

ORE-TEXTURAL AND GEOCHEMICAL FEATURES OF BOHNERZ AND RASENERZ CONCRETIONS IN GUTLAND (LUXEMBOURG)¹

P. A. RIEZEBOS², M. DE BRUIN³ & R. P. W. DUIN⁴

ABSTRACT

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Rasenerz and Bohnerz concretions from Gutland have been studied geochemically and by reflected light microscopy. The greater part of either type can be characterized by a single microscopic feature: more than 50% of the Rasenerz samples has an oolitic texture which is considered indicative of the Minette Formation; about 65% of the Bohnerz samples displays festoon development that is regarded as a sign of supergene origin. Festoons that occur in ooid-lacking Rasenerz (27%) suggest that Rasenerz also derives in part from destructed iron-bearing crusts. Common population statistics of individual trace element abundances fails to discriminate between the two types, but a statistical interpretation of 13 normalized concentrations enables their distinction.

When clustered on textural grounds into oolitic Rasenerz, festoon-bearing Rasenerz, and festoon-bearing Bohnerz categories, only the Na values of the first and the second category are significantly different. Especially on the basis of the rare earth chemistry, the festoon-bearing Rasenerz and Bohnerz concretions are thought to derive from different surface crusts.

INTRODUCTION

Bohnerz and Rasenerz are found in Gutland, the southern part of the Grand-Duchy of Luxembourg (Fig. 1). These iron concretions occur closely associated with surficial loams and as constituents of fluvial deposits. They differ in a number of properties. The first of these properties is their character as a raw material in the ancient Lotharingian iron industry (LUCIUS, 1948): Bohnerz yielded iron of good quality, while the product obtained from Rasenerz was of considerably inferior quality. The second is their phosphorous content: Bohnerz appears to contain a perceptibly lower concentration than Rasenerz (SCHILTZ, 1925). Furthermore, their regional and altitudinal distribution is different: Bohnerz seems to occur exclusively in loams covering the Bajocien limestone on the southernmost parts of the 400 m Gutland surface level while Rasenerz is found in sandy loams on more or less distinct planation

surfaces in a much greater number of areas varying in altitude from 240 to 395 meter (Fig. 1). Moreover, it forms a component of fluvial terraces and valley infills (LUCIUS, 1948). Finally, they differ in appearance. The usual form of Bohnerz concretions suggests that they are layered and have grown in a concentric manner while Rasenerz specimens are mostly irregular in outline consisting of angular blocky, nodular, or platy lumps sometimes with rounded edges and corners (LUCIUS, 1948). In addition, they are generally larger than the Bohnerz concretions, at least when randomly collected populations from the type localities are compared.

According to SCHILTZ (1925, 1927), LUCIUS (1948) and KABOTH (1969) Bohnerz was formed from the iron produced by laterite formation under a tropical climate during the Eocene. Rasenerz was considered by SCHILTZ (1927, 1937) and LUCIUS (1948) as a product of bog-iron formation in accumulated waste material in shallow lakes and swampy areas during the beginning of the Miocene. KABOTH's microscopic study, however, revealed that the Rasenerz concretions 'weitgehend aus oolithischem Material bestehen' (KABOTH, 1969, p. 99). These ooids are considered as atypical for bog-iron. Because in the type localities of the Rasenerz in Luxembourg no oolitic deposits are known to occur in the underlying Lias, KABOTH regards these ooids as residues of the Minette Formation. This

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² Fysisch Geografisch en Bodemkundig Laboratorium, Universiteit van Amsterdam, The Netherlands.

³ Interuniversitair Reactor Instituut, Delft, The Netherlands.

⁴ Afdeling Technische Natuurkunde, Technische Hogeschool, Delft, The Netherlands.

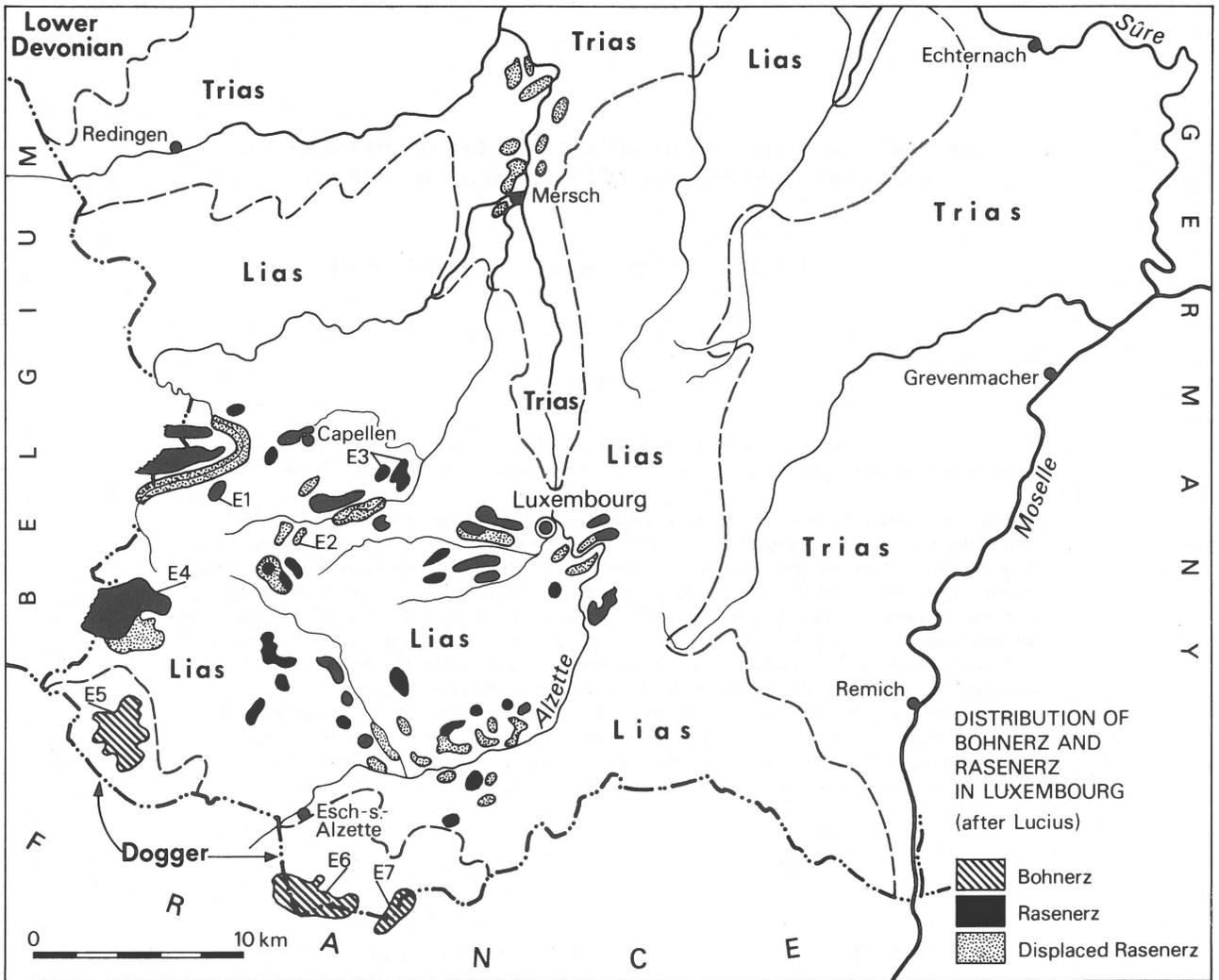


Fig. 1
Simplified geological map showing the distribution of Bohnerz and Rasenerz areas (after Lucius, 1948) and the sample sites E1 up to and including E7.

is a typical sedimentary facies in the Upper Lias and Lower Dogger of Middle Europe that is characterized by the occurrence of oolitic iron ore. In Luxembourg this facies is merely found today in two small areas adjacent to the French border (Fig. 1).

PURPOSE OF THE STUDY

This paper reports on the results of preliminary investigations on the erosional history of southeastern Gutland. Remnants of former weathering zones and geological strata that are now disintegrated, give important clues for the reconstruction of the erosional development of a modern landscape. As mentioned before, the two types of concretions are macroscopically discernable when sufficient large collections from a Rasenerz and Bohnerz type locality are compared. Non-specific individual specimens of about similar dimensions that

occur in 'secondary positions' are often hard to distinguish from each other (Fig. 2). So the first objective was to find out to what degree the oolitic texture could help discriminate between Rasenerz and Bohnerz concretions in 'secondary positions', especially as KABOTH (1969) stated: 'dass die untersuchten Luxemburger Proben: . . . weitgehend aus oolithischem Material bestehen'. A secondary objective was to assess whether chemical elements could be used to distinguish the two types of concretions.

PROCEDURE

Field sampling

A large number of concretions and fragments found on the surface was collected in four locations of the Rasenerz areas (E1, E2, E3 and E4, Fig. 1) and in three of the Bohnerz areas

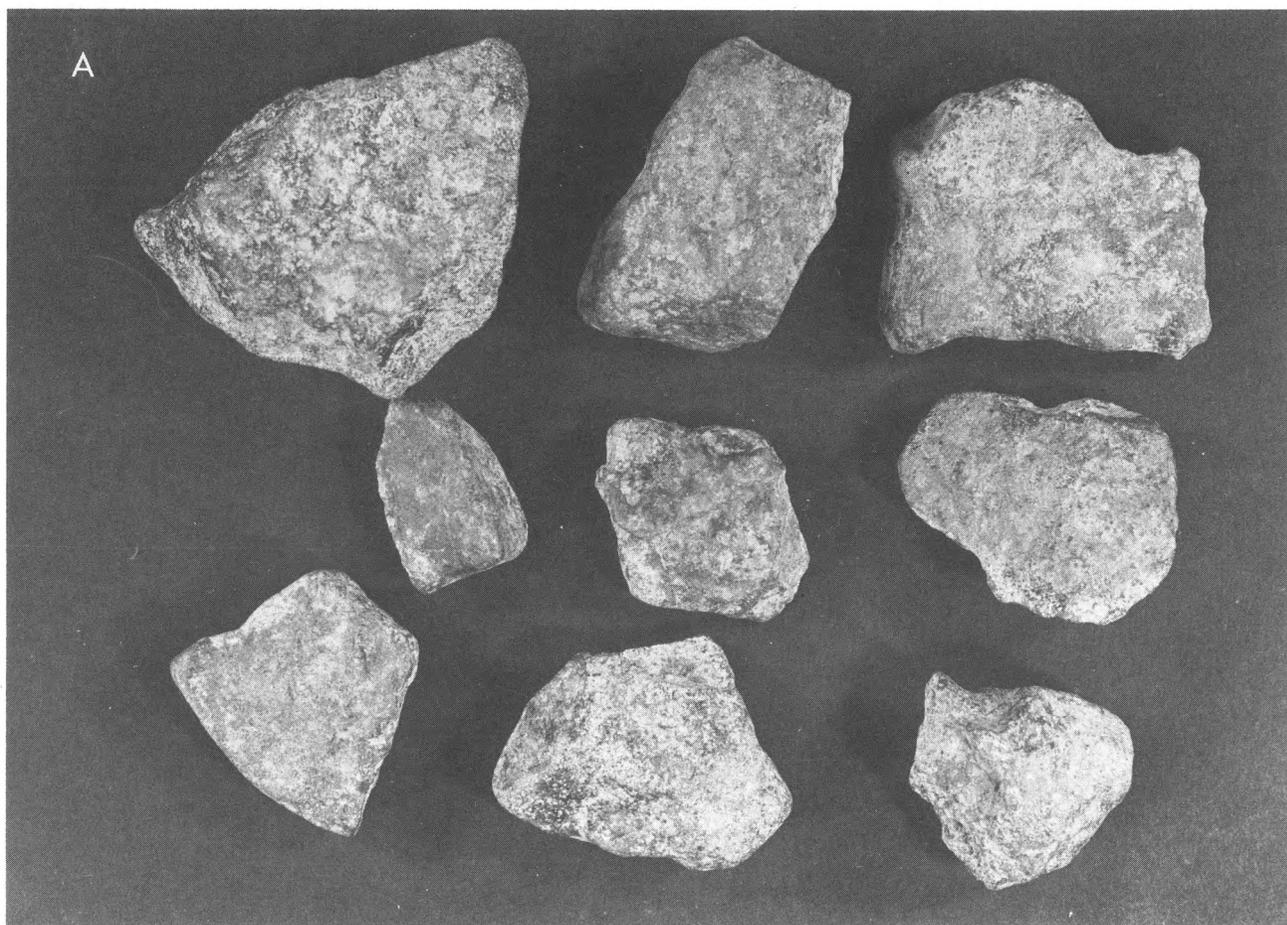


Fig. 2A
Examples of non-specific Rasenerz concretions.

(E5, E6 and E7, Fig. 1). Macroscopically, it was possible to distinguish one, two, or three groups, within each of these seven collections (Table I). From each of the fifteen groups distinguished three or four samples were taken at random and used for analysis.

Microscopical analysis

A section was cut from each sample, mounted in polyester resin, and subsequently ground and polished for analysis in incident light. Attention was focussed on the opaque material, the constituents if discernable, the fabric, the mutual relationships with other non-opaque components, etc. Plates 1 and 2 are photomicrographs that show some of those textural properties.

Neutron activation analysis

From the inside of the remaining sample portions, cubes of about 1 cm^3 were cut for multi-trace element analysis. The standard instrumental neutron activation analysis procedure for geological materials in use at the Interuniversity Reactor

Institute was applied (DE BRUIN & KORTHOVEN, 1972).

It is basically a single comparator method using zinc as a single element standard. The analysis comprises two irradiations both at a neutron flux of $10^{17} \text{ n/m}^2 \text{ s}$ and three measurements. After a first 30s irradiation, the samples are counted after a decay time of 20 minutes. A second irradiation of one hour is followed by measurements after 5 and 30 days respectively. The spectra of the γ -radiation emitted by the activated samples are measured with γ -ray spectrometers with solid or well-type detector directly connected to a DDC.POP-11/10 computer. The spectra are automatically analysed and interpreted using the program ICPEAX (KORTHOVEN & DE BRUIN, 1976). The concentration of at least the elements As, Al, Ce, Co, Cr, Eu, Fe, Hf, La, Mn, Na, Sc, Th and Yb were obtained.

Statistical interpretation of the trace-element contents

The concentration data were statistically interpreted using discriminant analysis techniques. For more details, the reader is referred to Appendix.

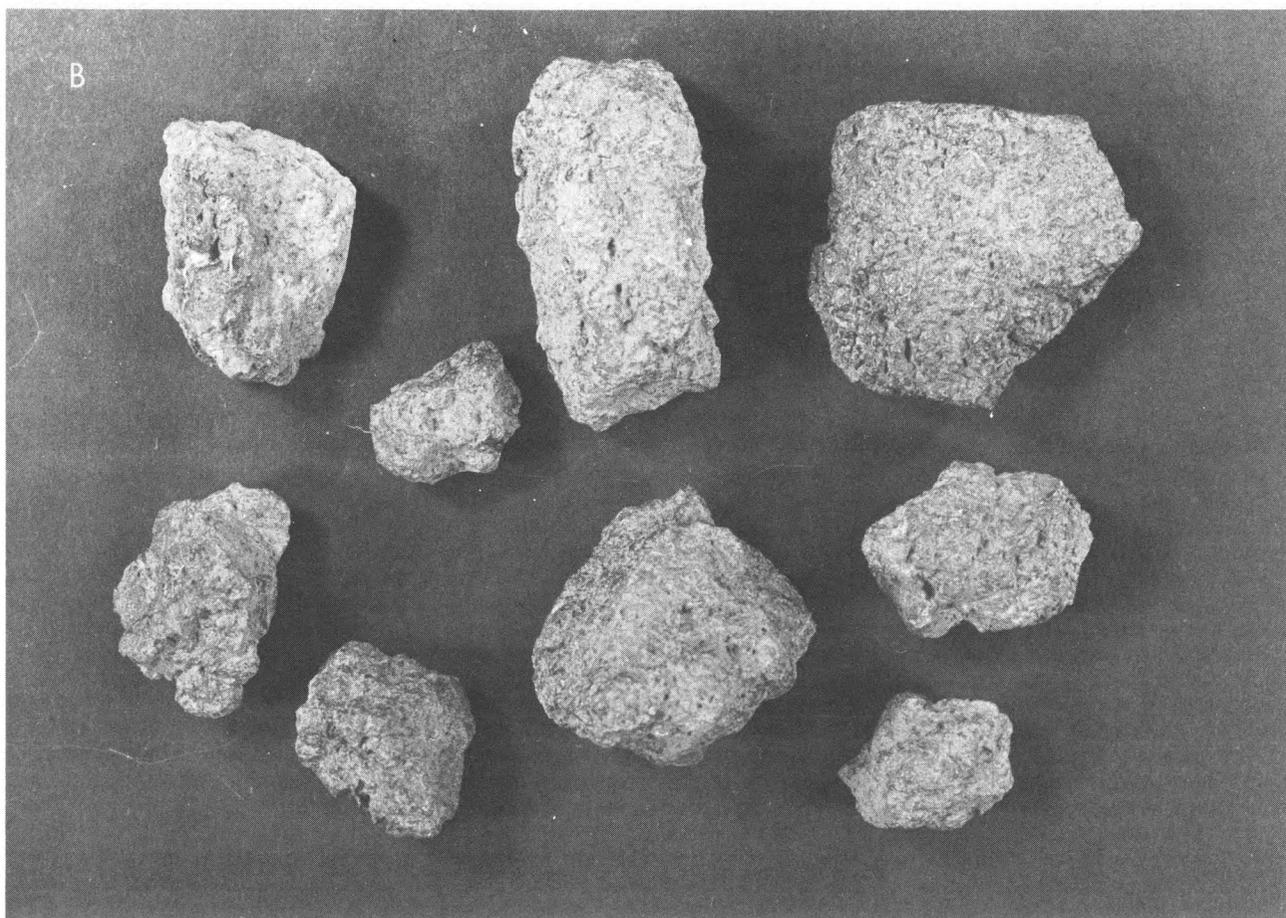


Fig. 2B
Examples of non-specific Bohnerz concretions.

RESULTS

Microscopical data

The bulk of the opaque and semi-opaque matter consists of iron hydroxides and earthy material with a varying iron content. Goethite is the most abundant constituent which is recognizable under the microscope. The concretions range between rather dense iron hydroxide lumps (Plate 1 D) and 'sedimentary particles' cemented in different degrees (Plate 1 A). These particles may be transparent mineral grains of varying shape and size, discrete iron hydroxide particles, diffuse iron-containing loamy areas (Plate 1, A, B, C and E) etc. The interstitial material varies from rather pure goethite to iron-bearing loam (Plate 1, A, B, E and F). Textural differences may be found within one section.

Two features, however, are rather conspicuous and common; ooids and festoons. The ooids are exclusively found in 18 of the 30 Rasenerz samples studied (Table I). The festoons consist of distinctly banded or layered areas of rather pure iron hydroxides. Festoons occur in both Bohnerz and Rasenerz samples but not in all of them. Table I indicates that

festoons are more frequently associated with the Bohnerz. In the Rasenerz samples festoon and ooid occurrences are almost mutually exclusive.

The ooids occur as more or less complete spherical and ellipsoidal specimens with varying dimensions. Measurement of 300 specimens provided lengths between 0,880 and 0,048 mm and widths between 0,600 and 0,048 mm. Ooid fragments are scarce. The thickness and distinctness of the concentrically laminated portions is variable (Plate 1, B and C) but in naturally and artificially etched examples, the laminated structure is well illustrated (Plate 1, F; Plate 2, C). Also the nucleus is frequently only discerned with difficulty (Plate 1, B, C; Plate 2, C), especially when the core is mainly composed of similar matter as the cortex. If the nucleus is discernible, its dimensions may range from virtually nothing to almost the entire ooid diameter.

The mutual orientation, packing, and nature of contact of the ooids is variable. In places they may be densely packed with little room for matrix and empty spaces. But they are also found widely scattered in the cementing material (Plate 1 B, C and F; Plate 2, C).

The laminar and banded nature of the festoons is produced

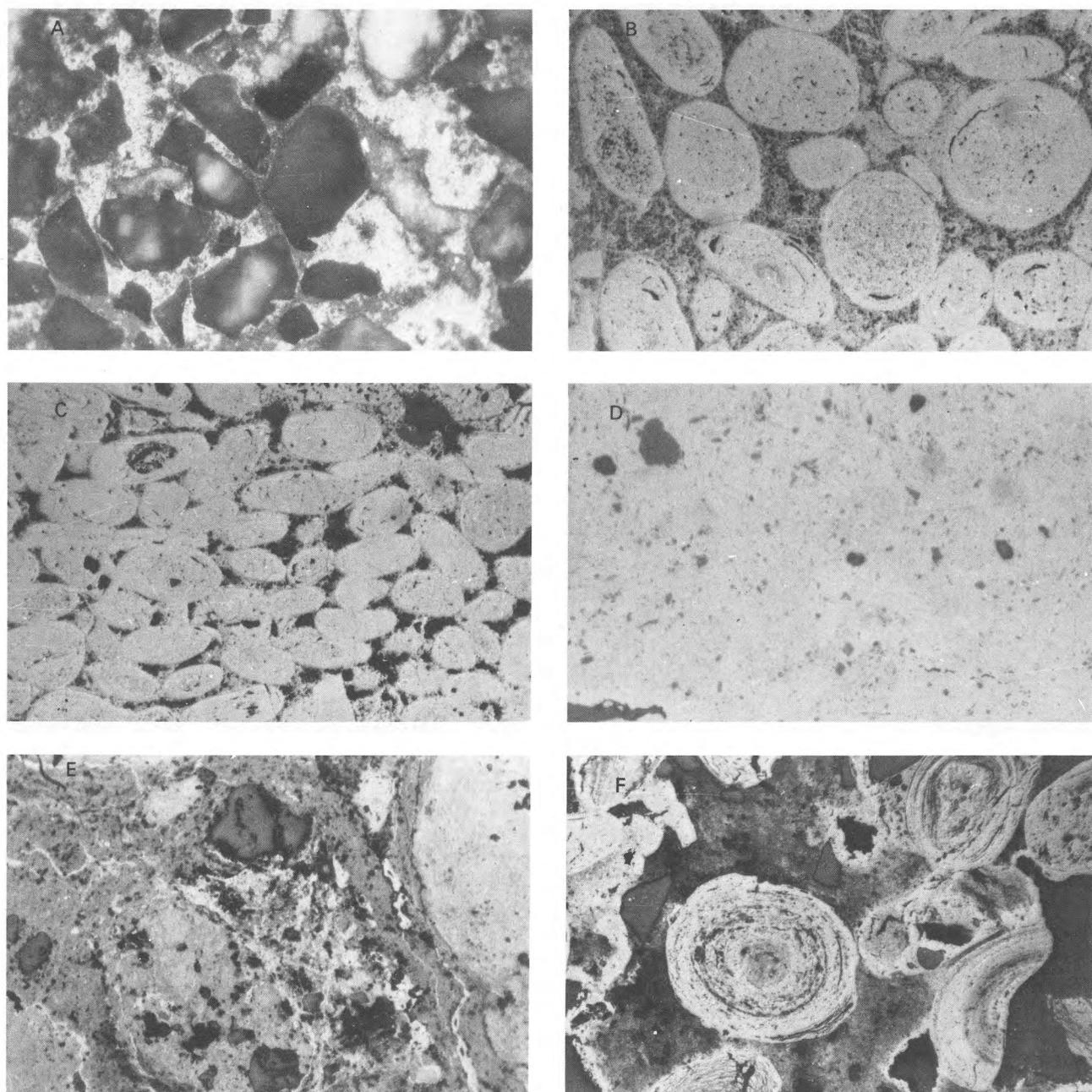


Plate 1

Photomicrographs illustrating the textural diversity of Bohnerz and Rasenerz concretions.

- A. Bohnerz sample (E6 collection). Note the angular nature of the transparent mineral grains. The matrix consists of porous iron hydroxide (whitishly speckled) and clayish loam locally rich in minute iron hydroxide particles (ocular Periplan 10×, objective 25/0.65 P, oil immersion).
- B. Rasenerz (E2 collection) showing ooids cemented by porous iron hydroxide material (ocular Periplan 10×, objective P5.6/0.15). Note the absence of transparent mineral grains.
- C. Rasenerz (E3 collection) showing a parallel orientation of ooids (ocular Periplan 10×, objective P5.6/0.15).
- D. Bohnerz (E5 collection) exemplifying a dense goethite concretion (ocular Periplan 10×, objective P16/0.40).
- E. Bohnerz (E5 collection) showing festoon development on a small scale (ocular Periplan 10×, objective P16/0.40).
- F. Rasenerz (E2 collection) exhibiting naturally etched ooids. Varying reflectivity of ooids, ooid shales, and matrix probably corresponds with fluctuating loam contents (ocular Periplan 10×, objective P5.6/0.15).

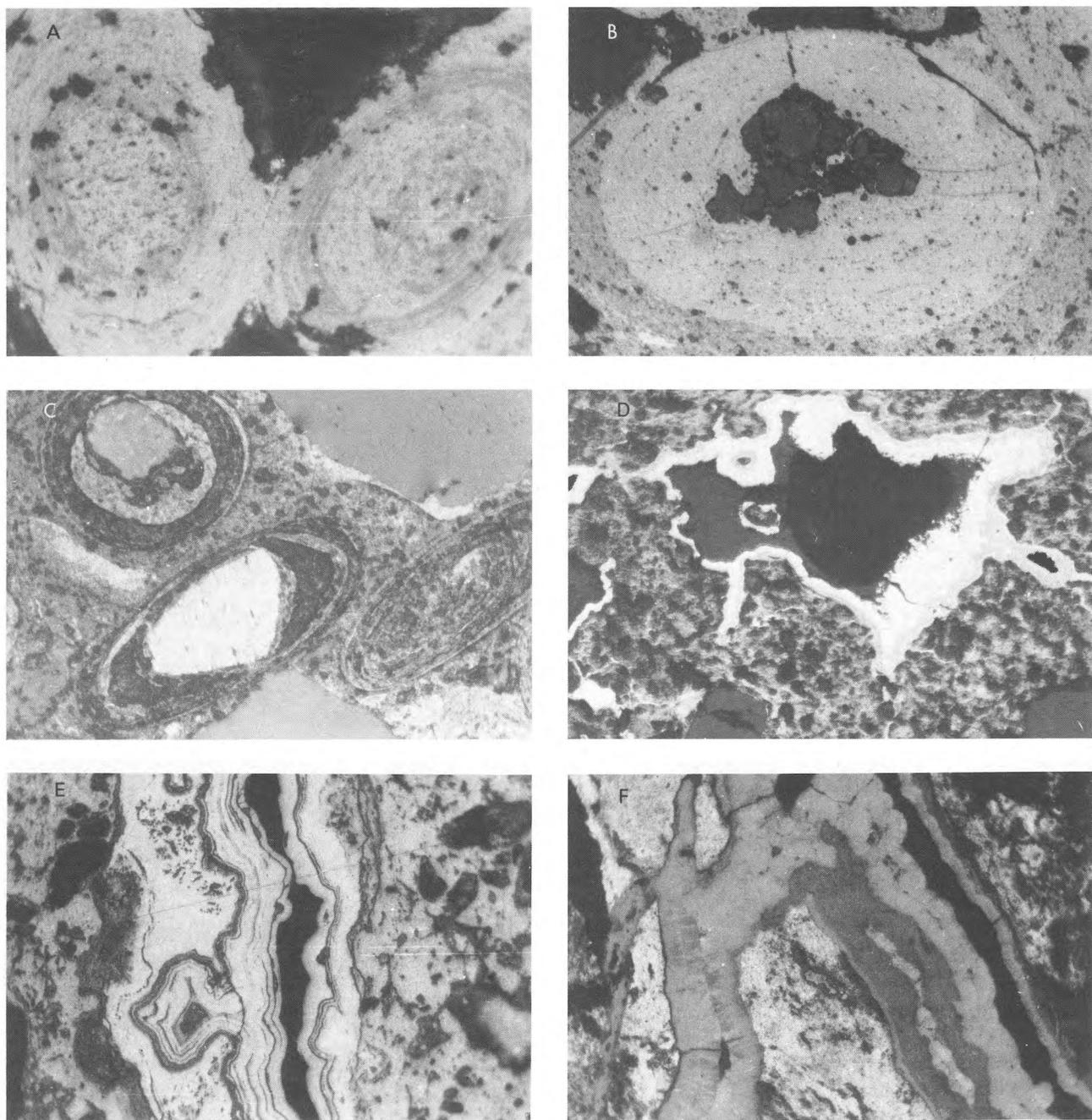


Plate 2

Examples of ooids and festoons.

A. Corroded ooids (E4 collection). In the empty interstitial spaces loam (dark-grey) has mantled the corroded walls of the ooids (ocular Periplan 10×, objective 25/0.65 P).

B. Example (E2 collection) with a core of transparent mineral particles (ocular Periplan 10×, objective P16/0.40).

C. Ooids (E1 collection) etched with hydrochloric acid in polished section and exemplifying the variable nature and mutual relationship of core and cortex (ocular Periplan 10×, objective P16/0.40).

D. Cavity (E2 collection) partly filled up by festoon-developed iron compounds and clay (grey-black). The white zone (hematite or lepidocrocite) has locally been dissolved (ocular Periplan 10×, objective 25/0.65 P).

E. A festoon area (E6 collection), displaying a laminately developed filling up of a fissure (ocular Periplan 10×, objective 25/0.65 P).

F. The ramifying festoon (E5 collection) exhibits locally radially arranged goethite crystals (ocular Periplan 10×, objective 25/0.65 P).

TABLE I

Rasenerz					Bohnerz				
Collection	Group	Nr.	Ooids	Festoons	Collection	Group	Nr.	Ooids	Festoons
E1	Gr. I	1	x	x	E5	Gr. I	1	-	x
E1	Gr. I	2	-	x	E5	Gr. I	2	-	x
E1	Gr. I	3	-	-	E5	Gr. I	3	-	-
E1	Gr. II	1	-	x	E5	Gr. I	4	-	x
E1	Gr. II	2	-	x	E5	Gr. II	1	-	x
E1	Gr. II	3	-	x	E5	Gr. II	2	-	x
E2	Gr. I	1	-	x	E5	Gr. II	3	-	-
E2	Gr. I	2	x	x	E5	Gr. II	4	-	x
E2	Gr. I	3	x	-	E5	Gr. III	1	-	-
E2	Gr. I	4	-	-	E5	Gr. III	2	-	-
E2	Gr. II	1	-	x	E5	Gr. III	3	-	x
E2	Gr. II	2	x	-	E6	Gr. I	1	-	x
E2	Gr. II	3	-	x	E6	Gr. I	2	-	x
E2	Gr. II	4	x	-	E6	Gr. I	3	-	x
E3	Gr. I	1	x	-	E6	Gr. I	4	-	x
E3	Gr. I	2	x	-	E6	Gr. II	1	-	-
E3	Gr. I	3	x	-	E6	Gr. II	2	-	x
E3	Gr. I	4	-	x	E6	Gr. II	3	-	x
E3	Gr. II	1	x	-	E6	Gr. II	4	-	-
E3	Gr. II	2	x	-	E6	Gr. III	1	-	x
E3	Gr. II	3	x	-	E6	Gr. III	2	-	x
E3	Gr. II	4	x	-	E6	Gr. III	3	-	x
E4	Gr. I	1	x	-	E6	Gr. III	4	-	-
E4	Gr. I	2	x	-	E7	Gr. I	1	-	-
E4	Gr. I	3	x	-	E7	Gr. I	2	-	x
E4	Gr. I	4	x	-	E7	Gr. I	3	-	-
E4	Gr. II	1	x	-					
E4	Gr. II	2	-	-					
E4	Gr. II	3	-	-					
E4	Gr. II	4	x	-					

x: observed in polished section
 -: not observed in polished section

Table I
 Distribution of ooids and festoons among the concretions examined.

by a variety of processes, e.g. an alternating deposition of pure and less pure goethite, a gradual or abrupt increase or decrease of minute inclusions normal to the free surface, radial growth of goethite crystals (Plate 2, F), successive accumulation of iron minerals with different reflectivities (Plate 2, D), alternating deposition of thin layers and accumulations of loamy and clayey material (Plate 2, E). The most beautifully developed examples are found at the margins of empty spaces and in former fissures and cavities which are now partly or completely filled (Plate 2, E and F). In the more massive portions of the concretions 'ghost festoons' can sometimes vaguely be distinguished. Obviously, the festoons represent the most recent hydrous Fe oxide deposition, and point to a form of internal crust formation that probably occurred frequently. There is also evidence for the removal of iron

compounds (Plate 2, A and D). Apparently, repeated growth and dissolution were rather common in these concretions.

Geochemical data

In Table II the highest and lowest values obtained for 14 elements together with the arithmetic mean and the standard deviation are given. The values of several other elements that were also determined (V, Zn, Tb, Ni, Lu, Dy) have been omitted as the greater part of these values appeared to be under the detection limit. Although the averages of Th, Hf, Yb, Eu, Ce, La, As, Co and Cr of the Bohnerz samples are somewhat higher, common population statistics do not permit a distinction between Bohnerz and Rasenerz.

According to Table III there also is no significant chemical

TABLE II

	Rasenerz (n=30)				Bohnerz (n=26)			
	values		\bar{m}	s	values		\bar{m}	s
	lowest	highest			lowest	highest		
Na	33	540	163.9	100.4	45	221	120.4	39.0
Al*	0.3	7.8	2.6	1.7	0.3	7.3	2.4	1.8
Sc	5.3	300	33.4	52.0	4.6	79	21.0	19.5
Cr	38	213	125.7	39.1	14.5	570	144.6	119.2
Mn	200	6300	1778	1489.6	250	9000	1312.7	1778.2
Fe*	28.0	72.0	46.8	8.9	24.6	61.0	43.0	9.7
Co	7.4	115	35.1	21.4	4.2	360	55.1	85.8
As	85	1370	407.6	290.2	19.7	1270	519.4	349.2
La	4.5	53	25.0	12.9	6.8	50	28.8	10.8
Ce	10.4	152	55.4	32.5	4.0	182	63.4	40.9
Eu	0.2	3.2	1.4	0.9	0.7	5.2	2.2	1.1
Yb	0.9	10.3	3.7	2.1	1.0	12.4	5.4	3.0
Hf	0.8	12.5	2.4	2.2	0.7	11.9	4.0	3.4
Th	2.1	14.6	6.7	3.1	0.5	50.0	13.6	14.0

Table II

The average element abundances (\bar{m}) and standard deviations (s) in addition to the lowest and highest values observed in the Rasenerz and Bohnerz samples (in p.p.m.). Asterisks indicate concentrations in percentages.

TABLE III

	Exclusively oolitic Rasenerz (16)		Exclusively festoon- bearing Rasenerz (8)		Exclusively festoon- bearing Bohnerz (17)	
	\bar{m}	s	\bar{m}	s	\bar{m}	s
Na	183.4	58.4	89.9	27.9	118.9	29.9
Al*	2.5	1.0	3.8	2.4	2.7	2.1
Sc	29.5	13.7	18.0	7.3	23.6	23.2
Cr	140.4	34.1	119.6	37.6	134.9	138.3
Mn	2011.6	834.5	1890	2606.9	938.9	831.4
Fe*	48.2	8.3	44.8	5.6	42.5	10.5
Co	42.8	21.9	19.1	9.7	39.3	38.2
As	434.4	359.3	349.6	57.4	548.0	354.5
La	28.2	12.1	19.1	12.3	30.2	9.5
Ce	61.1	32.2	41.3	26.6	67.3	40.2
Eu	1.6	0.7	1.0	0.6	2.3	1.2
Yb	4.7	2.4	2.5	0.9	6.0	3.3
Hf	1.7	0.4	3.6	3.7	4.4	4.0
Th	6.7	3.5	5.9	2.4	15.5	15.9

Table III

Average element concentrations (\bar{m}) and standard deviations (s) in texturally different categories (in p.p.m.). Asterisks indicate percentages.

TABLE IV

k = 1		k = 2		k = 3		k = 13	
element	\hat{D}^2	element combination	\hat{D}^2	element combination	\hat{D}^2	element combination	\hat{D}^2
Eu	0.84	Eu-Ce	2.42	Eu-Ce-Hf	4.06	Eu-Ce-Hf-Yb-Sc	
Yb	0.44	Eu-Sc	2.19	Eu-Ce-Sc	3.67	-Mn-La-Na-Al-	
Sc	0.32	Eu-Na	1.56	Eu-Na-Sc	3.38	-Cr-As-Co-Th	8.28
Hf	0.24	Sc-Yb	1.45	Eu-La-Sc	2.87		
Mn	0.20	Eu-Hf	1.20	Eu-Ce-Na	2.54		
La	0.16	Eu-Cr	1.06	Eu-Ce-As	2.53		
Na	0.10	Eu-Al	1.05	Eu-Ce-Mn	2.48		
Al	0.08	Hf-Al	0.99	Eu-Ce-Th	2.41		
Cr	0.05	Eu-Mn	0.99	Eu-Ce-Cr	2.40		
As	0.05	Eu-Th	0.98	Eu-Ce-Al	2.38		
Ce	0.01						
Co	0.01						
Th	0.00						

Table IV

Mahalanobis' distances for the normalized individual element concentrations ($k = 1$), for the 10 best couples ($k = 2$), for the 10 best trios ($k = 3$), and for the combination of all trace elements established ($k = 13$). Concentrations of the trace elements normalized on the basis of Fe concentrations.

difference between the oolitic Rasenerz, festoon-bearing Rasenerz, and festoon-bearing Bohnerz.

Oolitic Rasenerz has indeed slightly higher average element abundances than the festoon-bearing Rasenerz, except for Al and Hf, but only the average Na content is significantly higher. Comparison of both festoon-bearing categories shows that, apart from Al, Mn and Fe, the average values of the Rasenerz samples are lower than those of the Bohnerz, but again, the differences are insignificant.

In general the data do not show much evidence for a close relationship between the elements, e.g. between Fe and Mn, Co or Cr. A linear relationship is suggested by the Fe-Sc diagrams of NORMAN & HASKIN (1968) for igneous and sedimentary rocks. For the Bohnerz samples such a relationship could be established at a 90% level of confidence using the Pearson correlation test.

In Figure 3 the geochemical relationship among the rare earth elements (REE) is illustrated. The average and also the ranges show that the relative abundances of La, Ce, Eu and Yb are rather similar to those found in intermediate rocks, shales and graywackes (WEDEPOHL, 1978: Tables 39, 57-17-E-4 and 39, 57-17-K-2).

In Table IV one of the two kinds of normalization discussed in the Appendix is presented as normalization on the basis of the Fe concentration. The other on the basis of $1-1.59 \times \text{Fe}$ concentration appeared to be almost equivalent. This is not surprising as the average Fe abundance amounts to about 45%. For $k=1$ all values for the 13 n.t.e. concentrations are given. For $k=2$ and 3 the 10 best combinations have been

selected. The corresponding \hat{D}^2 values are optimistically biased by this selection. The value for $k=13$, in which all elements are used for estimating the Mahalanobis' distance corresponds to a significance of 6.10^{-8} ; the corresponding 95 % confidence interval for P is: $0.845 < P < 0.960$. These figures prove that the difference in n.t.e. concentrations is significant for the Bohnerz and Rasenerz. It is interesting to note that the best combination of three n.t.e. concentrations does not correspond at all with the individually best n.t.e. concentration. Especially the Ce abundance retains its discriminating power only when it is related to the Eu concentration. The correlation between the normalized Ce and Eu concentrations appears to be 0.8.

DISCUSSION AND CONCLUDING REMARKS

The two salient features, goethite ooids and festoons, may each be considered as specific for a set of environmental conditions. Ooids, rather commonly originate in marine as well as in non-marine settings, and are generally believed to point to areas where tidal bar accumulate or areas within tidal deltas where rather strong bottom currents prevail. Festoons may be considered to be produced by repeated dissolution and precipitation of iron compounds in the supergene zone of landscapes where iron-rich rocks are abundantly present. Generally, this represents an environment where changes in flushing, temperature, pH, Eh, etc. are rather usual.

The occurrence of both features in the Rasenerz sample

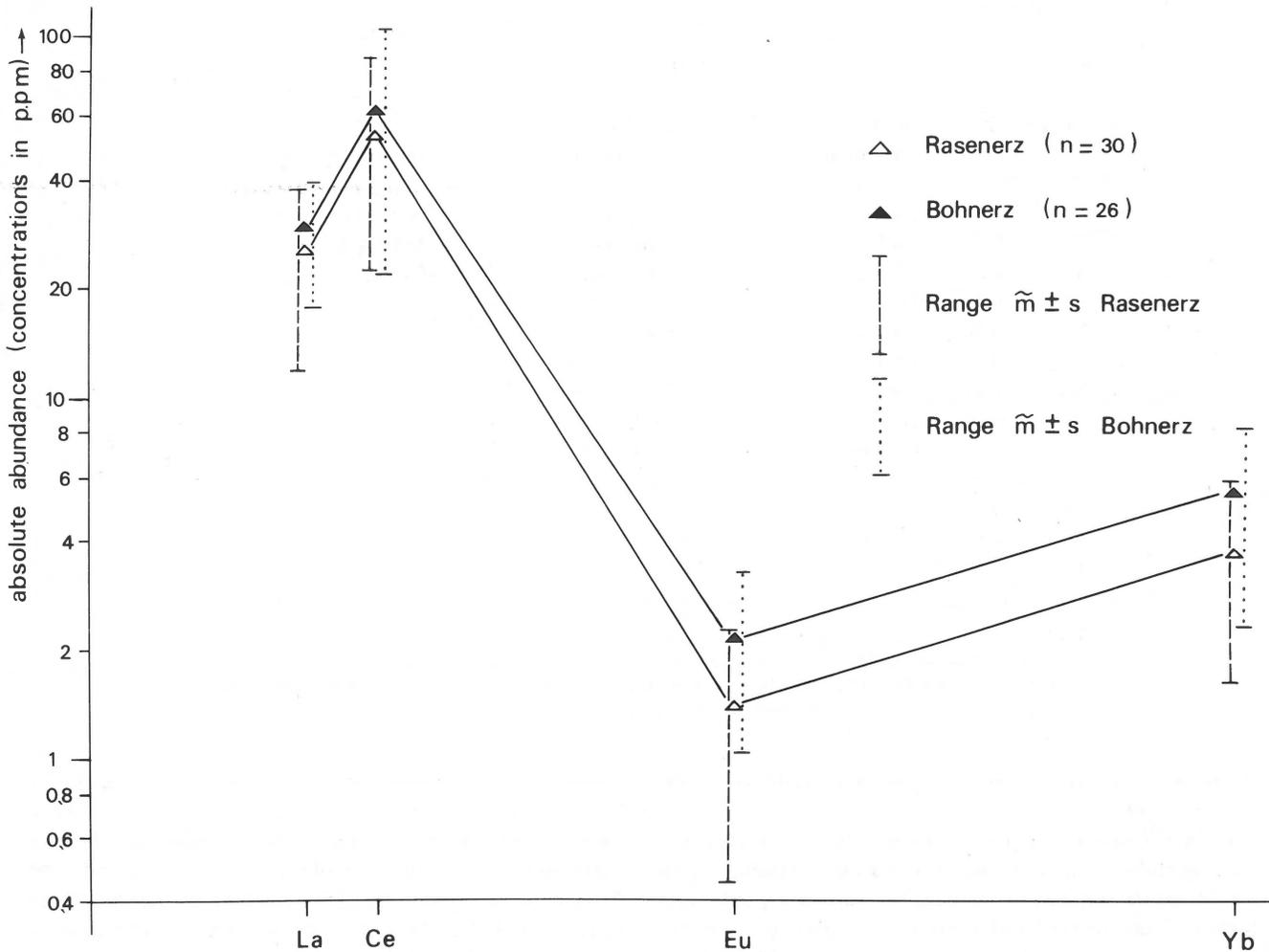


Fig. 3
Plot of La, Ce, Eu and Yb versus their respective averages (\bar{m}) in the Rasenerz and Bohnerz concretions.

population supports KABOTH'S (1969) conclusion that the Rasenerz concretions presently found at the surface are detrital remnants of the Minette Formation that were cemented by iron precipitation from solutions that originated under terrestrial conditions.

The fact that festoons in the Rasenerz concretions are mainly found in ooid-lacking specimens is somewhat surprising. It seems to suggest that in some of the Rasenerz localities, especially E1 and E2, not only concretions are found that were derived from the cemented Minette Formation but also specimens that were produced by the disintegration of lateritic or other iron-rich crusts which developed at the earth's surface. The significantly different Na contents of the oolitic and the festoon-bearing Rasenerz and also the higher averages of most elements in the first category are in favour of this suggestion (Table III). In any case, the presence of festoons in both Rasenerz and Bohnerz concretions restricts their distinction in 'secondary positions' on textural grounds.

A differentiation between the two festoon-bearing

categories on the basis of geochemical criteria is, as Table III shows, also difficult. This is to be expected because the lateritization that produced the Bohnerz concretions as well as the crusts of the Minette Formation took place in sedimentary rocks that were already geochemically differentiated. Mn, Co, and Cr abundances e.g. fall largely within the background range of common igneous and sedimentary rocks (Table II). Arsenic indeed displays an enrichment of about 100 times its lithospheric abundance, but the As averages of both festoon-bearing categories, although different, are in the same order of magnitude as the average value of the oolitic category (Table III).

In intermediate igneous rocks, shales and graywackes a close correspondence exists between the average La, Ce, Eu and Yb contents (WEDEPOHL, 1978: Tables 39, 57-17-E-4 and 39, 57-17-K-2), which indicates that these REE hardly show an enrichment or loss. RONOV ET AL. (1967), however, concluded that humid conditions apparently can cause different REE concentrations and distribution patterns. Also BALASHOV ET AL.

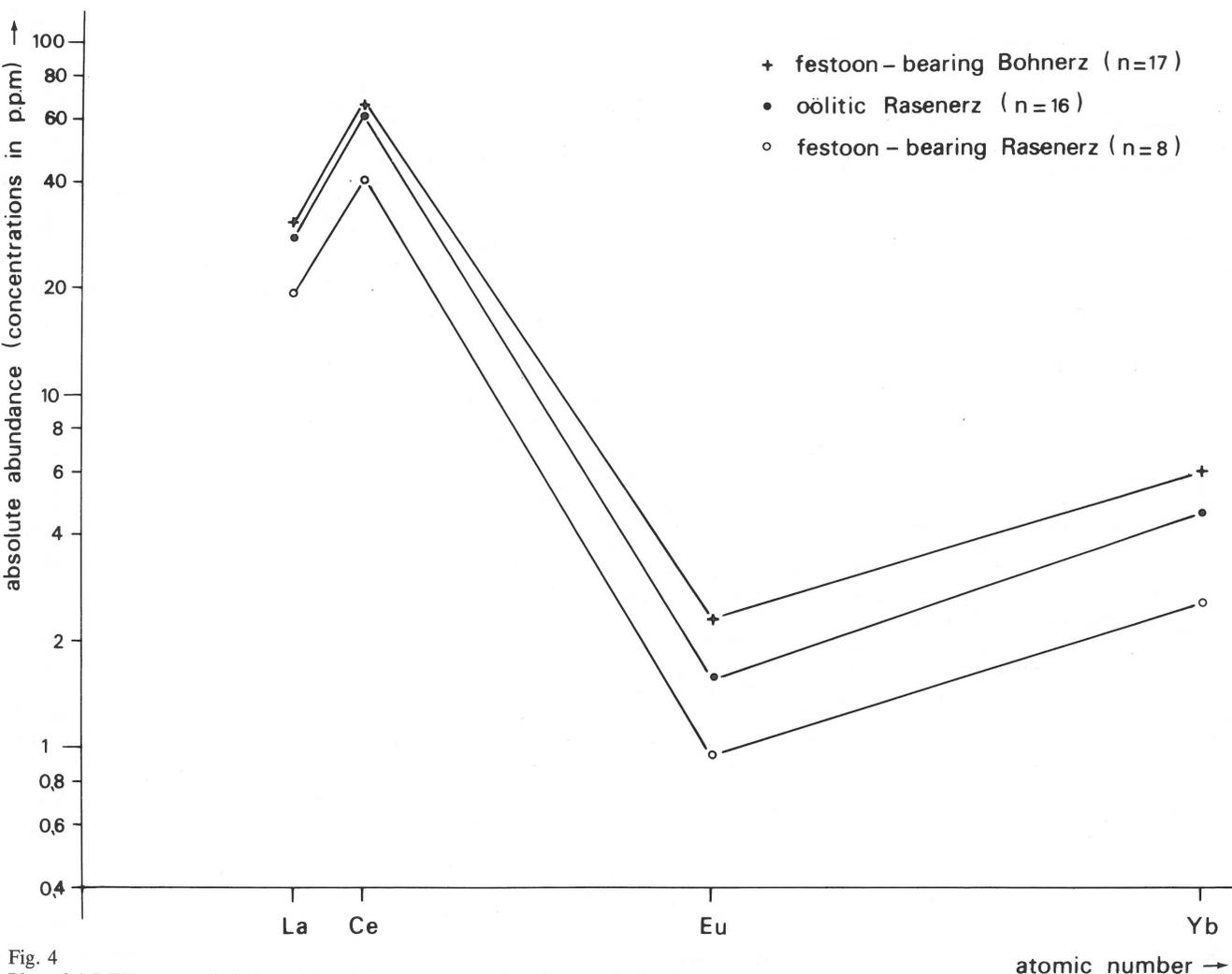


Fig. 4
Plot of 4 REE versus their respective average contents in microscopically different categories of concretions.

(1964) assumed that an increase in alkalinity of weathering solutions produces precipitation and fixation of the REE while a low pH favours their dissolution and removal.

From Table IV it is apparent that REE play an important part in producing the best combinations of 2 and 3 n.t.e. concentrations. Moreover, their absolute averages in the Bohnerz and Rasenerz classes show consistently, though not significantly, different values (Fig. 3). Also, plotting of their average abundances in the 3 texturally distinguished categories (Table III) yields clear differences, especially between the two festoon-bearing categories (Fig. 4). This suggests that if the festoon-bearing concretions are remnants of destructed surface crusts, the 'parent crusts' of the Rasenerz and Bohnerz categories concerned must have been different.

Summarizing, it appears that a statistical interpretation of no less than 13 n.t.e. concentrations is needed to discriminate between the sample populations collected from the Rasenerz and Bohnerz concretions. Further, that the oölitic texture is

only of limited value to discriminate between specimens from these populations. Finally, that textural evidence in combination with geochemical data suggest that the Rasenerz population, besides detrital relics of the cemented Minette Formation, also contains remnants of iron-rich surface crusts which, in particular in view of their REE chemistry, were produced under conditions different from those under which the Bohnerz-producing crusts originated.

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APPENDIX

The observed Fe concentrations indicate that the abundance of this element varies considerably. As iron hydroxide is a very effective sorbent of trace elements, some normalization has to be applied to the observed trace-element concentrations. When it is assumed that the trace-elements are solely or mainly associated with the iron-bearing minerals, the concentrations have to be normalized on the basis of the iron

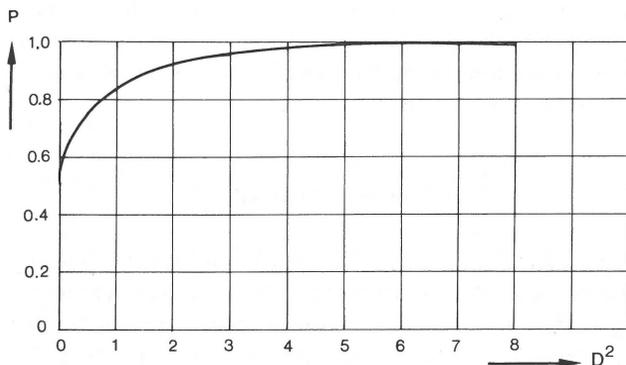


Fig. 5
The discriminating power P as a function of the Mahalanobis distance \hat{D}^2 .

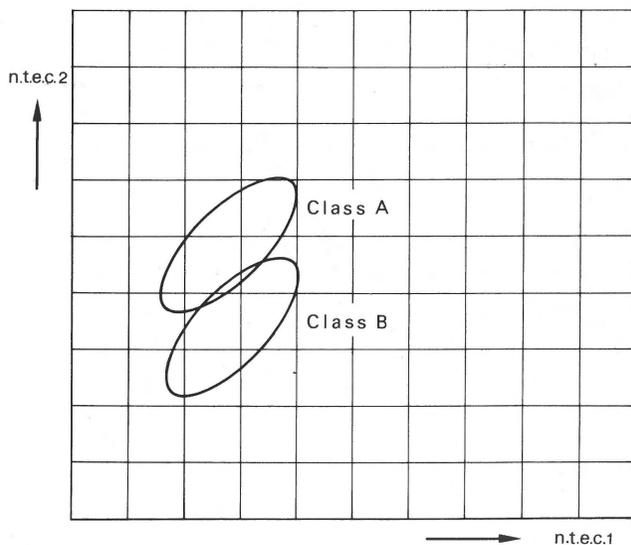


Fig. 6
Graph illustrating that a single n.t.e. concentration 1 is unsuitable to distinguish class A from class B, but may give a very good discrimination in combination with n.t.e. concentration 2.

concentration. But when these elements are part of the remaining minerals, the concentrations have to be normalized on the basis of $1 - 1.59 \times \text{Fe}$ concentrations (atomic weight of FeOOH is used). Since it is unknown a priori which assumption is valid, both normalizations have been applied.

To evaluate the discriminating ability of the normalized trace-elements (n.t.e.) concentrations, Mahalanobis' distance (\hat{D}^2) was used:

$$\hat{D}^2 = (\hat{\mu}_1 - \hat{\mu}_2)^T \hat{C}^{-1} (\hat{\mu}_1 - \hat{\mu}_2) \quad (1)$$

in which $\hat{\mu}_1$ and $\hat{\mu}_2$ are the respective estimated mean vectors in the multidimensional concentration space of the two classes of Bohnerz and Rasenerz, while \hat{C}^{-1} is the inverse of the estimated joint covariance matrix of the two classes. In general \hat{D}^2 gives a biased estimate of the true Mahalanobis distance. An unbiased estimator for the for the case of normally distributed classes is given by SCHAAFSMA (1977).

$$\hat{D}^2 = \frac{m-k-3}{m-2} \hat{D}^2 - \frac{mk}{m_1 m_2} \quad (2)$$

in which m_1 and m_2 are the sample sizes of the classes (in our case 26 for Bohnerz and 30 for Rasenerz). $m = m_1 + m_2$ while the dimensionality k equals the number of n.t.e. concentrations used in equation (1). To improve the normality of the data, the logarithms of the n.t.e. concentration values have been used.

In Fig. 5 the relation is given between the discriminating power P and \hat{D}^2 ; $P = \phi(\sqrt{\hat{D}^2})$, in which $\phi(\cdot)$ is the cumulative normal distribution. P is the probability that an arbitrary new sample is classified correctly. Mahalanobis' distance may be computed for the combined as well as for the individual n.t.e.

concentrations. It is important to notice that a single n.t.e. concentration may have very poor discriminating power but that it may be superior in combination with a second n.t.e. concentration (see Fig. 6). Two highly correlated n.t.e. concentrations may result in a much larger Mahalanobis' distance than two uncorrelated ones.

For normally distributed classes the statistical distribution of \hat{D}^2 is known and related to the non-central F-distribution. From that, the significance of the difference (i.e. the probability that the difference is caused by chance alone) between n.t.e. concentrations of the two classes, as well as a confidence interval for P, may be calculated.