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ABSTRACT

In the SW area of the Grand Duchy of Luxembourg ferruginous concretions of various size and shape are found in locally occurring, surficial loams underlain by Dogger and Lias deposits. The loam accumulations are supposed to be primarily weathering products of mainly Tertiary age. In the Pleistocene reworking and admixture with airborne sediments took place. Two types of iron concretions are distinguished: Bohnerz and Rasenerz. The first is exclusively found in loam occurrences overlaying the Bajocien limestone (Dogger), whereas the second one occurs in more sandy loams on the various Liassic sediments at topographically lower levels. Field evidence showing that both types formed in their present host-sediment is lacking. Rasenerz concretions have generally an oölitic texture rather similar to that of the ironstones of the Minette formation. This is a typical sedimentary facies of the Upper Lias and Lower Dogger in Middle Europe. In Luxembourg this facies is restricted today to a small area near the French border.

A geomorphogenetic model is proposed in which the present Rasenerz-bearing loam occurrences are explained as erosional remnants of a land surface, that for a great part consisted of a crust-covered Minette formation. To test this model Minette bulk samples (25), Rasenerz (30) and Bohnerz concretions (26) were subjected to neutron activation analysis (NAA). From the univariate statistics of 16 out of 36 measured chemical elements, it is inferred that the application of classical multivariate statistical techniques is not advisable, because of the highly irregular distribution of the individual variables.

Dynamic cluster analysis of a screened subset of the NAA output, comprising only 10 elements, indicates that within the total sampled population subgroups are distinguishable. These subgroups show at a certain level of homogeneity an obvious linkage between the Minette ironstone and the majority of the Rasenerz samples, whereas the remaining Rasenerz samples are evidently related to the Bohnerz samples. Correspondence analysis reveals that the variable As characterizes the Bohnerz samples and about 30% of the Rasenerz samples, and that the Minette ironstone and the majority of the Rasenerz samples are characterized by Co, Cr, Sc and a number of Lanthanides. So the present data supports the idea that the majority of the Rasenerz concretions can be considered as residual fragments of iron crusts developed in the Minette formation.

RESUME

Dans des limons de surface, qui recouvrent localement des sédiments du Jurassique moyen, dans le sud-ouest du Grand-Duché de Luxembourg, on trouve des concrétisations ferrugineuses de forme et de taille diverses. Ces limons sont supposés être constitués principalement de produits d'altération, qui se sont formés essentiellement pendant le Tertiaire. Depuis le Quaternaire ces limons ont été remaniés et mélangés avec des sédiments éoliens. Deux types de concrétions ferrugineuses sont discernés: le minerai de fer pisolithique (Bohnerz) et le minerai de fer des prés (Raseneisenerz). Le premier se trouve exclusivement dans des limons qui recouvrent les calcaires du Bajocien, tandis que le deuxième est trouvé dans des limons sableux qui se situent sur des sédiments du Lias. Ces derniers sont placés morphologiquement à des altitudes plus basses. Il n'y a pas d'indications intraformationnelles qui montrent que les deux types ont été formés dans leur matrice limoneuse actuelle. En général les concrétions du Raseneisenerz possèdent une texture oolithique assez semblable à celle que l'on rencontre dans les composantes ferrugineuses de la formation de la minette. Cette formation est développée dans un faciès sédimentaire caractéristique pour le Jurassique moyen en Europe Centrale. De nos jours ce faciès est limité au Luxembourg à une région de faible extension, qui se situe dans la partie SW du pays.

Un modèle géomorphologique est proposé. Dans ce modèle les présences locales des limons renfermant des concrétions du Raseneisenerz sont expliquées comme les restes d'une ancienne surface de terre ferme qui ont échappé à l'érosion. Cette surface était en grande partie constituée par la formation de la minette affleurant et recouverte d'une croûte d'altération superficielle. Pour tester ce modèle, des échantillons de minette (25), des concrétions du Raseneisenerz (30) et des concrétions du Bohnerz (26) ont été soumis à une analyse NAA (neutron activation analysis). Par les statistiques univariables de seize éléments chimiques sur un total de trente-six, il est conclu que l'application des techniques classiques de statistique multivariable n'est pas recommandable à cause des distributions très irrégulières des variables individuelles.

La "dynamic cluster analysis" d'une partie nettoyée des résultats de NAA, et comprenant seulement dix éléments, montre qu'on peut distinguer des sous-groupes dans la population entière. A un certain niveau d'homogénéité ces sous-groupes présentent une connexion nette entre les échantillons de la minette et de la majorité des concrétions du Raseneisenerz, tandis que les autres concrétions du Raseneisenerz sont liées d'une façon évidente avec les concrétions du Bohnerz. La "correspondance analysis" indique que les concrétions du Bohnerz et environ 30% des concrétions du Raseneisenerz sont caractérisées par la variable As, et que les échantillons de minette et la majorité des concrétions du Raseneisenerz sont caractérisés par Co, Cr, Sc et un nombre de lanthanides. Ainsi les données présentées ici semblent appuyer l'idée que la majorité des concrétions du Raseneisenerz peut être considérée comme des fragments résiduels des croûtes ferrugineuses provenant de l'altération de la minette affleurante.

INTRODUCTION

Detrital components derived from the source-rocks of a depositional basin can be of great help in disclosing the geologic development of that basin. In a similar way eluvial residues from lithologic units eroded in the past, may be used in the reconstruction of the erosional history of a modern landscape, provided these residual clasts can be recognised as such in the mantle of rock waste and derived surficial deposits.

In southwestern Gutland (Grand Duchy of Luxembourg) - which constitutes a part of the northeastern borderland of the Basin of Paris - indurated iron concretions of various shapes and sizes are encountered within surficial loam accumulations. These loams, considered as products of weathering (Lucius, 1948; Levelt, 1965), occur in places on the Bajocien limestone of the southern most parts of the 400 m Gutland surface level. Further in a much greater number of locations on more or less distinct planations surfaces below 395 m altitude and developed in older Jurassic stages (Fig. 1). The latter loams are generally more sandy than those on the Bajocien limestone. Hence some of them are seen as loams admixed with fluviatile or aeolian sediment, and/or as loams reworked by surface processes (Levelt, 1965). In Figure 1 the in situ („primäre Lagerstatte") and reworked occurrences as mapped by Lucius (1948) are presented.

According to the Carte Géologique Générale du Grand-Duché de Luxembourg, the loams are of Tertiary and Pleistocene ages, although no direct means are available to establish the exact age of the in situ loam accumulations. Evidence indicating that the included iron concretions originated within the present in situ loam occurrences, has not been observed nor reported in the literature.

PREVIOUS WORK ON THE IRON CONCRETIONS

For a long time two types of ferruginous concretions are distinguished: Bohneisenerz and Raseneisenerz (Schiltz 1925, 1927, Lucius 1948). The Bohnerz concretions are thought to be eluvial products of disintegrated lateritic formations developed in Bajocien limestone and possibly younger rock units during Eocene (Schiltz 1925, 1927, Lucius 1948, Kaboth 1969). The Rasenerz concretions were interpreted by Schiltz (1927, 1937) and Lucius (1948) as fragmentary remnants of early Miocene bog-iron formation in waste material accumulated in shallow lakes and swampy areas.

Their distinction is further based on a number of properties. First their nature as raw material in the ancient Lotharingian iron industry: Bohnerz concretions yielded iron of good quality whereas the iron gained from Rasenerz concretions was of inferior quality (Lucius 1948). Secondly Bohnerz contained a perceptibly lower phosphorous content (Schiltz 1925). Furthermore, the usual form of Bohnerz concretions suggests that they are layered and have grown in a concentrical manner. The Rasenerz specimens are generally larger and mostly irregular in outline, consisting of angular blocky, nodular or platy lumps, sometimes with rounded egdes and corners (Lucius 1948). Finally, Bohnerz concretions were thought to be found exclusively in loams covering the Bajocien limestone whereas those of Rasenerz were confined to the sandy loams on the Liassic series. Individual Rasenerz concretions were also met in gravels at the bottom of Holocene valley-fills and in relics of river terraces at topographically higher levels (Lucius 1948).

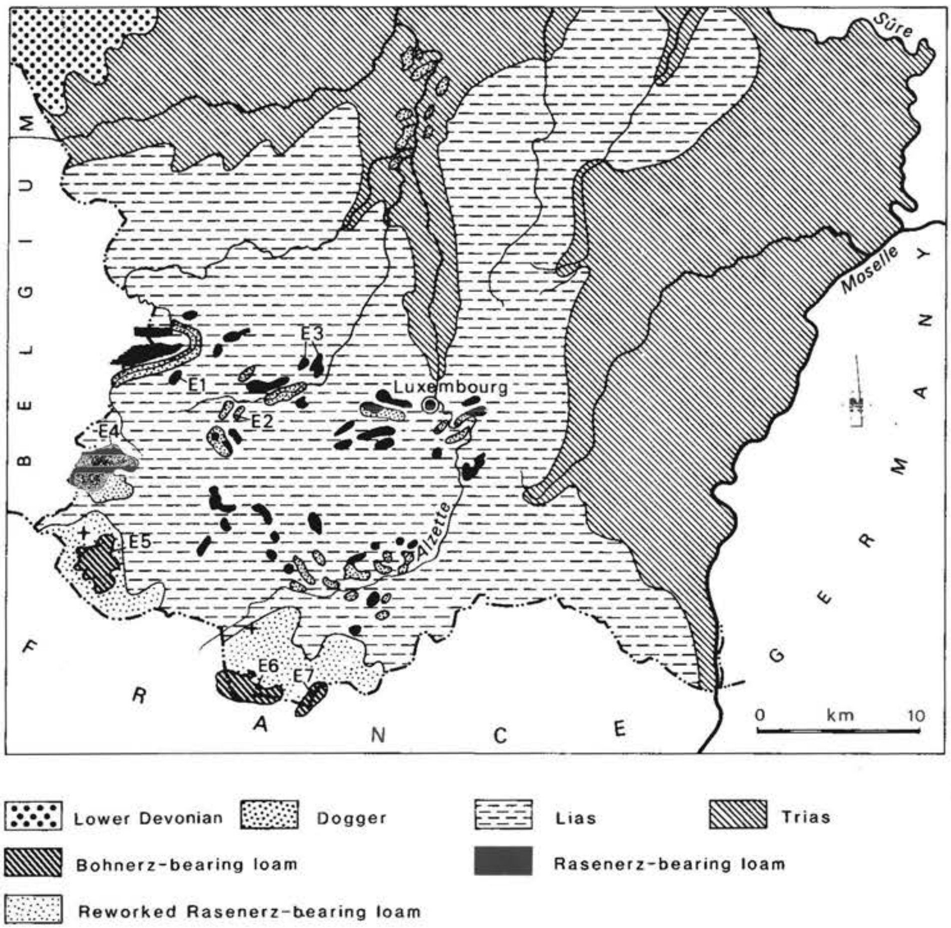

Fig. 1 Geological map copied from Carte géologique générale du Grand-Duché de Luxembourg, Echelle 1: 100.000. Ministère des Travaux Publics, Service Géologique, Deuxième édition 1974. The map shows also the Rasenerz and Bohnerz occurrences after Lucius (1948). E1-E4 indicate areas where Rasenerz, E5-E7 areas where Bohnerz concretions have been collected at the land surface. The two crosses indicate the locations of the sampled sections in the Minette formation (western cross: Differdinger Becken; eastern cross: Escher Becken).

Later on evidence was presented that a substantial portion of the iron-rich concretions from Rasenerz type localities shows on microscopic scale an oölitic texture. In iron concretions collected from Bohnerz type localities, this feature was never observed (Kaboth 1969, Riezebos et al, 1981). As ooids are atypical for bog-iron and as the Minette formation is the only known „parent rock" in Gutland which comprises strata with abundant iron ooids, it was inferred that the oölitic Rasenerz concretions represent fragments of surface crusts developed in the Minette formation. This inference implies that the Minette formation extended much farther to the north than today, and was lying at the landsurface during that crust formation.

THE PROPOSED GEOMORPHOGENETIC MODEL

In Figure 2 an hypothesis to elucidate genesis and distribution of the Rasenerz-bearing loams is schematized. It suggests that the loam occurrences, indicated by Lucius (1948) as „primäre Lagerstätte", reflect more or less the locations of former outliers, mesas or buttes. These landforms were probably developing during the last period of the Dogger scarp retreat. The scarp is now located near the French border (see Fig. 1).

The landforms were isolated by incision and erosion of a crusted land surface (Fig. 2, transition between stages 3 and 4). As a consequence they were initially covered by iron crusts formed in the Minette formation, and possibly even by remnants of even older caprocks. In fact, their formation and the duration of their existence as individual landforms must have been highly favoured by these crusts. Eventually however, these geomorphologic features were worn down, and the Rasenerz concretions embedded in the loam today represent the last eluvial remains of these crusts.

The present distribution of the Rasenerz-containing loams as mapped by Lucius (1948) supports the proposed model. These loams are mainly confined to the southwestern part of Luxembourg. Moreover, as „primäre Lagerstätte" they are frequently found on, or adjacent to topographic heights. Regional and altitudinal distributions seem thus to be in harmony with a gradual wearing away of the land surface by river systems operating from the east and northeast.

DISCUSSION OF THE PETROGRAPHIC EVIDENCE

It may be questioned whether the presence of ooids in both Rasenerz concretions and Minette ironstones, justifies to relate the Rasenerz-bearing loams with the Minette formation as done in the above model. In other words, does this common petrographic feature provide sufficient evidence as an argument in favour of the geomorphogenetic model proposed? In spite of the fact that oölitic iron-rich rocks have been studied for more than a century, there is still no unanimous opinion as to the mode of formation of ferruginous ooids (cf., Nahon et al., 1980).

Among the hypotheses dealing with their formation, one group proposes the ooids are products of subaerial bauxitic or lateritic weathering, whereas another group considers them to be the result of subaqueous growth in conti-

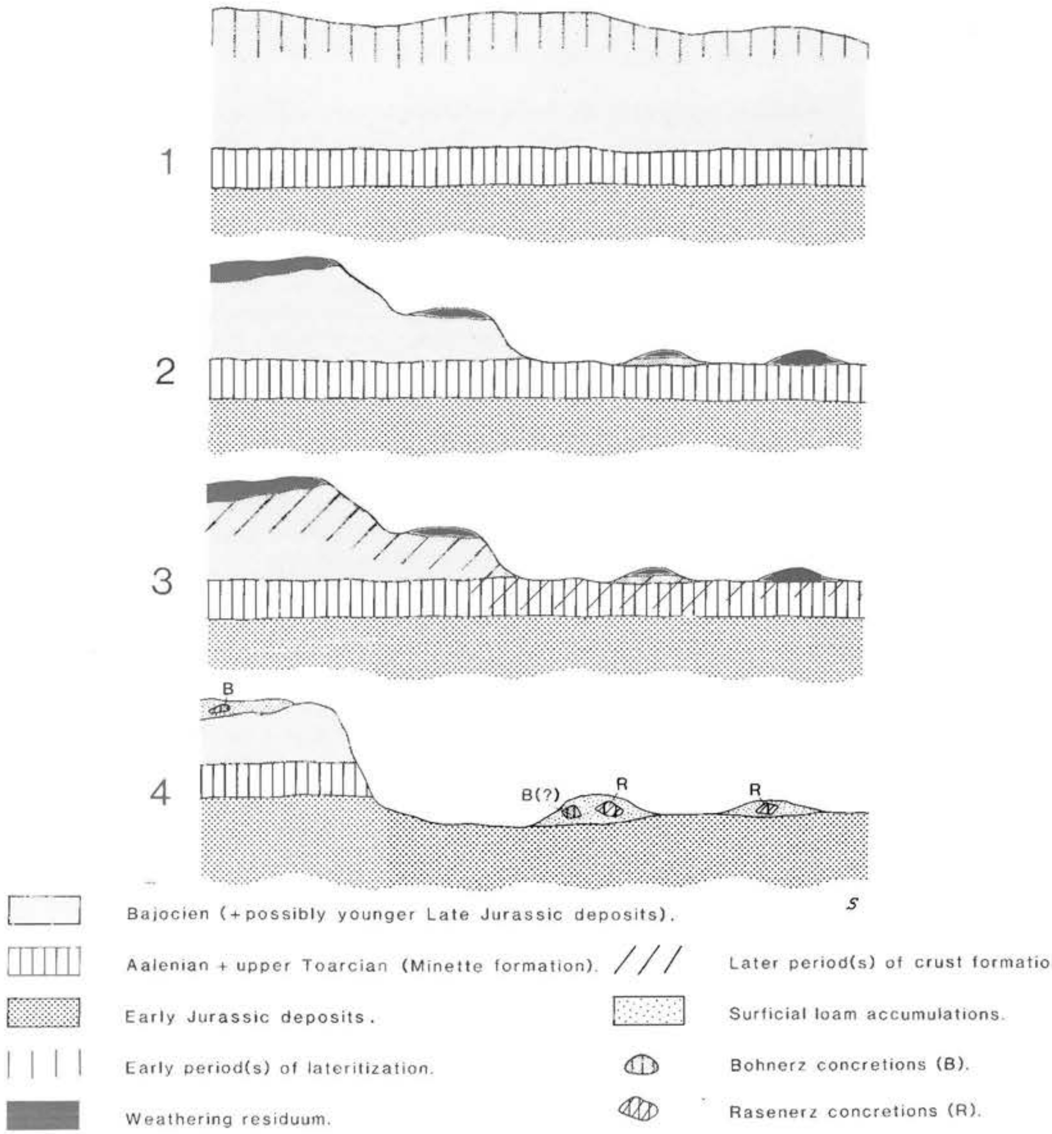

Fig. 2 Schematic representation of the proposed geomorphologic evolution leading to the present Rasenerz and Bohnerz occurrences in SW Gutland. The sketched profiles running from south to north illustrate four development stages. *Stage 1* represents a hypothetic starting-surface subjected to lateritization during one or more time-intervals. *Stage 2* gives the resulting topography after the northern areas had been drastically lowered by erosion. In the course of this lowering, the Minette formation was exposed. *Stage 3* presents this topography undergoing a following period of crust formation. *Stage 4* illustrates the present situation that evolved by severe erosion and denudation. In the course of lowering of this surface, a large-scale removal of the crusted Minette formation occurred, continuing probably into the Quaternary.

nental to marine settings. In a geochemical study of the Minette, Siehl and Thein (1978) reconciled these extreme views in concluding that the ferruginous ooids in the Minette ironstones of Luxembourg represent detrital particles, set free from lateritic caprocks in the source area by weathering and erosion, and then deposited in the high-energy environments of a wide shelf area.

Studies and experimental work on carbonate ooids (Simone, 1981), suggest that careful and detailed studies of their cortex structures might reveal more about their genesis. Sheaths within the cortex showing a radial fabric are related to completely different environmental conditions than those with a concentric fabric (Davies et al., 1978; Ferguson et al., 1978). A radial-concentric orientation of the constituent particles is attributed to crystallinisation-precipitation processes on nucleating surfaces, whereas a tangential-concentric orientation in the sheaths is thought to indicate mechanical accretion on the nuclei. The first mechanism operates in wet subaerial and quiet subaqueous environments, whereas the second is thought to be confined to the sediment-water interface under high-energy conditions.

In a SEM study, Bhattacharyya and Kakimoto (1982) demonstrated that sheaths in the cortex of ironstone ooids mostly show the tangential concentric fabric, whereas those of pisoids/ooids from lateritic or bauxitic formations are characterised by a radial-concentric fabric. A radially arranged pattern of (mostly) fibrous crystals is a well-known and frequently noted phenomenon associated with suitable nucleating surfaces and unimpeded growth conditions.

Figure 3 shows SEM images of features, observed in polished surfaces of Bohnerz and Rasenerz concretions and described as „festoons" (Riezebos et al., 1981). They are banded to laminated infills of fissures and cavities inside these concretions, and the laminae are made up of iron hydroxide minerals admixed in varying amounts with clay and other material. The origin of the individual laminae within the festoons probably took place under conditions comparable to those controlling the genesis of sheaths with a radial fabric inside pisoids and ooids (Bhattacharyya and Kakimoto, 1982). The pictures in Figure 3 demonstrate the expected radial growth of the constituent crystals.

Thus, to determine whether there exists a genetic relationship between the ooids from the Rasenerz concretions and the Minette ironstones, the study of their individual cortex sheaths, as done by Bhattacharyya and Kakimoto (1982) seems to be an appropriate approach. We will try this approach in an following study.

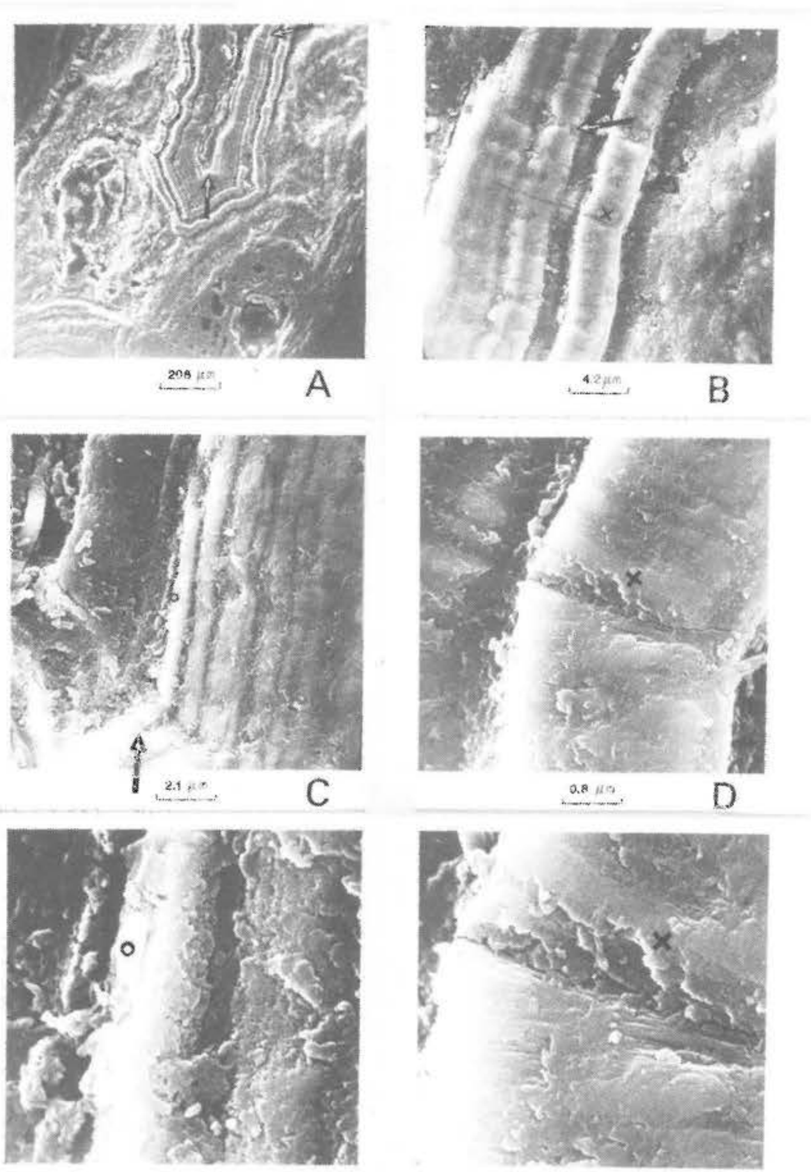

Fig. 3 Scanning electron micrographs displaying increasing magnifications of sites (see arrows in the upper left picture) in a polished and subsequently etched festoon (sample E1 III1, Riezebos et al, 1981). Irrespective of the rounding effects of the hydrochloric acid applied in etching, the radial crystallization fabric of the platelets in the individual iron-rich laminae is clearly illustrated in the large magnifications. Arrows, circles and crosses indicate ca. corresponding sites in the enlargements.

PURPOSE OF THIS STUDY

The aim of the work presented here is an attempt to corroborate the inferred relationship between the Rasenerz concretions and the Minette ironstones, by investigating their bulk geochemistry. Apart from Rasenerz and Minette ironstone samples, Bohnerz samples were also included in the study because earlier work suggested that these concretions deviate geochemically from the Rasenerz concretions (Schiltz, 1925; Riezebos et al., 1981).

A meaningful pattern in the distribution of chemical elements, which the three types of iron-rich rocks have in common, was searched after. If such pattern exists, it will provide additional evidence for the suggested connection between the Rasenerz concretions and the Minette ironstones. It will also support the hypothesis that Rasenerz-bearing loam occurrences are actually remnants of worn-down inselbergs and the included iron concretions eluvial fragments of iron crusts developed in the Minette formation when it was at or very near the land surface.

SAMPLING, SAMPLE PREPARATION AND METHOD

The Rasenerz and Bohnerz samples were taken from existing collections used for an earlier study (Table 1, Riezebos et al., 1981). Figure 1 indicates sites at which these collections have been sampled. From each of these seven collections ($E_1 - E_7$) and the groups therein, an equal number of individual specimens were randomly selected as in the previous study.

The samples of Minette ironstones were taken from a sequence exposed in the Lallingerberg in the Escher Becken (14 samples) and from a section in the Differdinger Becken (11 samples). From each of the individual iron-ore beds and barren strata („Erzlagern" and „Zwischenmitteln") of the cyclic repetitions one or more samples were collected (Table 1). Thein (1975) emphasized however, that due to frequently changing juxtaposition of the various lithofacies in space and time, a correlation between the stratigraphic units in the basins mentioned is hard to establish. Therefore, the correlations and stratigraphic positions of the samples, as indicated in Table 1, are only tentative.

A subsample of approximately 1 cm^3 was cut out of each specimen, crushed and milled down in an agate ball-mill to a grain size of about 2 μm. Ten milligrams of the powered material were placed in a sealed capsule and submitted for neutron-activation analysis (NAA) at the Interuniversity Reactor Institute at Delft. The standard procedure of instrumental neutron activation analysis for geological material was applied (de Bruin and Kortenhove, 1972). Basically it is a single comparator method, using zinc as a single element standard. The analysis comprises two irradiations, both at a neutron flux of $10^{17} n/m^2s$, and three measurements. Twenty minutes after a first irradiation of 30 sec. the samples are counted. The second irradiation of one hour is followed by measurements after decay times of 5 and 30 days respectively.

The spectra of the γ-radiation emitted by the activated samples are measured with γ-ray spectrometers using solid or well-type detectors, directly connected to a PDP-11/34 computer. The spectra are automatically analysed and interpreted, using the program ICPEAX (Kortenhoven and de Bruin, 1976). The concentrations of 35 chemical elements in 81 samples were measured.

SCREENING AND SUMMARY STATISTICS OF THE NAA OUTPUT

In the NAA output the information on the chemical elements consists of an estimation of their abundances (in ppm) followed by indications of the precision of estimate. These indications are the detection limit and the instrumental coefficient of variation (in %). To obtain a reliable set of date, the NAA outcomes were screened on the presence of gross instrumental errors, detection limits, and magnitudes of the coefficient of variation. Two samples had to be discarded due to gross errors. Further, all variables with a coefficient of variation greater than 10% were deleted. This operation reduced the initial dimensions of variable space from 35 to 16. The variables remaining are Na, Sc, Cr, Fe, Co, Zn, As, La, Ce, Sn, Eu, Tb, Yb, Lu, Hf and Th.

In order to acquire uni- and bivariate information on the statistical behaviour of the 16 variables and to facilitate choosing among alternative multivariate methods, summary statistics were prepared with program BASTAT (Ten Kate and Sprenger, 1986). BASTAT processes a multidimensional data-array in which missing values may occur. Also the data can be collectively transformed by one of a set of transformation functions. For each variable the program yields (a) sample mean, median, mode, range, variance, standard deviation, coefficient of variation, skewness and kurtosis, (b) a test of normality, and (c) 95% confidence limits about the population mean and variance. The program also computes standardized scores, linear correlation coefficients and linear regression equations. It plots histograms and produces scatter diagrams and regression curves of pairs of variables with a correlation coefficient greater or equal than 0.70.

The main results are listed in Table 2. Most variables have a substantial range (rows d and e); measures of central tendency do not coincide, hence the sample frequency distributions are asymmetric (row f, g and h); measures of dispersion are high, e.g. all coefficients of variation are greater than 43% (row i and j), and the majority of the frequency distributions have a positive skewness and are too peaked (rows k and l). Hence, only three variables (Sc, Co and Zn) pass the test on normality at 95% confidence level (rows m-q).

Ahrens (1945a, b, 1957) and Koch and Link (1970) suggested that trace elements in rocks are lognormally distributed. When the data set is logarithmically transformed, the situation only slightly improves: Na, Sc, Co, Ce, Tb, Yb and Lu pass the test on lognormality. Moreover Na and Tb have to much values below the detection limit (Table 2, row b and c). Therefore these results are nor reported here.

Meanwhile the bivariate plots in Figures 4, 5, 6 and 7 are interesting. In Figure 4 a cluster of Bohnerz samples, relatively low in Na and high in As values, is separated from a cluster of Minette ironstones with low As and

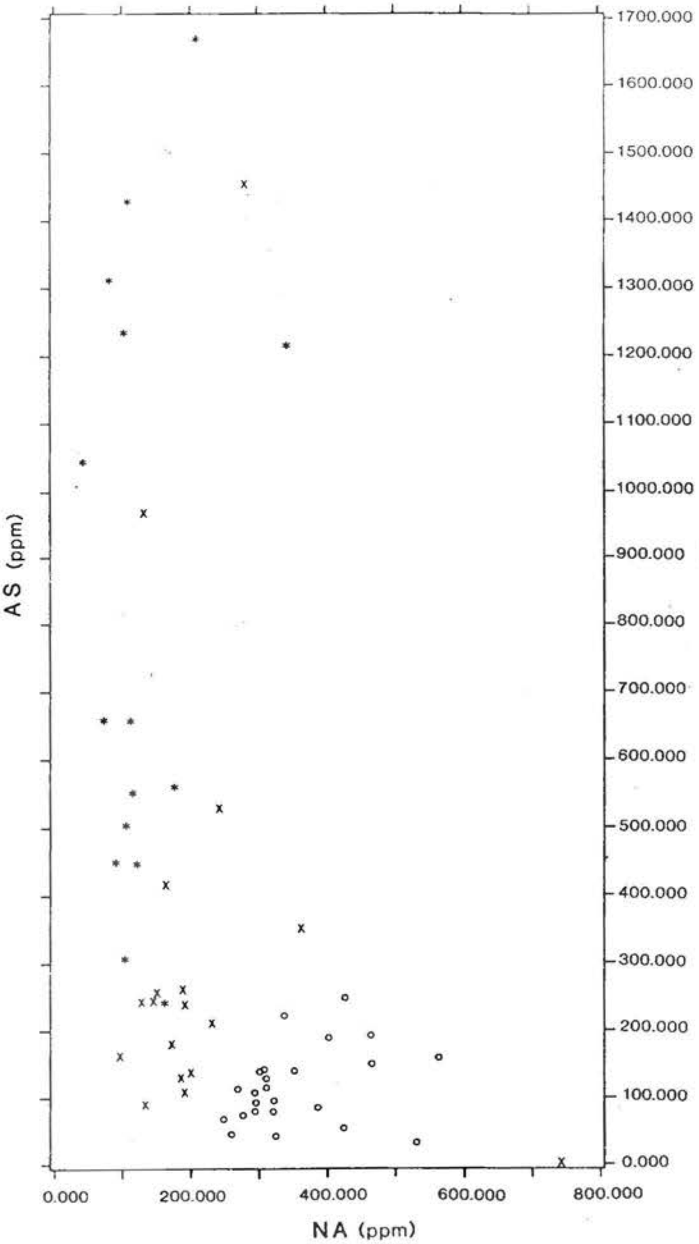

Fig. 4 Bivariate Na-As plot obtained with BASTAT (Ten Kate and Sprenger, 1986). Circles indicate Minette, crosses Rasenerz and stars Bohnerz samples.

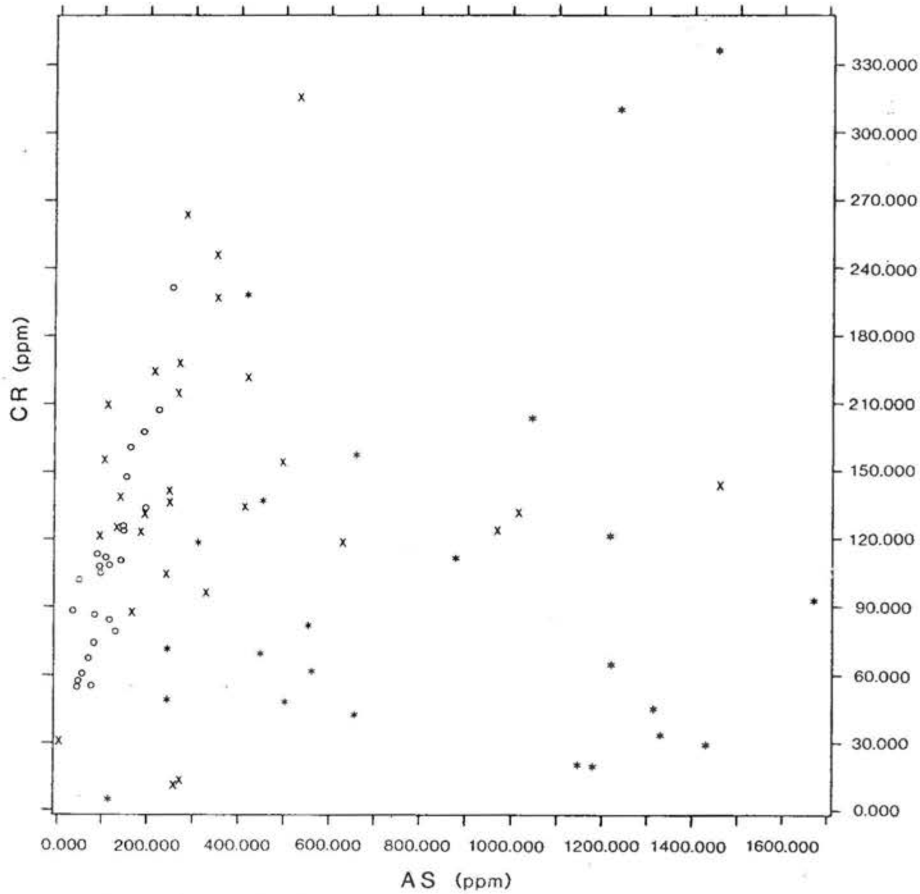

Fig. 5 Bivariate As-Cr plot. For legends see Figure 4.

high Na contents. The majority of the Rasenerz values form an intermediate cluster between these two. The same tendency, although progressively less distinct, is observable in the plots of variable pairs As-Cr (Fig. 5), As-Ce (Fig. 6) and Cr-Ce (Fig. 7).

The results of the univariate statistics indicate that methods, free from multivariate statistical requirements, and more in agreement with the amount and nature of the data, have to be applied. This leads to numerical classification, a tool frequently applied in many branches of science.

NUMERICAL CLASSIFICATION

Numerical classification is a branch of pattern analysis and concerns itself with pattern extraction. It uses mathematical tools and concepts, and aims at simplification and efficient ordening of a data set too large to process with the human mind (Williams, 1976). In contrast to multivariate statistical methods, no statistical conditions are assumed or tested. If a sample from a set of 79 samples is characterized by its contribution to a set of 16 variables

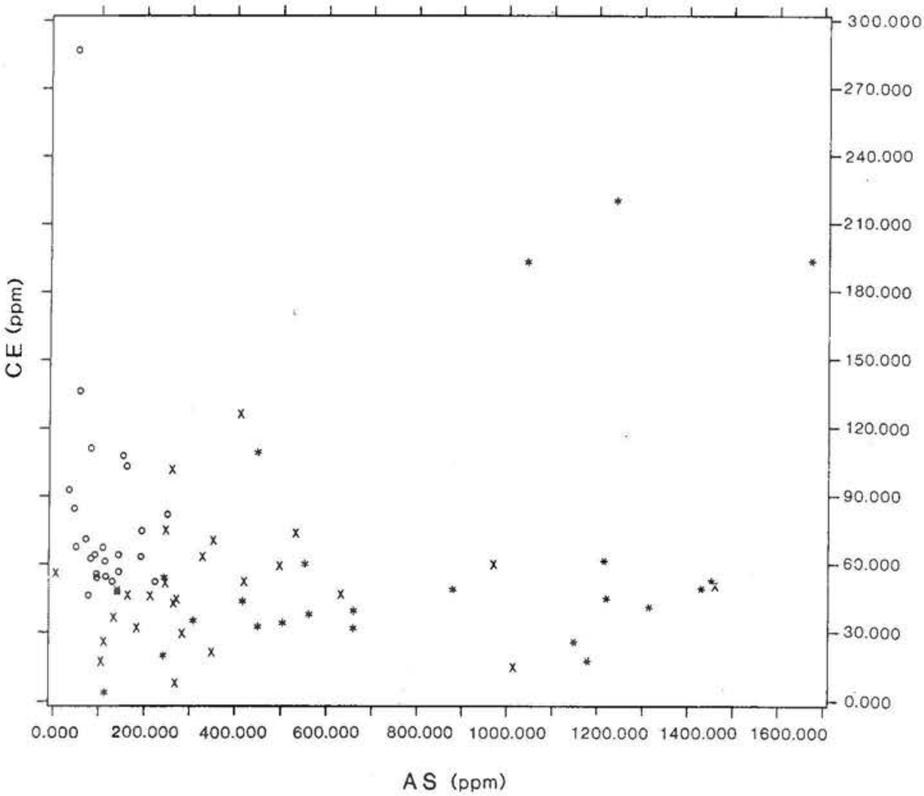

Fig. 6 Bivariate As-Ce plot. For legends see Figure 4.

common to all these samples, it can be presented as a point in a coordinate system spanned by 16 variables (R-space). Its coordinates correspond with its contributions to the variables, and, when this is done for all the samples, a configuration of points will result.

However, before constructing such configuration, i.e. before deciding on a proper strategy of classification, it is necessary to consider the purpose of the investigation in relation to the mathematical quality, quantity and nature of each measured variable. For instance, heterogeneity of dimensions and of scales of measurement among variables confine the choice of similarity or distance measures between the samples, and may push the strategy either to some type of ordination method, or to a type of cluster analysis.

Further, when such a configuration of sample points has been produced, two questions are of interest. The first is whether clusters are recognizable, and thus the set of samples is classifiable in subsets. If so, the second question is: are certain clusters determined by a characteristic combination of variables. Hence, in this paper two complementary methods of numerical classification are employed: Dynamic Cluster Analysis (DYCLAN) as conceived by Diday (1973) and programmed by Bochi (1973) and Correspondence Analysis (CORRES), the theoretical background of which is extensi-

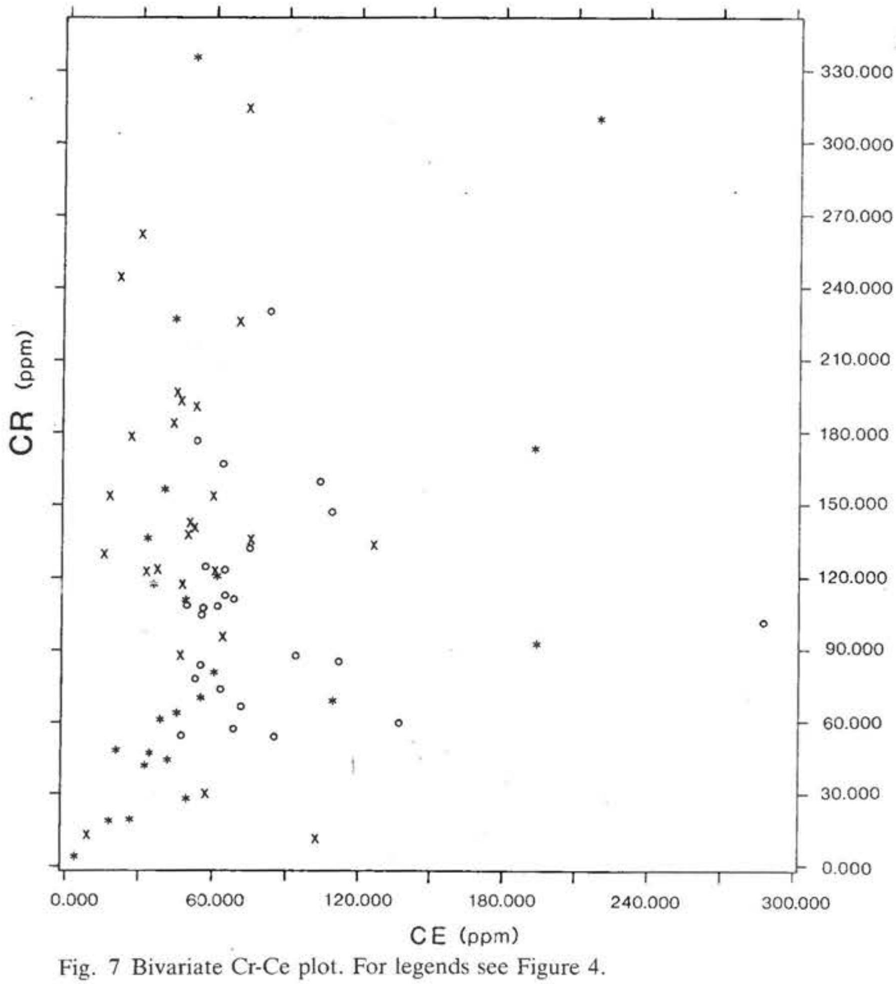

Fig. 7 Bivariate Cr-Ce plot. For legends see Figure 4.

vely treated in Benzecri et al. (1973), Lebart and Fénelon (1975) and Hill (1974). Lefebvre and David (1977) and Guillaume (1977) give a lucid description of both methods applied to geological problems.

Both use the same measure of similarity, i.e. the chi-square distance function. DYCLAN examines whether a set of samples can be divided into a finite number of subsets, the so-called 'strong patterns'. The variation among samples belonging to the same strong pattern is minimised and in terms of the chi-square distance they resemble each other as much as possible. So DYCLAN answers the question as to a collection of samples, characterized by the same set of variables, are classifiable into subsets, but it does not indicate the reason. CORRES - as proposed by Benzecri (1973) - is a particular form of principal component analysis. It combines Q- and R-mode and has the ability to illustrate graphically the connection between variables and samples.

Row c of Table 2 shows that in the reduced data matrix several variables have a high number of values below detection limit. Here they are considered as missing values and they form a problem because in the selected methods of numerical classification they are not allowed. Rigorous elimination of the variables concerned would waste valuable information, cause a further reduction of sample and variable space, and counteract our purpose. The problem was solved by discarding all variables containing more than five missing values, so Na, Zn, Tb, Hf and Th have not been included in the numerical classifications. If the total of missing values was 5 or less, these values have been replaced by the mode of that particular variable. Although this substitution is not entirely up to standards, it is thought that the effect on the final result of DYCLAN and CORRES will be minor.

A trial run of CORRES on the 11 variables showed that the factor plots were difficult to interpret, owing to the domination of Fe. For that reason, iron also had to be eliminated.

DISCUSSIONS OF RESULTS OF NUMERICAL CLASSIFICATION

The results of DYCLAN applied on the remaining 10 variables are presented in Table 3. Thirteen strong patterns appear to be recognizable at the highest degree of homogeneity, ten of them comprising only one sample. The remaining three, however, are the numbers 1, 4 and 8, which contain 69 out of the total of 79 samples (ca. 87%). Strong pattern no. 1 unites eight Minette and two Rasenerz samples; no. 4 fifteen Minette, sixteen Rasenerz and two Bohnerz samples, whereas strong pattern no. 8 includes 21 Bohnerz and 5 Rasenerz samples. It is striking that no. 1 is mainly made up of Minette samples, no. 4 of Minette and Rasenerz samples whereas no. 8 contains primarily Bohnerz samples. At lower levels of homogeneity this tendency becomes in particular evident. At level 7 (Table 3) two groups are distinguishable: one comprising all the Minette, 66% of the Rasenerz and only two Bohnerz samples; the other group holds the remaining Bohnerz and 33% of the Rasenerz samples.

The results of the CORRES are summarized in Table 4, which lists among others the loadings on the variables. Factors 1 and 2 account for 91.76% of the total variation. Figure 8 shows the plane containing these two factor axes. The objects (samples) and the variables (elements) have been projected on this plane. The figure clearly illustrates the close relationship between the Minette and Rasenerz samples, and the divergent position of the Bohnerz samples. The majority of the Rasenerz samples partially envelopes the more scattered cloud of Minette samples. Also the plane containing factor axes 1 and 3 demonstrates this trend (Fig. 9).

CORRES shows that the first three factors explain 95.5% of the variation (Table 4). Therefore, it seems permissible to neglect the higher factor axes accounting for less than 5% of the total variation, and to confine the discussion to the plots of the factors 1 and 2 (Fig. 8) and 1 and 3 (Fig. 9).

Factor 1 is clearly dominated by As, pulling all but two Bohnerz samples and about 33% of the Rasenerz samples in a direction opposite to that of the other variables. Factor 2, which explains 20.51% of the variation, is the

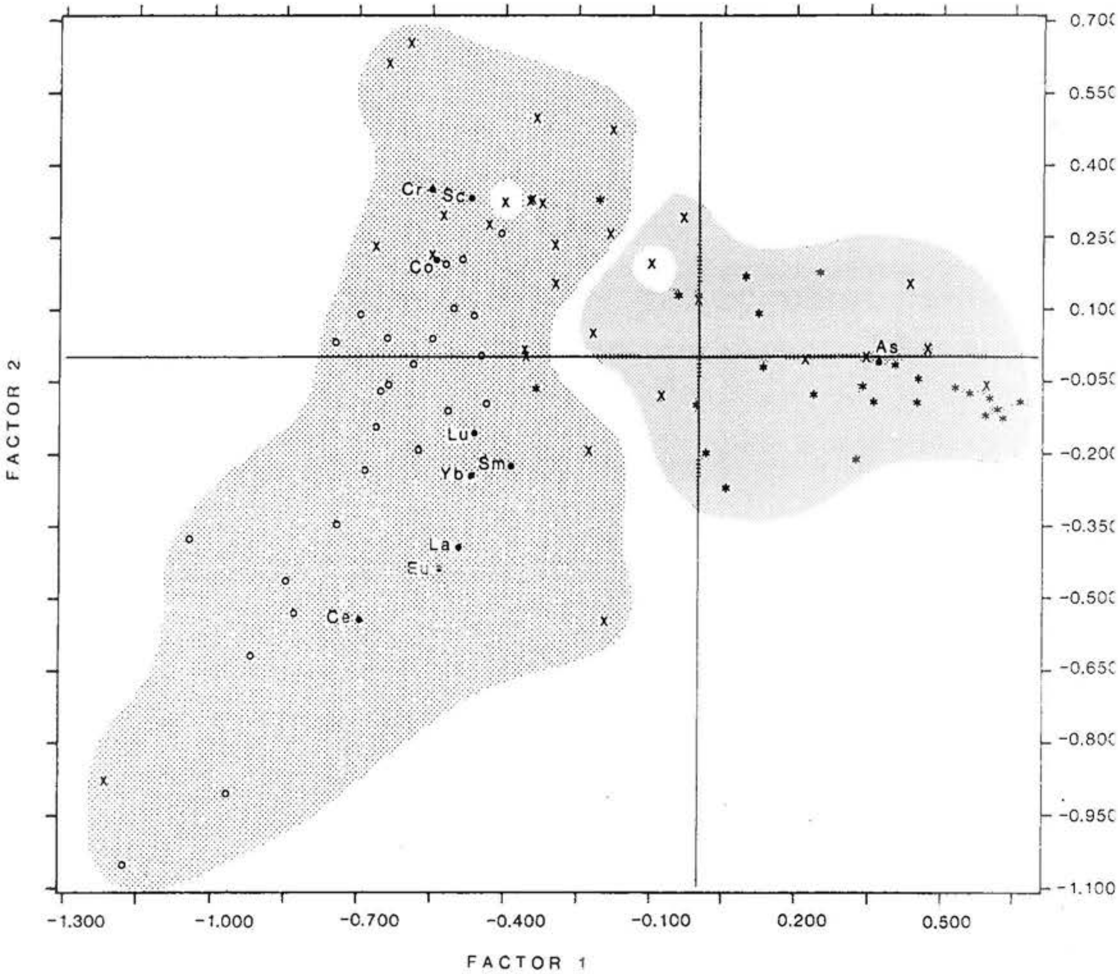

Fig. 8 Plot of the first two axes of CORRES. Samples and elements have been projected on this plane with Factors 1 and 2, that explain together 91.67% of the total variation. The light shading indicates the distribution of strong patterns 1-5, the dark one that of strong patterns 8-13 while that of strong patterns 6 and 7 are represented by included unshaded spots (Table 3) .
o Minette, x Rasenerz and * Bohnerz samples and • are elements.

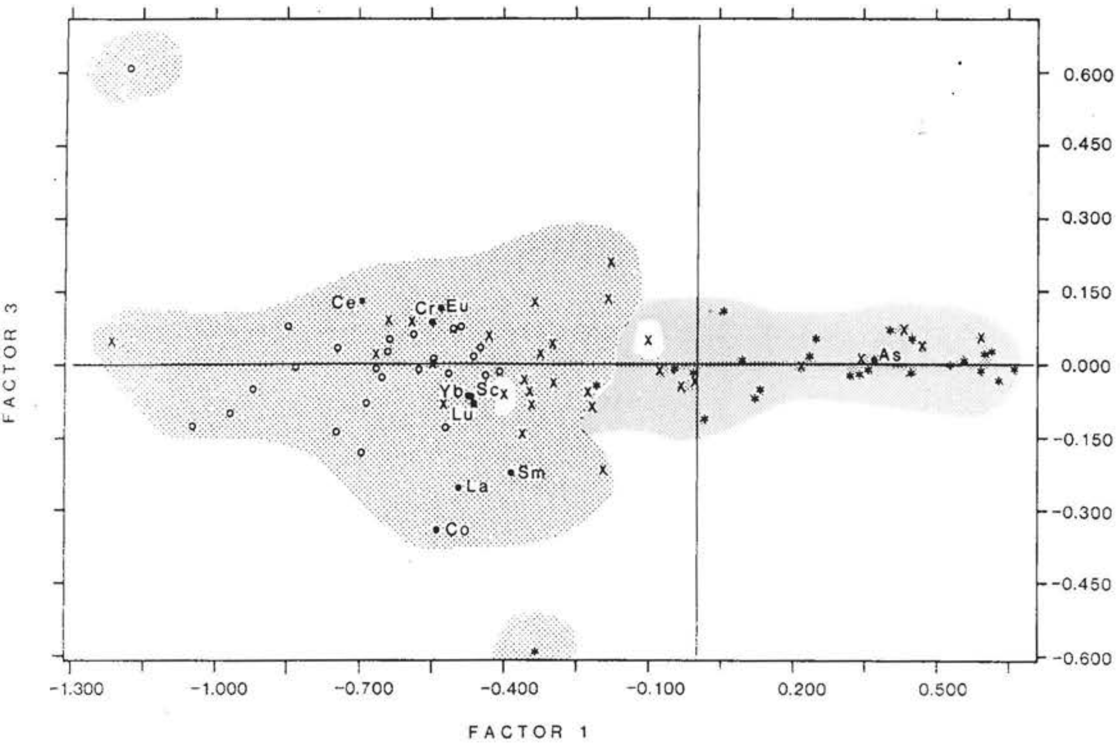

Fig. 9 Projection plane with the second and third factor axes explaining just 24.39% of the total variation. For legends see Figure 8.

result of the interaction of the lanthanides and the minor elements Co, Sc and Cr. The elements contributed to factor 2 are arranged in a conspicuous way, going from the lanthanides in the lower part to the minor elements Co, Sc and Cr in the upper part. The pattern of sample points more or less matches this trend of the element points (Fig. 8). Going from the top to the bottom of this plot, a cloud of points first representing the majority of Rasenerz and thereafter the Minette samples are encountered. Sample points representing all but two of the Bohnerz samples and part of the Rasenerz samples fall outside this trend and are concentrated around the As projection.

The plot in Figure 9 showing the projection of samples and elements on the plane factor 1 - factor 3 does not add much more information and confirms the picture already obtained. It does display the anomalous location of one of the two deviating Bohnerz samples (no. 73), and illustrates further the rather insignificant role of the third factor.

In summary, analyses on 10 variables allow grouping of the samples in subsets similar to those predicted in a geomorphogenetic model conceived on the basis of field and microscopic data, and stress the close relationship between the Rasenerz and the Minette. Further, the distribution of sample projections belonging to the groups distinguished might suggest certain trends in the geochemical mobilities of the elements involved.

IDENTIFICATION OF THE FACTORS

The first factor reflects the importance of As enrichment during the formation of the lateritic crusts from which the Bohnerz concretions are derived. Enrichment is suggested, because an average arsenic content of 428 ppm (Table 2) is high compared to presently known abundances in other rock types. As is found in rock-forming minerals, and is a major constituent in a large number of minerals (Wehdepohl, 1978; Chapter 33). The highest values occurring in some „brines" and phosphatic limestone do not exceed 23.5 ppm, whereas an average abundance in shales is 13 ppm. In soils the mean values of As vary between 5 and 10 ppm.

The arrangement of the element projections along the second factor axis, apparently reflects a differentiation among the lanthanides on the one side and Co, Cr and Sc on the other. The proximity of these latter element projections and those of a great number of Rasenerz and Minette samples seems to indicate a certain affinity. The remaining Minette samples together with 2 Rasenerz samples – representing Strong Pattern 1 – are separated from that combined Rasenerz-Minette cloud by the lighter lanthanides. It should be noted that the lighter lanthanides Ce, La and Eu in particular contribute to this trend.

The number of primary and secondary minerals containing Cr, Co and Sc as a major constituent are limited. In many minerals however, these elements can substitute the more common ones, especially if their ions have similar sizes and chemical properties. Hence, Cr, Co and Sc tend to behave rather similarly during the various petrogenetic, diagenetic and weathering processes (Wehdepohl, 1978: Chapters 21, 24 and 27).

Sedimentary iron ores and lateritic/bauxitic residual deposits are generally both enriched in Cr, Co and Sc. In residual formations, the higher abundances are ascribed to secondary enrichment, whereas in sedimentary iron ores the higher contents are connected with Fe - Al in colloidal state and with clay (Frölich, 1960). Trivalent chromium is effectively absorbed from seawater by hydrous Fe and Mn oxides; Sc^{3+} is believed to be absorbed by colloidally divided clays and hydrous Al and Fe^{3+} oxides (Vlasov, 1966). Norman and Hask (1968) presented a possible linkage between Sc and Fe in sedimentary rocks, and ascribe this phenomenon either to coprecipitation of Sc with ferric hydroxide or to adsorption on colloidal iron hydroxides and clay.

On the basis of current knowledge, it seems impossible to compare the geochemical mobilities of the lanthanides with those of Cr, Co and Sc. (Wehdepohl 1978, chapter 57, 58, 62, 63, 70, 71). Ronov et al. (1967) communicate that in both sandstones and shales, the lanthanides decrease to a minimum towards the center of a basin. Moreover, there is a considerable change in the ratio: Σ La-Eu/Σ Gd-Lu, Y from continental to nearshore sandstones and shales due to a relative increase in the „heavy" lanthanides. This suggests that atomic weight may play a role in the geochemical mobility. The atomic masses of Cr, Co and Sc are far below those of the lanthanides. If the atomic weight indeed is a deciding factor, than Co, Cr and Sc might be remobilized more readily than the lanthanides during the alteration, and subsequently concentrated in that weathering system by reprecipitation. In any case this would explain why a great portion of the Rasenerz samples has been concentrated in the scattered Minette-Rasenerz cloud near the Co, Cr and Sc poles.

CONCLUDING REMARKS

The paleogeographic reconstructions of Ziegler (1982) of the tectonic and stratigraphic development of Western and Central Europe show that since the Late Kimmerian tectonism, the territory of the Grand Duchy of Luxembourg has formed part of the Brabant-Rhenish-Bohemian Massif. An exception might have been the SW part of Gutland during the Aptian-Albian (Ziegler, 1982, Encl. 22), but Muller (1980) considers the Bajocien deposits as the last marine formations in Luxembourg. Evidently the shape and attributes of the surface in Gutland are the product of a geomorphological development lasting 140 Ma. During this long period of time, covering the Cretaceous and Cenozoic, ample opportunities existed for iron-crust formation alternating with their dissection and erosion. These erosional periods might have been closely connected with, or induced by the tectonic development of the Massif. The evolution of the Rhine, Ruhr and Leine volcanic-rift systems during the Tertiary for instance, might have greatly affected and intensified periods of erosion just as the epeirogenetic movements of the Brabant-Rhenish Massif itself.

For the time being there is no firm evidence available to assess a time-equivalence between the iron crusts and Bohnerz and Rasenerz occurrences. Bohnerz probably represents remnants of lateritic crusts developed in Bajocien or possibly post-Bajocien Jurassic deposits, as already surmised by early investigators (Lucius, 1948). But with our present knowledge, it seems impossible to establish whether this crust formation occurred during the Cretaceous or during the Tertiary.

As is suggested in Figure 2, and more or less supported by the affinity of a number of the Rasenerz concretions to the majority of the Bohnerz concretions (Fig. 8 and 9), part of the iron concretions presently found at the localities of the typical Rasenerz occurrences, might actually be residual fragments of the Bohnerz-producing crusts (Table I; Riezebos et al., 1981). This would signify that, at that time when the surfaced Minette formation was subjected to iron-crust formation (Fig. 2, stage 3), remnants of „Bohnerz crusts" were still present at the land surface. In any case, the present study corroborates the view that the majority of the Rasenerz concretions derived from crusts originated in the Minette formation. These Aalenian-Toarcian deposits were exposed in a preceding period of erosion and denuation, during which the overlaying strata bearing the „Bohnerz crusts" were fragmented and largely removed (Fig. 2, stage 2).

Finally, the results of this work suggest that specific textural rock features, e.g. an oölic texture, might be inherited. In studies investigating the environmental significance of iron ooids, this possibility might not always be fully realized.

ACKNOWLEDGMENTS

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Table 1

Escher Becken		Sample	Label of strong pattern
Rotes sandiges Lager	L4	ME 13	1
	L3B/L4	ME 12	1
Oberes rotes Lager	L3B	–	–
	L3A/L3B	ME 10 ME 11	4 4
Unteres rotes Lager	L3A	–	–
	L3/L3A	ME 9 ME 14	1 1
Rotes Hauptlager	L3	–	–
Gelbes Nebenlager	L2A	–	–
	L2/L2A	ME 8	4
Gelbes Hauptlager	L2	ME 7	4
	L1/L2?	ME 6	4
Graues Lager	L1	ME 5 ME 4 Me 3	4 4 4
	L1/LI?	ME 2 ME 1	1 4
Braunes Lager	LI	–	–

Differdinger Becken		Sample	Label of strong pattern
Oberkalk	L3	ME 15	1
Zwischenmittel	L2	ME 16	2
Unterkalk	L1	ME 17 U ME 17 M ME 17 L	3 4 4
	L1/LI?	ME 18	1
Rotes Lager	LI	ME 19 ME 23	4 4
Gelbes Lager	LIa	–	–
	LIa/LII?	ME 20	4
Graues Lager	LII	ME 21	1
Schwarzes Lager	LIII	ME 22	4

Table 1 Tentative lithostratigraphic correlation between the sampled lithologic units of the sections exposed in the Escher and Differdinger Becken. Nomenclature is related to common mining practice. „Lager" and „Zwischenmittel" indicate comparatively iron-rich and iron-poor units (Thein, 1975). Corresponding sample and strong pattern numbers (see Table 3) are in the second and third column.

Table 2

a : Variable	1 Na	2 Sc	3 Cr	4 Fe	5 Co	6 Zn	7 As	8 La
b : Sample size :	58	78	79	79	79	73	79	77
c: Values below detection limit :	21	1	0	0	0	6	0	2
d : Minimum value :	45.200	1.122	5.010	36080.00	1.339	4.570	2.623	3.710
e : Maximum value :	744.900	69.970	336.590	572300.00	94.360	557.400	1671.000	97.030
f : Model value :	133.989	17.067	114.243	523374.17	26.653	126.396	164.964	24.081
g : Median value :	229.119	18.669	113.416	454659.89	27.570	173.540	274.182	25.953
h : Mean value :	252.416	20.243	120.381	382628.73	29.991	199.283	428.126	28.936
i : Stand. dev. :	138.101	13.207	69.673	164765.14	18.889	114.935	431.749	17.655
j : Coef. of var. :	54.01%	65.24%	67.88%	43.0%	62.98%	57.67%	100.85%	61.01%
k : Skewness. :	1.045	1.385	0.839	0.638	1.230	0.905	1.336	1.846
l : Kurtosis :	1.436	2.701	0.995	1.197	2.031	0.801	0.543	4.534
m: Chi-square :	6.746	4.998	7.742	77.635	5.042	5.042	67.939	12.501
n : D.F. :	2	2	3	4	2	2	3	2
o : P (Chi-square) :	96.57%	91.78%	94.84%	99.99%	91.96%	91.96%	99.99%	99.81%
p : (1-a) :	95%	95%	95%	95%	95%	95%	95%	95%
q : Test N (μ, o^2) :	reject	accept	undecided	reject	accept	accept	reject	reject

Table 2 Summary of sample statistics. The values in rows d up to and including i are in ppm.

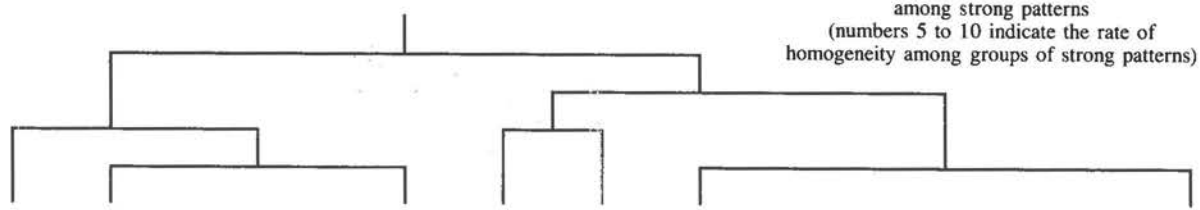
Table 2 (continued)

a : Variable :	9 Ce	10 Sm	11 Eu	12 Tb	13 Yb	14 Lu	15 Hf	16 Th
b : Sample size :	75	79	79	69	79	74	72	70
c: Values below detection limit :	4	0	0	10	0	5	7	9
d : Minimum value :	0.879	0.879	0.194	0.265	0.332	0.054	0.100	0.010
e : Maximum value :	286.700	41.600	12.900	6.560	15.070	2.518	17.290	43.110
f : Model value :	49.893	7.367	1.921	1.536	3.597	0.609	1.458	8.412
g : Median value :	53.124	7.783	2.045	1.751	4.036	0.722	1.718	9.404
h : Mean value :	63.850	9.232	2.473	2.059	4.688	0.841	2.046	10.308
i : Stand. dev. :	46.965	6.706	2.019	1.217	2.835	0.481	2.233	6.650
j : Coef. of var. :	73.55%	72.64%	81.67%	58.10%	60.46%	57.14%	109.14%	64.51%
k : Skewness. :	2.478	3.094	3.200	1.819	1.858	1.538	5.008	2.073
l : Kurtosis :	7.529	11.418	11.728	4.166	3.863	2.644	29.755	7.498
m: Chi-square :	22.196	33.874	31.406	13.375	23.722	17.411	33.453	10.209
n : D.F. :	2	1	1	2	3	3	1	2
o : P (Chi-square) :	99.99%	99.99%	99.99%	99.88%	99.99%	99.4%	99.99%	99.39%
p : (1-a) :	95%	95%	95%	95%	95%	95%	95%	95%
q : Test N (μ, o^2) :	reject	reject	reject	reject	reject	reject	reject	reject

Table 3

Dendograrh based an descending connectivities among strong patterns (numbers 5 to 10 indicate the rate of homogeneity among groups of strong patterns)

5
6
7
8
9
10



	1	2	3	4	5	6	7	8	9	10	11	12	13
1	ME13												
2	ME12												
3				ME10									
4				ME11									
5	ME9												
6	ME14												
7	ME15												
8				ME8									
9				ME7									
10		ME16											
11				ME6									
12				ME5									
13				ME4									
14				ME3									
15			ME17U										
16				ME17M									
17				ME17L									
18	ME2												
19				ME1									
20	ME18												

Table 3 Distribution of the samples over the strong patterns (col 1-13) recognized by DYCLAN. Nr. 1-25 are Minette ironstone samples arranged in stratigraphical order (Table 1); Nr. 26-55 are Rasenerz samples from the locations E1-E4 (Fig. 1); Nr. 56-79 are Bohnerz samples from the sites E5-E7 (Fig. 1).

Table 3 (continued)

	1	2	3	4	5	6	7	8	9	10	11	12	13
21				ME19									
22				ME23									
23				ME20									
24	ME21												
25				ME22									
26				E1/1/D									
27								E1/1/E					
28				E1/1/F									
29								E1/2/D					
30						E1/2/E							
31										E1/2/F			
32											E2/1/E		
33				E2/1/F									
34				E2/1/G									
35				E2/1/H									
36								E2/2/E					
37				E2/2/F									
38				E2/2/G									
39				E2/2/H									
40				E3/1/E									
41				E3/1/F									
42				E3/1/G									
43								E3/1/H					
44							E3/2/E						
45								E3/2/F					
46				E3/2/G									
47													E3/2/H
48				E4/1/E									
49					E4/1/F								
50												E4/1/G	
51				E4/1/h									
52				E4/2/E									
53				E4/2/F									
54	E4/2/G												
55	E4/2/H												

Table 3 (continued)

	1	2	3	4	5	6	7	8	9	10	11	12	13
56								E5/1/E					
57								E5/1/F					
58									E5/1/G				
59								E5/1/H					
60								E5/2/E					
61								E5/2/F					
62								E5/2/G					
63								E5/2/H					
64								E5/3/D					
65								E5/3/E					
66								E5/3/F					
67								E6/1/E					
68								E6/1/F					
69				E6/1/G									
70								E6/1/E					
71								E6/2/F					
72								E6/2/G					
73				E6/2/H									
74								E6/3/F					
75								E6/3/G					
76								E6/3/H					
77								E7/1/D					
78								E7/1/E					
79								E7/1/f					

Table 4

		FACTOR 1			FACTOR 2			FACTOR 3		
EIGEN VALUE		0.2095			0.0606			0.0133		
PERCENTAGE		71.10%			20.56%			3.83%		
CUM. PERCENTAGE		71.10%			91.67%			95.50%		
Var.	WEIGHT	Proj.	RC1	AC1	Proj.	RC2	AC2	Proj.	RC3	AC3
Sc	0.0285	−0.4706	45.86	3.01	0.3335	23.02	5.23	−0.0682	0.96	1.17
Cr	0.1701	−0.5498	69.10	24.54	0.3514	28.23	34.67	0.0878	1.76	11.60
Co	0.0424	−0.5403	57.56	5.90	0.2024	8.08	2.87	−0.3421	23.07	43.93
As	0.6049	0.3677	99.87	39.03	0.0115	0.10	0.13	0.0055	0.02	0.16
La	0.0407	−0.4943	46.17	4.75	−0.3948	29.45	10.48	−0.2542	12.21	23.32
Ce	0.0890	−0.6953	60.17	20.55	−0.5455	37.04	43.74	0.1299	2.10	13.32
Sm	0.0130	0.3864	53.40	0.93	0.2247	18.07	1.09	−0.2230	17.78	5.75
Eu	0.0035	−0.5326	52.52	0.47	0.4384	35.59	1.11	0.1157	2.48	0.41
Yb	0.0066	−0.4688	75.54	0.69	0.2442	20.49	0.65	0.0671	1.55	0.26
Lu	0.0012	−0.4624	84.50	0.12	0.1566	9.69	0.05	0.0795	2.50	0.07

Table 4 (continued)

		FACTOR 4			FACTOR 5		
EIGEN VALUE		0.0063			0.0047		
PERCENTAGE		2.14%			1.59%		
CUM. PERCENTAGE		97.63%			99.23%		
Var.	WEIGHT	Proj.	RC4	AC4	Proj.	RC5	AC5
Sc	0.0285	−0.0764	1.12	2.64	0.3739	28.95	84.79
Cr	0.1701	0.5050	0.58	6.88	−0.0376	0.32	5.13
Co	0.0424	−0.2162	9.21	31.43	−0.1027	2.08	9.50
As	0.6049	−0.0028	0.01	0.08	−0.0015	0.00	0.03
La	0.0407	0.2527	12.06	41.26	0.0237	0.11	0.49
Ce	0.0890	−0.0745	0.69	7.84	0.0009	0.00	0.00
Sm	0.0130	0.1730	10.71	6.20	−0.0109	0.04	0.03
Eu	0.0035	−0.2242	9.31	2.79	0.0228	0.10	0.04
Yb	0.0066	−0.0837	2.41	0.74	0.0045	0.01	0.00
Lu	0.0012	−0.0905	3.24	0.15	0.0133	0.07	0.00

Table 4 Summary of the results of Correspondence Analysis (CORRES).
Weight: relative mass of the j^{th} chemical variable (j=1, 2, ..., 10); Proj: projection of the j^{th} variable on the k^{th} factor axis (k = 1, 2, ..., 5); RCj: relative contribution of the j^{th}-variable to the k^{th}-factor (rowwise the RCj's sum to 100%); ACj: absolute contribution of the j^{th}-variable to the k^{th}-factor (columnwise the ACj's sum to 100%).

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