and differences in the hydrological regimes the expression of the two components is not the same. The equivalent of the surface/depth dipole component (component 3) of the schist waters is difficult to assess in the granite waters: there are features of components 2, 3

and 4 of the granite waters combined in the third component of the schist waters. However, NO₃ is related to fertilizers, i.e. contamination, which makes the fertilizer component (component 3) in the granite waters in some aspects similar to the surface/depth dipole component of the schist waters.

WATER TYPES: CLUSTER ANALYSIS

The spatial distribution of the evapotranspiration components within the granite and schist could easily be linked over the contact. The other processes described in these models are less easily related over the two geological units (see above). This is mainly caused by differences in the chemical and mineralogical compositions and different hydrological regimes on either side of the contact. This results in component models with overlapping interpretations for only partially equivalent components which, in such cases, are not easy to match. Rotation of the second and third components of the schist waters in their plane perpendicular to the first one does not lead to an improved match with the granite water components.

An alternative for an interpretable grouping

Table 1. Component models for the granite and schist waters

Component loadings	Granite waters				Schist waters		
	Component 1	Component 2	Component 3	Component 4	Component 1	Component 2	Component 3
pH				0.80			0.73
Eh				-0.86		-0.70	-0.36
Ec	0.82	0.34	0.32		0.84	0.35	
Na	0.80	0.29	0.31		0.88		
K	0.33		0.71			0.69	
Ca	0.81	0.42			0.58	0.70	
Mg	0.94				0.79	0.51	
HCO ₃	0.30	0.74		0.36	0.25	0.68	0.36
Cl	0.89				0.90		
SO ₄	0.87				0.70		
NO ₃			0.84				-0.79
F		0.83	0.33		0.47		0.72
Additional correlations							
U			0.30			-0.26	
Fe		-0.27		0.31			0.26
Mn						0.53	0.51
Al							
H ₄ SiO ₄	-0.32		0.38				
DOC	0.64			0.33			0.33
PO ₄	-0.46	0.39			-0.58		
Li		0.25			0.43	0.37	0.33
Sr	0.91				0.74	0.53	
Ba	0.65		0.31		0.29		

Only loadings and correlations outside the range of +0.25 and -0.25 are given. The eigenvalues of the components prior to rotation are respectively for the granite waters 6.12, 1.56, 1.18 and 0.94; for the schist 5.46, 2.07 and 1.08. The variables included in the PCA model comply to two criteria: (1) they are measured with good analytical precision and (2) they have reasonable communality within the chosen PCA model. Variables which did not comply to these criteria were excluded from the calculation of the final robust models. The correlations of these variables with the calculated scores for the different components of the robust models are given for comparison under "Additional correlations".

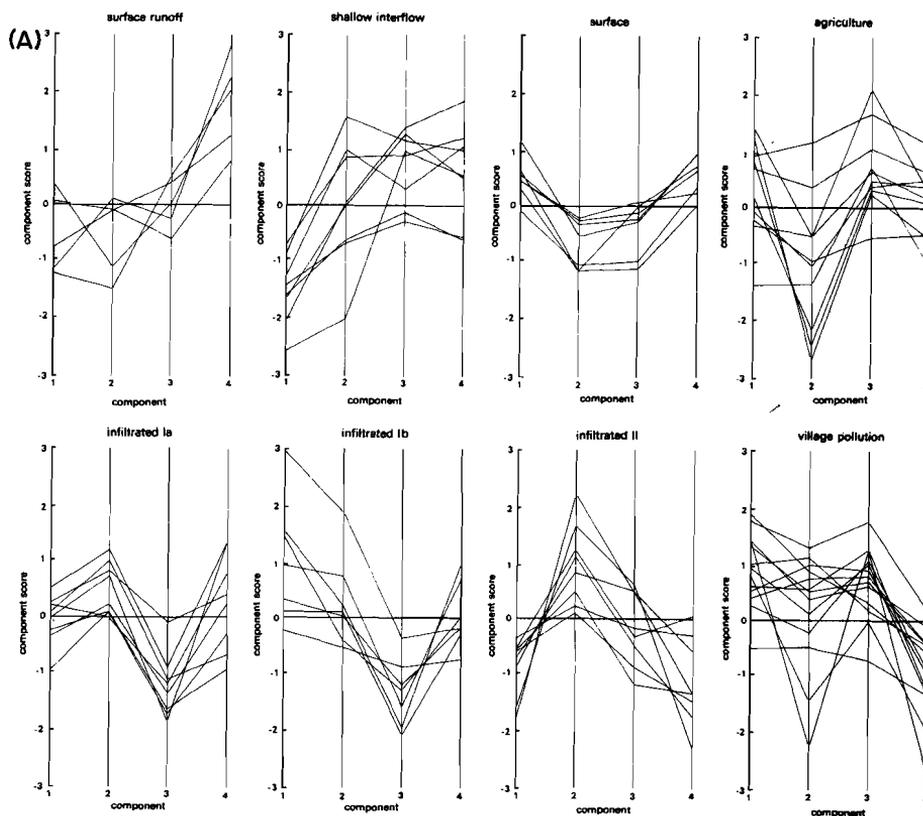


FIG. 6(A).

amongst the granite and schist water samples may be the outcome of a Q-mode cluster analysis (DAVIS, 1986) applied separately to both data sets. This type of similarity cluster analysis leads to a number of groups which each have different hydrogeochemical signatures. These signatures may extend over the contact zone. For this homogeneous dataset cluster analysis may seem less appropriate. However, it does lead to interpretable clusters with distinctive features; of course the cluster division has a gradual character.

The component scores of the samples are used as input in the cluster analysis (applied program taken from DAVIS, 1973, pp. 467–473), while the correlation coefficients between samples are used as similarity measure. Clustering on component scores rather than on raw data was chosen because the component scores reflect the important hydrogeochemical processes which are described by more than one variable. Thus the communal influence of variables is emphasized, while the unique variation of separate variables—which may be considered as “noise”—is reduced. Correlation coefficients as a similarity mea-

sure compare the relative impact of the processes to each other, rather than the absolute impact of each process. Because evapotranspiration is the most important process, this procedure seems justified. Thus waters which have similar process patterns are grouped. Experience with comparable datasets corroborates these findings (VAN DIEST *et al.*, 1982).

Interpretation

A heuristically determined similarity level of >0.55 yields six clusters for the schist waters and eight clusters for the granite waters. The within-cluster variation in the granite waters is larger than in the schist waters (cf. Fig. 6).

Characteristic typologies, which are used to label the clusters with appropriate geochemical meanings, can be derived for each cluster. Cluster names were chosen to represent the processes that govern the chemical composition of the waters. For example, the name of the agriculture waters of the granite group is deduced as follows. These waters are evapo-

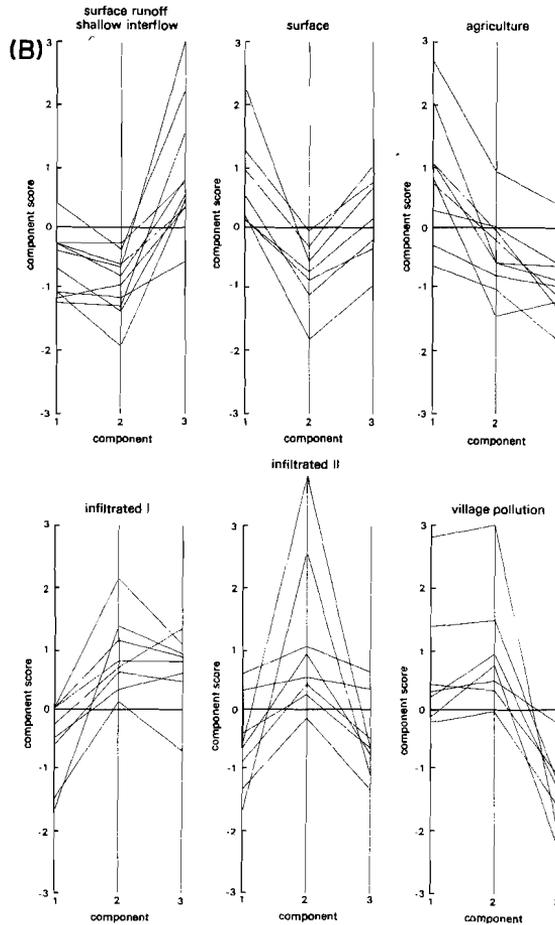


FIG. 6. Principal Component Analysis Score pattern for each cluster in the waters from the granite (A) and schist (B). For the geochemical meaning of the components see Table 1. The selected Q-mode clustering technique groups samples with similar patterns. The cluster names are derived through geochemical interpretation (cf. Fig. 7).

transpired (i.e. relatively high score on component 1), of surficial origin (relatively low score on component 2), contaminated (relatively high score on component 3, indicating influence of fertilizer) and relatively oxidizing (relatively low score on component 4). The labels of the other clusters are derived along similar lines (cf. caption Fig. 7) leading to the following typological names for the granite clusters: surface runoff (SR), shallow interflow (SI), surface (S), infiltrated Ia and Ib (In Ia; In Ib), infiltrated II (In II), agriculture (A) and village pollution (VP). The approach proves its validity by the fact that similar clusters are found in the analysis for the schist domain, i.e. surface runoff/shallow interflow (SR-SI), surface (S), infiltrated I (In I), infiltrated II (In

II), agriculture (A) and village pollution (VP) waters.

A model for the genetic relation together with the processes that cause the transition from one cluster to another is given in Fig. 7. The granite SR and SI clusters as well as the infiltrated Ia and Ib clusters, which show a great similarity between pairs, are combined in the model.

Geographical distribution of the clusters: matching of the granite and schist areas

The model, outlined in Fig. 7, comprises the following clusters in each sample group: surface runoff, surface, agriculture, infiltrated I and II and village

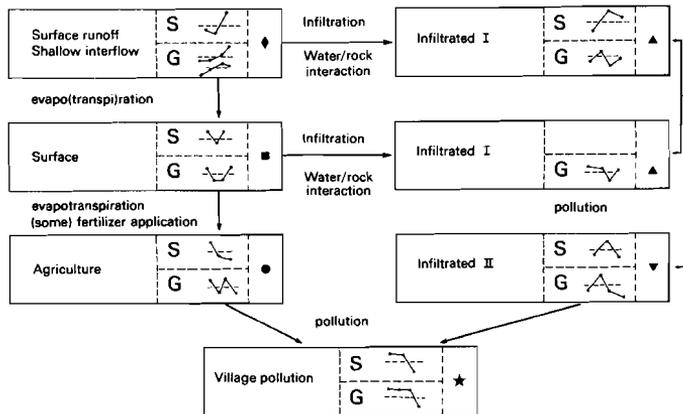


Fig. 7. A model for the genetic relation of the clusters; S and G denoting schist and granite, respectively. The general PCA score pattern is derived schematically from Fig. 6. The horizontal hatched line indicates zero level for the component scores. The relation between the different clusters can be described as follows: waters mainly determined by the rainwater composition combined with some evapotranspiration are Surface runoff (SR)-Shallow interflow (SI) clusters. In the granite waters these clusters can be distinguished (SR upper curve, SI lower one). In the schist waters this subdivision is not seen. Through evapo(transpiration) the SR-SI cluster passes into the Surface cluster. More extreme evapotranspiration with some fertilizer application leads to the Agriculture cluster. Through infiltration the SR-SI cluster passes into the Infiltrated I cluster. In the granite waters a subdivision can be made: when surface waters infiltrate, a slightly different Infiltrated I cluster is obtained. In the schist waters this subdivision could not be unraveled. When Infiltrated I type waters are contaminated (e.g. by fertilizer application) they blend into the Infiltrated II cluster. The "final" evolution is achieved when the pollution increases through use and re-use of the waters in the direct vicinity of the villages. This final cluster is therefore termed Village pollution cluster.

pollution. Figure 8 shows their geographical distribution. The boundary between the granite and schist domains is no longer evident, an interesting result given the differences in element concentrations and hydrological regimes. Cluster analysis is successful in distinguishing similar groups of water samples in different geological domains, by combining the characteristics expressed by the component scores of each sample.

The most pronounced feature on the map (Fig. 8) is, not unexpectedly, the aureole of contaminated waters around the villages. The agriculture type is indeed mainly located in agricultural areas, while the contaminated infiltrated II waters are concentrated in areas characterized by waters of deeper origin, where agriculture is applied. Surface waters are encountered in the artificial lake and in areas where forests are dominant. Surface runoff water is found in

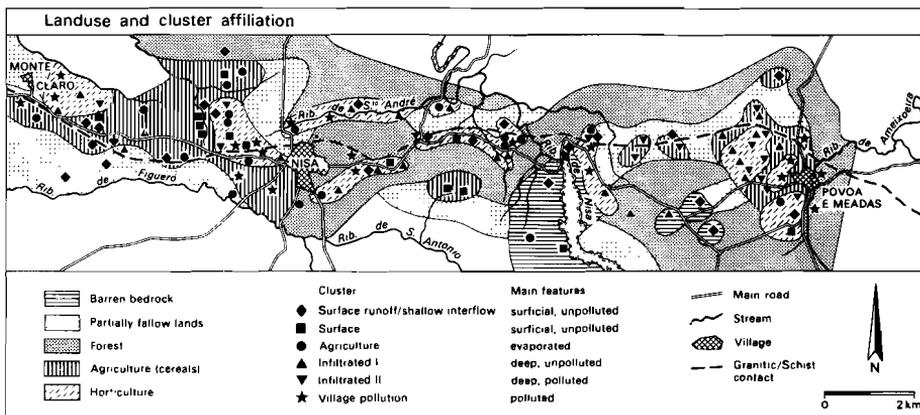


Fig. 8. Land-use map of the study area combined with the cluster affiliation of the waters. Similar clusters in the granite and schist waters have the same symbols.

areas devoid of human activity and it is an indication of the low capacity of the wells and springs in these areas, making agriculture or even forestry impossible. The waters in the neighborhood of Pova e Meadas are generally from deeper origin, in accordance with the greater amount of fractures and veins (sometimes mineralized) in this area. The statistical significance of clustering is difficult to assess theoretically. However, the observed spatial coherence and the consistency of the cluster model gives confidence in the soundness of the interpretation.

URANIUM DISTRIBUTION IN THE WATER SAMPLES

Thermodynamic calculations on uranium speciation and supersaturation

The determination of the degree of saturation is of importance for the interpretation of the U-threshold values in waters. It is likely that a high U-concentration will be a reliable ore-indicator in those waters which are undersaturated with respect to all U minerals. However, a water with a low U concentration, which is nevertheless supersaturated with respect to a U-mineral phase, may equally point to a mineralized zone (cf. LANGMUIR and CHATHAM, 1980).

Aqueous speciation of U and saturation indices (SI) for the more common minerals were calculated with a modified version of the WATEQ chemical speciation program (PLUMMER *et al.*, 1976; VAN GAANS, in press) with data for U from LANGMUIR (1978) and VAN GENDEREN and VAN DER WEIJDEN (1984). The logarithm of the computed ion-activity products of minerals divided by their respective solubility products represents the saturation index. Supersaturation is indicated by positive numbers. The outcome of the thermodynamic saturation calculations has to be used with care because dissolution-precipitation reactions in supergene environments are often kinetically determined and do not reflect strict equilibrium conditions as is assumed in the thermodynamic calculations (e.g. BOWIE and THORNTON, 1985).

An important parameter in the calculation of SI values of species amenable to redox reactions is the redox-potential in the waters. As is well-known (e.g. MORRIS and STUMM, 1967; LINDBERG and RUNNELLS, 1984) redox couples in natural waters are often not in mutual thermodynamic equilibrium (e.g. MORRIS and STUMM, 1967; HENRY *et al.*, 1982; LINDBERG and RUNNELLS, 1984). Slow electron transfer at the electrode-solution interface of the platinum electrode then results in mixed potentials. However, in the present study the measured Eh/pH values lie, for the greater part, in the field for which WHITFIELD (1974) argues that operational use of platinum electrode measured Eh values is warranted. Although relatively high DOC contents in the Nisa waters show

that biological influence may be of importance, the calculated SI for $\text{Fe}(\text{OH})_3$ approaches equilibrium fairly well, pointing towards reasonably internally consistent Fe, Eh and pH determinations. This justifies a semi-quantitative use of the redox potential for the measured Eh-range.

Supersaturation with respect to clay minerals is ubiquitous and with respect to Al-, Fe- and Mn-bearing (hydr)oxides common. Supersaturation of Fe- and Mn-bearing phases could partly be overstated due to the fact that organic complexes are not taken into account in the WATEQ calculations. Humic and fulvic acids are strong complexing agents especially for elements of the first row transition elements (Fe, Mn) in waters like the ones investigated (BOWIE and THORNTON, 1985). Their presence may be inferred from the DOC content of the samples. The apparent supersaturation could also be due to the existence of suspended (colloidal) particles in the solution. This applies especially for Al. Colloidal particles are important in dilute waters from crystalline bedrock (e.g. BOWIE and THORNTON, 1985). Particles with sizes $<0.45 \mu\text{m}$ pass through the filter and are measured adding to the total concentration in true solution (ROSE *et al.*, 1979). However, kinetics are possibly more important because we find the majority of the samples close to equilibrium with amorphous $\text{Al}(\text{OH})_3$. Equilibrium (defined as SI between -1 and $+1$) is also attained between amorphous silica and the solutions in virtually all samples and, to a lesser extent, between amorphous $\text{Fe}(\text{OH})_3$ and the solutions. The latter is undersaturated in waters with a $\text{pH} < \sim 5$. The equilibrium situation between the solution and these amorphous phases indicates the general importance of kinetic factors under the prevailing supergene conditions. Whenever supersaturation occurs, crystal growth in supergene environments is greatly hampered by the presence of silica because it adsorbs onto nuclei, thereby occupying "growth places" (e.g. SCHWERTMANN and TAYLOR, 1972; KÄMPF and SCHWERTMANN, 1982).

The above considerations undoubtedly have implications for the speciation and solubility of U in the waters. In the presently available thermodynamic calculation models these are hardly incorporated. It can be presumed, however, that these aspects will not greatly influence the relative predominance of U-species, though an increased solubility of U is envisioned.

The predominant U-species is calculated to be $\text{UO}_2(\text{HPO}_4)_2^{2-}$ under the prevailing neutral to slightly acid pH regime. The concentration of this complex is up to three orders of magnitude higher than the second most important complex. Differences in the remaining complex concentrations are much smaller from the second most important complex downward. With increasing pH (>7.5) the UO_2 -carbonate complexes become more important and occasionally surpass the $\text{UO}_2(\text{HPO}_4)_2^{2-}$ concentration. In more acid waters ($\text{pH} < 4.5$) the UO_2^{2+} -hydroxy complexes are

dominant. The concentration of uranyl-carbonate complexes is negligible in this low pH regime.

Uranium minerals are undersaturated in virtually all samples; the SI values range down from about -5 . Autunite-like minerals have SI values from -9 downward; typical SI values are some orders of magnitude lower. This, despite the fact that the U-mineralization consists of autunite-like minerals (veins in the granite and disseminated ores in the contact zone). The present-day composition of the water samples cannot reflect mineralization-precipitation conditions. The U minerals which are closest to saturation (but still far away from equilibrium conditions) are uraninite, coffinite, rutherfordite, schoepite and β -schoepite.

A few samples have SI values for uraninite and coffinite > -3 . Occasionally, even a small positive SI is calculated. These samples are all from waters in the schist, which have a lower average Eh than the granite waters, in part because of associated organic matter (cf. Fig. 2). Those samples with an Eh above the bulk of Eh-values appear to be associated with radiometric anomalies. Those samples with a lower Eh than the bulk of the samples are point anomalies, unrelated to radiometric anomalies. These latter anomalies could reflect very local U-saturation through oxidation/reduction mechanisms. In the present survey, erratically distributed samples with low Eh (and thus supersaturated with respect to U-minerals) should therefore be assigned a relatively low prospecting priority.

In conclusion it may be stated that the U distribution in the majority of the waters is not influenced by supersaturation of U minerals. Hence, supersaturation with respect to U-bearing minerals does not affect the interpretation of the U-anomaly pattern in the Nisa area.

Anomaly assessment

The following points are of importance for the recognition of U anomalies:

(1) Recent studies emphasize the necessity of background adjustment for varying geochemical environments (DI ZHOU, 1985; ROQUIN and ZEEGERS, 1987). Similarly, in the present study different geometric means for dissolved chemical constituents are calculated for waters from the granite and the schist areas (Fig. 2).

(2) The U concentration in the waters may increase solely due to evapotranspiration because the waters are undersaturated with respect to U compounds. Thus evapotranspiration may cause false anomalies. To compensate for this effect the ratio of U over Ec (U_{Ec}) instead of the U concentration is sometimes used (DALL'AGLIO, 1971).

(3) Differences in the genetic histories of the groundwater samples, as have been outlined above, may have implications for the significance of the

anomalies. Waters reflecting a deeper origin are of special interest in prospecting for hidden U-deposits.

The U-anomalies defined by the U concentrations and the U_{Ec} values will be evaluated within these different perspectives. Cumulative frequency curves (SINCLAIR, 1976) do not show a distinct bimodality, neither for the total data set nor for the separate granite and schist data sets. Multiple impacts of different processes on each water sample apparently obscure patterns in the U distribution.

Another means to assign a threshold in a data set is the so-called gap test (MIESCH, 1981). The gap test determines the maximum gap between adjacent values in a standardized distribution. The values below the gap may be considered as background values, with the gap value being the threshold value. The significance level of the gap can be used in the interpretation. Applying this test to the total data set leads to the trivial result of a separation of the granite and schist waters (the granite waters contain considerably more U, Fig. 2). These differences are enhanced in the U_{Ec} values owing to the lower Ec values of the granite waters (Fig. 2). In the following, the granite and schist waters will be considered separately.

The trivial and often used mean-plus-two-standard-deviation criterion for threshold estimation is obviously inappropriate in this area with a high incidence of U-mineralization (see also ROSE *et al.*, 1979 and HOFFMAN, 1988). Many known U-anomalies would be classed as background by this definition of anomaly. Therefore, this definition is too stringent. Samples with U content greater than this level (8.8 and 8.7 $\mu\text{g/l}$ for the granite and schist, respectively) are classed as "extra high values" (EHV). They are excluded from the data sets for further threshold determination.

A threshold value for U at the geometric mean-plus-one-standard-deviation is reasonable for the study area. Inspection of the response of known (radiometric) anomalies supports the validity of this choice. Also, the gap test, applied to the separate granite and schist water data sets, gave its most significant gap near this level (with a probability of about 0.20). The gap test applied to each cluster for U and U_{Ec} yielded similar results. The different threshold values for U and U_{Ec} for the total data set, separated in a granite and schist group and per cluster are given in Tables 2 and 3, respectively.

Noteworthy in Tables 2 and 3 are the varying background and threshold values of the clusters. The differences between granite and schist affiliation are most striking. Only values for the surface waters are similar, which is reasonable because rock interaction is minimal for this water type.

Uranium and U_{Ec} values can now be transformed to standard normal deviates from the respective means. The geographic distributions of these normalized U and U_{Ec} for the granite and schist sample group and per cluster are shown in Fig. 9A-D. A

U anomaly evaluation in groundwater, Nisa, Portugal

Table 2. Geometric means and geometric-means-plus-one-standard-deviation for the U contents of the clusters

	Geometric mean		G. mean + 1* st. dev.		
	Granite	Schist	Granite	Schist	
Undifferentiated	0.59		1.98		
Total	0.85	0.36	2.13	1.44	
Cluster I	0.94	0.34	2.29	1.57	Village pollution
Cluster II	1.50	0.38	2.92	1.43	Infiltrated II
Cluster III	0.76*	0.47	2.62	1.58	Agriculture
Cluster IV	1.02*	0.55	2.97	3.59	SR-SI
Cluster V	0.73*	0.11*	1.36	0.27	Infiltrated I
Cluster VI	0.44	0.48*	0.88	0.71	Surface

*One extra high U-value (EHV) is not included in the calculation of the mean.

Table 3. Geometric means and geometric-means-plus-one-standard-deviation for the (U/Ec)* 1000 ratios of the clusters

	Geometric mean		G. mean + 1* st. dev.		
	Granite	Schist	Granite	Schist	
Undifferentiated	4.6		18.4		
Total	8.6	2.0	23.4	8.0	
Cluster I	6.2	1.4	15.7	5.3	Village pollution
Cluster II	20.4	2.4	45.4	9.5	Infiltrated II
Cluster III	7.5*	2.1	28.0	8.7	Agriculture
Cluster IV	14.5*	3.8	42.3	22.4	SR-SI
Cluster V	6.9*	0.7*	11.7	1.8	Infiltrated I
Cluster VI	4.4	2.5*	8.6	5.0	Surface

*One extra high U-value (EHV) is not included in the calculation of the mean.

Table 4. Comparison of radiometric and hydrogeochemical U anomalies

Anomaly	Radiometric	Hydrogeochemical			
		G/S	CLUS	G/S _{Ec}	CLUS _{Ec}
R1	*	*	*	*	*
R2	*	*	*	*	*
R3	*	*	*	*	*
R4	*	no water available			
R5	*	*	*	*	*
R6	*	*	*	*	*
R7	*	—	—	—	*
R8	*	*	*	*	*
H1	—	*	*	*	*
H2	—	—	*	—	*
H3	—	—	*	—	*
H4	—	*	*	—	*
H5	—	*	*	—	—
H6	—	—	*	—	—
H7	—	*	*	—	—
H8	—	*	—	*	—

R8 was discovered during the hydrogeochemical sampling campaign. Hydrogeochemical anomalies are listed according to their various modes of assessment. G/S = U threshold defined per rock type; CLUS = U threshold defined per cluster; G/S_{Ec} = threshold defined per rock type for U/Ec; CLUS_{Ec} = threshold defined per cluster for U/Ec.

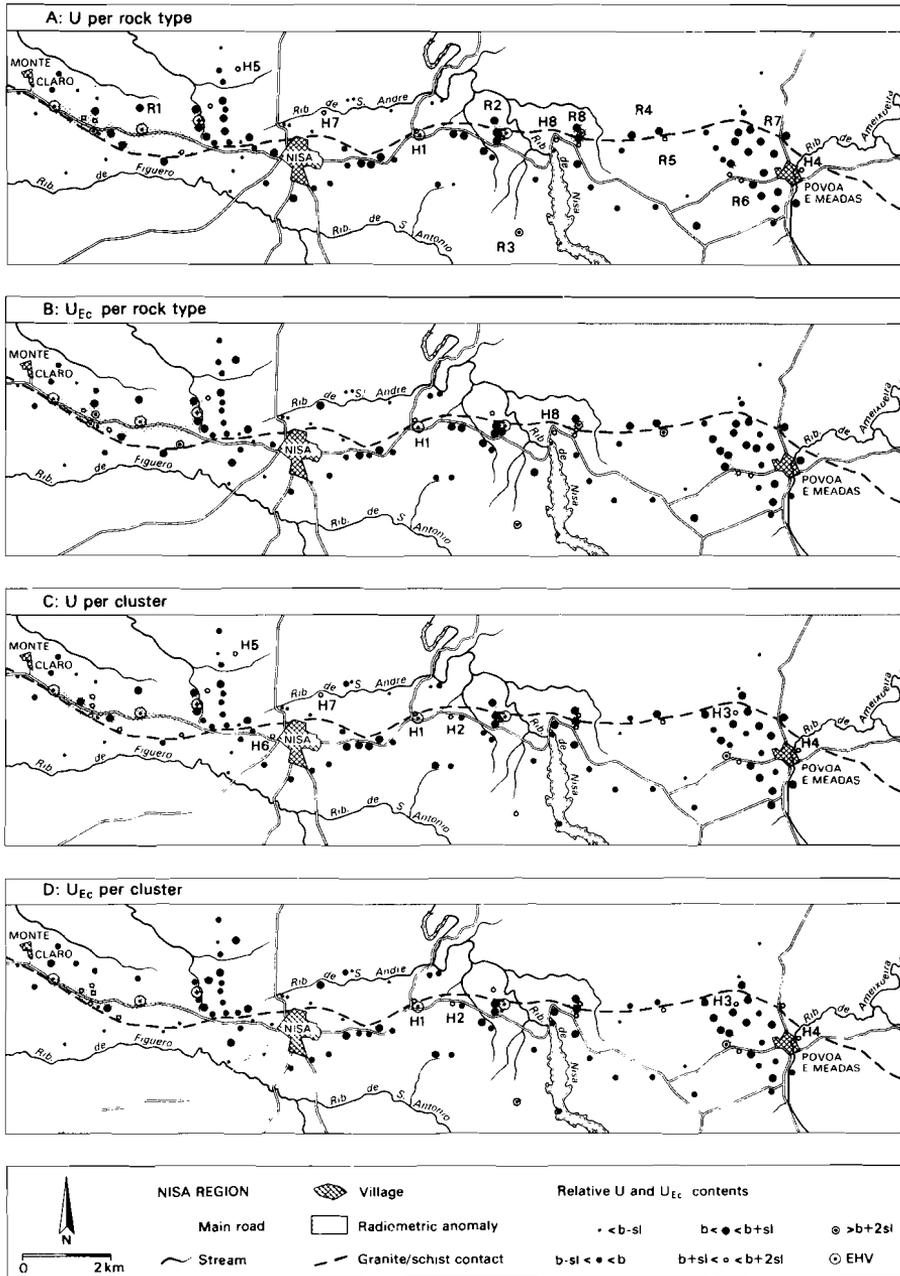


Fig. 9. Uranium and Ec-corrected U (U_{Ec}) distributions normalized to their geometric means (b) and standard deviations (sl) compared per rock type and per cluster. The radiometric anomalies are indicated with the dotted areas. (A) shows normalized U compared on rock type level; (B) U_{Ec} compared on rock type level. The cluster comparison level is shown in (C) for U and in (D) for U_{Ec} . Numbers of the radiometric anomalies (R1 to R8) correspond to Table 4; they are only indicated in (A). The additional hydrogeochemical U anomalies (H1 to H8), as generated by the different anomaly definitions, are shown in each figure; their numbering corresponds to Table 4.

comparison between the radiometric and hydrogeochemical anomaly pattern is made in Table 4.

The different normalized U and U_{Ec} patterns show subtle but important differences in general appearance (Fig. 9) and anomaly definition (Table 4). The cluster affiliation of an anomalous sample is an important parameter for the evaluation of the priority order of the anomalies. A group of anomalous samples with surficial characteristics, geographically close to each other, indicates an outcropping ore zone. Anomalous samples belonging to clusters of a deeper origin are interesting exploration targets for hidden ore deposits. Unfortunately, the exact relevance of our interpretation cannot be assessed because follow-up studies have not yet been carried out.

Hydrogeochemical anomalies are found in the vicinity of all known radiometric anomalies (Fig. 9). The good correspondence of the radiometric and hydrogeochemical approach is consistent with the relatively thin soil cover in the study area. The absence of water precludes a reflection of the Mato do Povoia vein in the hydrogeochemical anomaly pattern. All but one of the radiometric anomalies are

related to water from a deeper origin, thus they are probably not caused by local surficial U-enrichment.

Apart from the detection of the known radiometric anomalies, each hydrogeochemical approach gives different anomalous samples (cf. Fig. 9, Fig. 10 and Table 4). Their prospective values can be assessed with the hydrogeochemical features of the water chemistry. An ideal anomaly definition strictly distinguishes mineralization-related samples from the others. In practice, an anomaly definition should be neither too "loose" nor too "tight". The former leads to many false anomalies and the latter assigns anomalous samples to the background group. From Table 4 it appears that the evapotranspiration correction normalized per rock type (column 3 of the hydrogeochemical anomaly definitions) is too tight. This rather crude correction does not take into account the genetic history of the samples. The U_{Ec} of the waters increases due to evapotranspiration, agricultural influences etc., but also due to water-rock interaction. When correcting for the U_{Ec} and normalizing per rock type one cannot discriminate between these different contributions. The hydrogeochemical interpretation led to several groups of

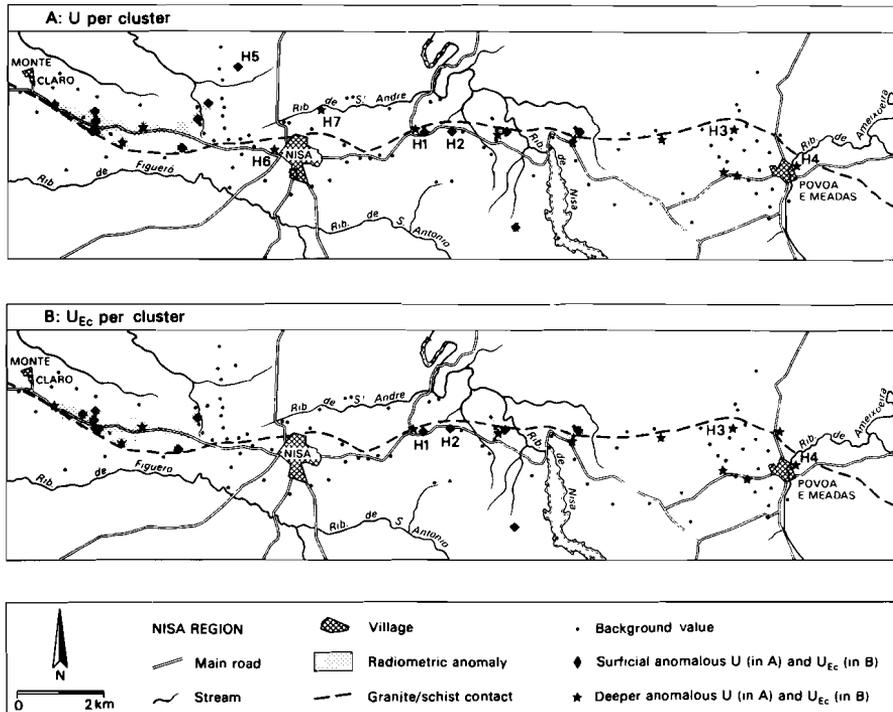


FIG. 10. Anomalous U in the cluster approach for U (A) and U_{Ec} (B). Surficial water is indicated with \blacklozenge symbols and deep water with \star symbols. Radiometric anomalies are indicated with the dotted areas. For clarity, only the additional hydrogeochemical U anomalies as defined by the respective definitions are indicated. Their numbering corresponds to those in Table 4.

waters with similar genetic histories, so when comparing normalized E_c corrected figures at cluster level one takes the genetic history of each sample into account.

This cluster approach is visualized in Fig. 10. The anomalous samples categorized on the basis of normalized U as well as normalized U_{E_c} are shown. Waters are discriminated into a surficial group and a group reflecting features from a deeper origin. With this division, important information on the character of each anomaly is obtained. The superiority of the U_{E_c} -approach is evident: the U -approach would miss a radiometric anomaly and leads to some additional anomalies. The U_{E_c} -approach traces all radiometric anomalies and leads to fewer additional anomalies. Each additional anomaly as defined by the U_{E_c} -approach is also anomalous in the U -approach. The anomalies of deeper origin defined only by the U -approach are confined to polluted waters, which makes them rather suspect. Indeed they are classed as non-anomalous with the U_{E_c} -approach.

The additional anomalies of the U_{E_c} -approach are indicated with H1, H2, H3 and H4 in Fig. 10B. Anomaly H2 is surficial; anomaly H3 has a deep origin. Anomaly H1 consist of two anomalous samples close to each other, so this anomaly could have a larger areal extent. Anomaly H4 is in the vicinity of a Pb-Zn vein. With the information obtained from the hydrogeochemical features it can be assessed that anomalies H1, H3 and H4 have a greater prospecting value for hidden U -mineralization than anomaly H2 because they are related to deeper (more evolved) waters.

SUMMARY AND CONCLUSIONS

Straightforward univariate and bivariate statistical procedures revealed important features of the water samples. Histograms showed logarithmic distributions for all constituents, apart from H_4SiO_4 and the intrinsically logarithmic variables (pH, Eh) which show normal distributions. The normal distribution of H_4SiO_4 is explained by equilibrium between dissolved silica and amorphous silica as demonstrated by WATEQ calculations. Scattergram interpretation allowed tracing of the origin of Cl (rainwater), NO_3 (fertilizer application) and SO_4 (fertilizer application and acid rain). Piperdiagrams also indicated that the water composition can only be explained by the combined influence of several processes, such as evapotranspiration, weathering and pollution.

The influence of such processes on the composition of each water sample was evaluated by multivariate statistics. Discriminant Function Analysis showed that waters originating from granite and schist are significantly different. Therefore, subsequent multivariate statistical techniques (Principal Component Analysis and Q-mode Cluster Analysis) were carried out on separate granite and schist groups. Principal

Component Analysis revealed four dominant processes determining the composition of the granite waters (evapotranspiration, relation to faults and fracture zones, fertilizer application and oxidation-reduction processes) and three dominant processes determining the schist water composition (evapotranspiration, water-rock interaction and a surface vs depth dipole). Only the evapotranspiration components could be matched over the granite-schist contact. The other components have only partially overlapping interpretations owing to differences in bedrock chemistry and hydrological regime between the granite and schist terranes. However, Q-mode Cluster Analysis on the Principal Component Scores led to the recognition of clusters with similar hydrogeochemical features. A genetic sequence of Surface Runoff-Shallow Interflow, Surface, Agriculture, Infiltrated I, Infiltrated II and Village Pollution clusters are distinguished for both rock types. The geographical cluster distribution reflects land-use. The cluster characteristics match across the contact zone, thus enabling a general interpretation of the U -distribution in the entire study area.

Thermodynamic calculations (WATEQX) of saturation indices and kinetic considerations showed that the samples are generally undersaturated by several orders of magnitude with respect to all U -minerals. The U -distribution in the waters is thus not limited by precipitation of U -bearing minerals. Four different U -anomaly displays are generated: U and U_{E_c} ($=U/E_c$) normalized per rock level and per cluster. Comparison of the hydrogeochemical anomaly patterns with the radiometric pattern shows that all radiometric anomalies are traced and several additional anomalies are defined. From a combination of hydrogeochemical characteristics as revealed by Principal Component Analysis and Q-mode Cluster Analysis it is concluded that the U_{E_c} pattern normalized on cluster level leads to the most promising hydrogeochemical anomaly definition. With the hydrogeochemical knowledge several additional anomalies related to polluted samples could be discarded. The hydrogeochemical approach permits the establishment of a priority level of additional anomalies by the distinction between waters with a surficial character and those displaying characteristics from a deeper origin with potential indications for hidden ore deposits. Furthermore, the hydrogeochemical results show that the radiometric anomalies have extension to deeper levels which enhances their prospective value. Thus, a hydrogeochemical survey significantly adds to a radiometric survey. Interpretations based on sophisticated multivariate techniques are to be preferred over interpretations which take only rock-type discrimination into account.

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Govers provided additional analyses. J. Kocken supervised the ICPES analyses. S. Frans and J. J. Berghenegouwen made the drawings. R. D. Schuiling, H. L. ten Haven and J. Oostindier critically read the manuscript. Suggestions made by R. G. Garrett, M. B. Goldhaber, B. Hitchon and two anonymous reviewers are gratefully acknowledged. This study was partly financed by grant No. 007.79.3 EXU NL of the European Community.

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REFERENCES

- BOWIE S. H. U. and THORNTON I. (eds) (1985) *Environmental Geochemistry and Health*. Reidel.
- CAITELL R. B. (1966) The scree test for the number of factors. *Multivariate Behavioral Research* **1**, 245–249.
- COMANS R. J. N., VAN DER WEIJDEN C. H. and VRIEND S. P. (1986) Geochemical studies in the drainage basin of the Rio Vouga (Portugal) IV: impact of land use on the hydrogeochemistry of natural waters in the Vouzela region. *Environ. Geol. Water Sci.* **9**, 119–128.
- DALL'AGLIO M. (1971) A study of the circulation of uranium in the supergene environment in the Italian Alpine Range. *Geochim. cosmochim. Acta* **35**, 47–60.
- DAVIS J. C. (1973) *Statistics and Data Analysis in Geology*. J. Wiley, 1st Edn.
- DAVIS J. C. (1986) *Statistics and Data Analysis in Geology*. J. Wiley, 2nd Edn.
- DEKKERS M. J., VRIEND S. P., VAN DIEST PH., VAN DER WEIJDEN C. H. and OOSTEROM M. G. (1983) Geochemical controls of transport and deposition of uranium from solution, case study São Pedro do Sul (Portugal), Publ. Inst. Earth Sci., University of Utrecht, Contract 007.79.3 EXU NL.
- DEKKERS, M. J., VRIEND S. P., VAN DER WEIJDEN C. H. and VAN DIEST PH. (1986) The São Pedro do Sul granite, Portugal: hydrogeochemistry related to the prospecting of uranium. *Uranium* **2**, 261–277.
- DEKKERS, M. J., VRIEND, S. P., WALEN C. G. and VAN DER WEIJDEN C. H. (1984) Geochemical controls of transport and deposition of uranium from solution, case study Nisa (Portugal), Publ. Inst. Earth Sci., University of Utrecht, contract 007.79.3 EXU NL.
- VAN DIEST PH., VRIEND S. P., VAN DER WEIJDEN C. H., ZUURDEEG B. W., OOSTEROM M. G. and KEUKEN M. P. (1982) Geochemical controls of transport and deposition of uranium from solution, case study Lachaux (France), Publ. Inst. Earth Sci., University of Utrecht, contract 007.79.3 EXU NL.
- DURRANCE E. M. (1986) *Radioactivity in Geology, Principles and Applications*. John Wiley.
- DE FARIA F. L. (1966) Gites d'uranium Portugais dans les formations metasedimentaires. *Port. Serv. Geol. Comun.* **50**, 9–50.
- FERNANDES A. P. (1970) Contribução para o estudo da região dos granitos radioactivos de S. Pedro do Sul. Junta de Energia Nuclear, Lisboa.
- FERNANDES A. P. (1971) A geologia da provincia uranífera do Alto Alentejo, Contribution to the *Economic Geological Congress Hispano-Luso-Americano*, Madrid and Lisbon, 19–25 Sept. 1971.
- FERNANDES A. P., PERDIGAO J. C., DE CARVALHO H. and PERES A. M. (1973) Carta Geologica de Portugal, escala 1:50,000, noticia explicativa da folha 28D: Castelo de Vide.
- FERREIRA P. V. (1971) Jazigos uraníferos Portugueses; jazigos de Au-Ag-sulfuretos do Norte de Portugal. Excursion Guide Book Vol. 5. *Economic Geological Congress Hispano-Luso-Americano*. Madrid and Lisbon, 19–25 Sept. 1971.
- VAN GAANS P. F. M. (1989) WATEQX—A restructured, generalized and extended FORTRAN 77 computer code and database format for the WATEQ aqueous chemical model for element speciation and mineral saturation, for use on personal computers or mainframes. *Comput. Geosci.*, in press.
- GARRELS R. M. and CHRIST C. L. (1965) *Solutions, Minerals and Equilibria*. Harper and Row.
- VAN GENDEREN A. C. G. and VAN DER WEIJDEN C. H. (1984) Prediction of Gibbs energies of formation and stability constants of some secondary uranium minerals containing the uranyl group. *Uranium* **1**, 249–256.
- GERMANOV A. I., BATULIN S. G., VOLKOV G. A., LISITSIN A. K. and SEREBRENNIKOV V. S. (1958) Some regularities of uranium distribution in underground waters. *Proc. Second U.N. Conf. on Peaceful Uses of Atomic Energy*, Vol. 2, pp. 161–177.
- GUTTMAN L. (1954) Some necessary conditions for Common-Factor Analysis. *Psychometrika* **19**, 149–161.
- TEN HAVEN H. L., KONINGS R., SCHOONEN M. A. A., JANSEN J. B. H., VRIEND S. P., VAN DER WEIJDEN C. H. and BUITENKAMP J. (1985) Geochemical studies in the drainage basin of the Rio Vouga (Portugal) II, a model for the origin of hydrothermal water in the Vouzela region. *Chem. Geol.* **51**, 225–238.
- HENRY C. D., GALLOWAY W. E., SMITH G. E., HO C. L. and GLUCK J. K. (1982) Geochemistry of ground water in the Miocene Oakville sandstone—a major aquifer and uranium host of the Texas coastal plain. Bureau of Economic Geology, Texas, Rep. of Invest. No. 118.
- HOFFMAN S. J. (1988) Notes from the Editor. *Explore* **63**, 2–3.
- HOWARTH R. J. and SINDING-LARSEN R. (1983) Multivariate analysis. In *Statistics and Data Analysis in Geochemical Prospecting—Handbook of Exploration Geochemistry*, Vol. 2 (ed. R. J. HOWARTH) pp. 207–289. Elsevier.
- JÖRESKOG K. G., KLOVAN J. E. and REYMENT R. A. (1976) *Methods in Geomathematics 1—Geological Factor Analysis*. Elsevier.
- KÄMPF N. and SCHWERTMANN U. (1982) The 5M-NaOH concentration treatment for iron oxides in soils. *Clays Clay Minerals* **30**, 401–408.
- KORKISCH J. and HECHT F. (1972) *Elemente der Sechsten Nebengruppe*. Springer (see esp. pp. 203–211).
- LANGMUIR D. (1978) Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits. *Geochim. cosmochim. Acta* **42**, 547–569.
- LANGMUIR D. and CHATHAM J. R. (1980) Ground water prospecting for sandstone-type uranium deposits: a preliminary comparison of the merits of mineral-solution equilibria, and single-element tracer methods. *J. geochem. Explor.* **13**, 201–219.
- LENCASTER J. DE and VAIRINHO M. M. (1970) Estudo de um mineral uranífero da região de Nisa (Portugal). Junta Energia Nuclear Rep.
- LINDBERG R. D. and RUNNELLS D. D. (1984) Ground water redox reactions: an analysis of equilibrium state applied to Eh measurements and geochemical modeling. *Science* **225**, 925–927.
- MIESCH A. T. (1981) Estimation of the geochemical threshold and its statistical significance. *J. geochem. Explor.* **16**, 49–76.
- MORRIS J. C. and STUMM W. (1967) Redox equilibria and measurements of potentials in the aquatic environment. In *Equilibrium Concepts in Natural Water Systems* (ed. W. STUMM) pp. 270–285. American Chemical Society.
- NEIVA J. M. C., DE QUEIROZ N. M. and DE FARIA F. L. (1953) Géologie et genèse des gisements Portugais d'apatite. *Int. Geol. Cong. 19th Algeria C.R.*, sec. 11, f. 11, pp. 145–159.
- NIE N. H., HULL C. H., JENKINS J. G., STEINBRENNER K. and BENT D. H. (1975) *Statistical Package for the Social Sciences*. 2nd Edn. McGraw-Hill.

- OLESEN B. L. and ARMOUR-BROWN A. (1984) Multivariate screening of training sets for classification and the definition of geochemical background. In *Geochemical Exploration 1983* (ed. A. J. BJÖRKLUND) pp. 471–479. Ass. Explor. Geochem.
- PILAR L. (1966a) Condicoes de formacao do jazigo uranifero de Nisa. *Port. Serv. Geol. Comun.* **50**, 51–83.
- PILAR L. (1966b) Petrografia das rochas metamorphicas e dos granitos de contacto de regio de Nisa. *Port. Serv. Geol. Comun.* **50**, 85–107.
- PIPER A. M. (1944) A graphic procedure in the geochemical interpretation of water analyses. *Am. Geoph. Union Trans.* **25**, 914–923.
- PLUMMER N. L., JONES B. F. and TRUESDELL A. H. (1976) A fortran IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters. U.S. Geol. Surv. Water Res. Invest. 76-13.
- RIBEIRO O., TEIXEIRA C., DE CARVALHO H., PERES A. M. and FERNANDES A. P. (1965) Carta Geologica de Portugal. escala 1:50,000; Noticia explicativa sa folha 28B: Nisa.
- ROQUIN C. and ZEEGERS H. (1987) Improving anomaly selection by statistical estimation of background variations in regional geochemical prospecting. In *Geochemical Exploration 1985* (ed. R. G. GARRETT) pp. 295–316. Ass. Explor. Geochem.
- ROSE A. W., HAWKES H. E. and WEBB J. S. (1979) *Geochemistry in Mineral Exploration*. Academic Press.
- SCHWERTMANN U. and TAYLOR R. M. (1972) The influence of silicate on the transformation of lepidocrocite to goethite. *Clays Clay Minerals* **20**, 159–164.
- SELINUS O. (1981) Lithochemical exploration data in prospecting in northern Sweden. In *Geochemical Exploration 1980* (eds A. W. ROSE and H. GUNDLACH) pp. 181–201. Ass. Explor. Geochem.
- SINCLAIR A. J. (1976) Applications of probability graphs in mineral exploration. Ass. Explor. Geochem. Spec. Vol. 4, Toronto.
- THADEU D. C. (1977) Hercynian paragenetic units of the Portuguese part of the Hesperic massif. *Bolm Soc. geol. Port.* **20**, 247–276.
- VAN DER WEIJDEN C. H., OOSTEROM M. G., BRIL J., WALEN C. G., VRIEND S. P. and ZUURDEEG B. W. (1984) Geochemical controls of transport and deposition of uranium from solution, case study Fundão (Portugal). Publ. Inst. Earth Sci., University of Utrecht, contract 007.79.3 EXU NL.
- WHITFIELD M. (1974) Thermodynamic limitations on the use of the platinum electrode in Eh measurements. *Limnol. Oceanogr.* **19**, 857–865.
- DI ZHOU (1985) Adjustment of geochemical background by robust multivariate statistics. *J. geochem. Explor.* **24**, 207–222.
- ZIELINSKI R. A., OTTON J. K., WANTY R. B. and PIERSON C. T. (1987) The geochemistry of water near a surficial organic-rich uranium deposit, Northeastern Washington State, U.S.A. *Chem. Geol.* **62**, 263–289.

CURRICULUM VITAE

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