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Geochemistry of Quaternary fluvial and eolian sediments in the southeastern Netherlands

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Abstract

Bulk chemical analyses of Quaternary sediments in the southeastern Netherlands show that sands from the middle terraces of the Meuse in South Limburg are significantly lower in SiO_2 and higher in almost all other analysed major and minor elements than mixed Meuse and Rhine sediments in North Limburg and adjacent areas. Within individual formations in North Limburg the Sterksel and Urk formation are characterized by relatively high Al, Fe, Mg, K and Rb and low Zr contents, the Kreftenheije Formation and Nuenen Group by low Rb and high Zr contents, whereas the Veghel Formation has both low Rb and low Zr contents.

Principal component analysis is used to assign well-correlated element groups to individual minerals. Factor 1 (65% of the total variance) is composed of Fe, Al, Mg, K, As, Sc, Cs, Rb, Th and the LREE and is interpreted as a muscovite/goethite factor. Factor 2 (13% of the total variance), is dominated by Na, Ca, Al, Mg, K, Th and Sr and is interpreted as a feldspar factor. Factor 3 (7% of the total variance), is composed of Zr, Nb, Cr, Ti, V and Lu, elements concentrated in some stable heavy minerals. High levels of Factor 1 elements in South-Limburg sands are interpreted to be due to admixture of large amounts of shale fragments, muscovite and goethite particles. Depletion of Rb in eolian sands is interpreted to differential winnowing of micas during deflation. The concentration of many elements is also strongly grain-size dependent. Geochemical analysis is shown to provide much additional information not normally detected in routine petrographic analysis.

Introduction

Characterization of Quaternary fluvial and eolian formations in the Netherlands up to now relied mainly upon grain size and heavy mineral composition and gravel counts (Doppert et al. 1975). This paper shows that bulk geochemistry of Quaternary sediments is an additional useful tool in stratigraphy, as it can provide information as to provenance, sorting and postdepositional processes, complementary to that obtained by classical sedimentary petrography (cf. Ronov et al. 1965, Kroonenberg et al. 1988).

Quaternary fluvial and eolian deposits of known lithostratigraphical position have been sampled in various sand pits in the SE Netherlands. The sedimentary petrography of fluvial deposits of the rivers Meuse and Rhine and derivative eolian deposits

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from this area has been studied extensively (Edelman 1933, Van Baren 1934, Van Straaten 1946, Zonneveld 1947, 1949, 1956, 1958, Van Andel 1950, Bisdom et al. 1978, Riezebos et al. 1978).

The area studied comprises two main regions: the South Limburg area, in which pure Meuse deposits occur in river terraces ranging from 20 to 170 m above present river level, and North Limburg, a lowland area in which Meuse deposits are mixed with Rhine deposits (Fig. 1). Low Late Weichselian terraces are present here (Miedema 1987), but the majority of Pleistocene fluvial formations are present only at some depth in the subsoil. The two regions are separated by the Feldbiss fault, which at the same time marks a terrace crossing. The formations studied are the Valkenburg, St. Geertruid and Caberg Deposits in South Limburg terraces, and the Tegelen, Sterksel, Urk, Veghel and Kreftenheije Formations and the Nuenen Group in North Limburg and adjacent areas. Sample locations are indicated on Fig. 1. The stratigraphic position of each formation is indicated in Fig. 2. Details about the geology are given in Zagwijn & Van Staalduinen (1975), Zagwijn (1985) and the explanatory notes to the 1:50,000 geological maps of sheets Tiel West 39W, Tiel East 39O, Venlo 52W and Heerlen 62W (Van den Toorn 1967, Kuyl 1980, Verbraeck 1984).

Materials and methods

At each sample point several samples of different grain size were taken, as previous research had indicated the importance of grain size for geochemistry of bulk sediments (Moura & Kroonenberg 1988, Kroonenberg et al. 1988, cf. also Strakhov 1969). The samples were air-dried and particles >2 mm were removed by sieving. The samples were split into two parts by means of a sample splitter. From one part free iron, calcium carbonate and organic matter was removed with standard methods. Also the fraction <16 μm was removed in order to be able to compare geochemistry with optically determinable mineralogy. The remaining sand and coarse silt fraction was then ground in a tungsten carbide mill, pre-ignited and smelt with lithium borate to a glass bead. In each bead the amounts of the major elements Si, Ti, Al, Fe, Mg, Mn, Ca, Na, K, and P and of the trace elements V, Cr, Ni, Cu, Ga, Rb, Sr, Zr, Nb, Ba, La and Pb were determined using X-ray fluorescence spectrometry (XRFS) on a Philips PW 1404 assembly. The system was calibrated using USGS geochemical standards as listed by Abbey (1980, p. 16). Analytical results summing <98% or >102% were repeated until a sum within these limits was obtained. Moreover, 50 samples were analysed at ECN at Petten using Instrumental Neutron Activation Analysis (INAA) for the elements Na, K, Fe, Zn, Co, Rb, Ba, Cr, Cs, Th, U, Mo, As, Sb, W, Ta, Hf, Sc and the REE La, Ce, Nd, Sm, Eu, Tb, Yb, and Lu. Those elements which were analysed by both methods showed a good correspondence, ex-

Table 1. Sample sites

Formation	Sample site and site number on Fig. 1	Number of samples
South-Limburg		
Valkenburg	Nekami (1)	2
St. Geertruid	Savelsbos (2)	4
Caberg	Belvédère (3)	5
North-Limburg		
Tegelen Fmn.	Tegelen (4)	2
Kedichem Fmn.	Maalbeek (5)	2
Sterksel Fmn.	Tegelen (4)	11
	Maalbeek (5)	3
	Fransche Kamp (6)	3
Urk Fmn.	Driessen (7)	7
	Bluijssen (8)	11
(Urk A)	Fransche Kamp (6)	2
(Urk B)	Fransche Kamp (6)	6
(Urk C)	Fransche Kamp (6)	2
Veghel Fmn.	Meijel (9)	5
Kreftenheije F.	Geijsteren (10)	2
	Bergerheide (11)	10
	Bergharen (12)	1
	Grubbenvorst (13)	2
Nuenen Groep	Grubbenvorst (13)	11
	Meijel (9)	1
Drente	Molenhoek (14)	4
	Fransche Kamp (6)	1
Twente	Bergerheide (11)	1
		—
Total		98

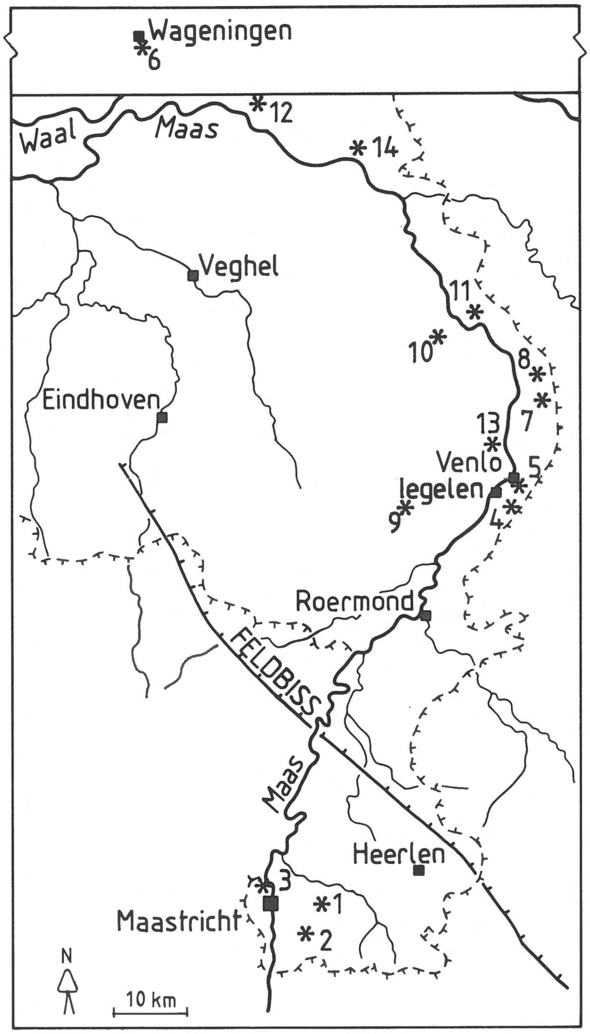

Fig. 1. Sample locations; for significance of numbers refer to Table 1.

cept for La-XRFS which gave unreliable results. W, Ta and Co were not considered in the calculations because contamination during milling was suspected. Also the data for Lu may be unreliable. It should be noted that many elements showed contents below the detection limit of specific elements.

Results

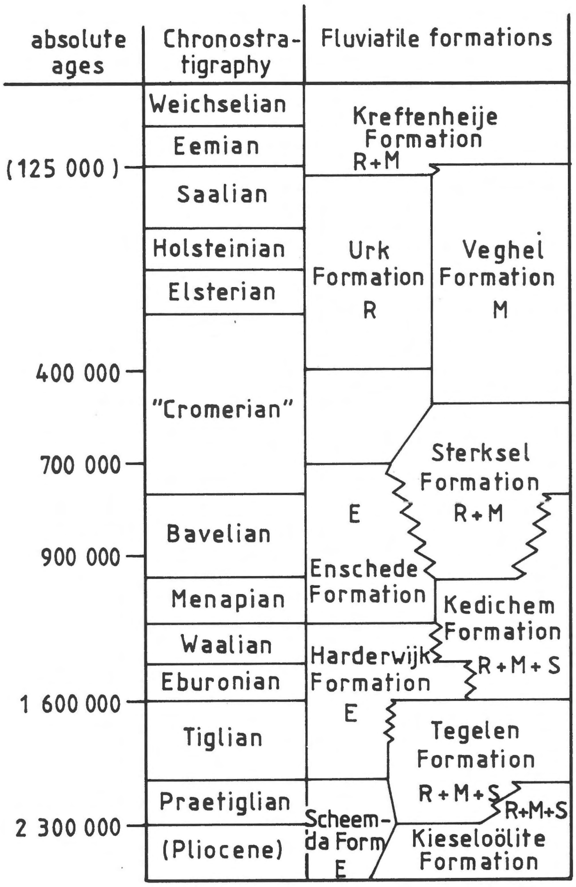

Fig. 2. Stratigraphical position of studied formations (after Zagwijn, 1985).

From the analytical data (Table 2) it is clear that all sandy sediments have high contents of SiO_2. South Limburg sand samples appear to have SiO_2 contents below 90%, all other ones above 90%. The lower SiO_2 content in South Limburg samples is compensated by higher contents of almost all other elements. A discriminant analysis using SiO_2 as a predictor classifies 100% of the samples in the correct group. That this is not simply due to different amounts of quartz but involves other minerals such as feldspars and ferromagnesians as well is shown by a plot of Na + K/Ti + Fe + Mg, which gives an excellent separation of the two populations (Fig. 3).

Perusal of the analytical data for North Limburg and adjacent areas per formation (Table 3) shows that the Sterksel and Urk formation are characterized by relatively high Al, Fe, Mg, K and Rb and low Zr contents, the Kreftenheije Formation and

Nuenen Group by low Rb and high Zr contents, whereas the Veghel Formation has both low Rb and low Zr contents. Of the other formations too few samples are available to draw any conclusions. A discriminant analysis using Rb and Zr as predictors classifies 85.4% of the samples correctly in the Sterksel + Urk group and 77.1% of the samples in the Kreftenheije + Nuenen + Veghel Group.

Statistical analysis of the data

Statistical analysis of the data, recalculated on a water-free base, has been carried out using the SPSS PC+ and FACTOR software packages. A correlation matrix for the elements analysed by XRFS show high correlations for many elements at $p = 0.001$. Some element associations that emerge are:

1. Good positive correlations (correlation coefficients (c.c.) commonly > 0.7) between Al, Fe, Mg, P, K, Rb, Sr, Ba, V, Ti, all having a good negative correlation with Si (c.c. commonly > 0.7; for the sake of brevity all major elements are stated as such, although they have been determined as weight percentages of the oxides).
2. Very strong positive correlation between Zr and Nb (c.c. > 0.9), with little correlation with other elements.
3. Strong positive correlations (c.c. > 0.8) between Na, Ca, and to some extent (c.c. > 0.5) with Sr, P, Al and Ga.
4. Good positive correlations between Ni, Al, Fe, Mn, Mg, P, Cu, Ga (c.c. > 0.7) and to some extent (c.c. > 0.6) Rb.

The matrix is not given here because of its size; full data are given by Moura & Kroonenberg (1988b).

Factor analysis

The data were examined using Principal Component Analysis (PCA) to attempt to identify clusters or associations within the data set (Krumbein & Graybill 1965, Jöreskog et al. 1976). This was carried out using the FACTOR routine of the SPSS-PC+ package (Norusis 1986). By application of PCA the complex data set is simplified by creating new variables or factors each representing a cluster of interrelated variables within the data set. Using major elements only, certain correlations may be biased as a result of the closed sum problem. However, trace elements do not give a closed sum, and still show the same correlations with or without major elements, suggesting that the closed sum problem does not seriously affect the correlations found.

The results of the factor analysis are summarized

Table 2. Chemical composition of Pleistocene sands from South and North-Limburg (major elements in wt %, minor elements in mg/kg; Loss On Ignition omitted). 1: average; 2: standard deviation; n: number of analysis. *: INAA analyses, others XRFS

Element	South-Limburg (n = 11)		North-Limburg (n = 72)	
	1.	2.	1.	2.
SiO_2	88.39	3.88	94.61	2.88
TiO_2	0.26	0.06	0.09	0.08
Al_2O_3	5.25	1.28	2.44	1.57
Fe_2O_3	2.34	0.88	0.32	0.29
MnO	0.01	0.01	0.00	0.00
MgO	0.31	0.08	0.13	0.11
Na_2O	0.18	0.08	0.22	0.36
K_2O	1.71	0.44	0.89	0.46
P_2O_5	0.07	0.02	0.01	0.01
V	47	7	23	10
Cr	16	8	10	3
Ni	12	6	3	3
Cu	9	4	3	1
Ga	7	3	4	2
Rb	63	25	15	13
Sr	61	11	40	14
Zr	87	103	64	109
Nb	10	5	8	5
Ba	327	70	188	84
Pb	12	4	8	3
(INAA)	(n = 6)		(n = 34)	
As*	8.6	3.8	1.7	0.9
Cs*	3.2	0.3	1.1	0.7
Sc*	4.7	1.2	1.9	1.4
Th*	4.1	0.7	2.3	1.4
REE (sum)*	82		29	

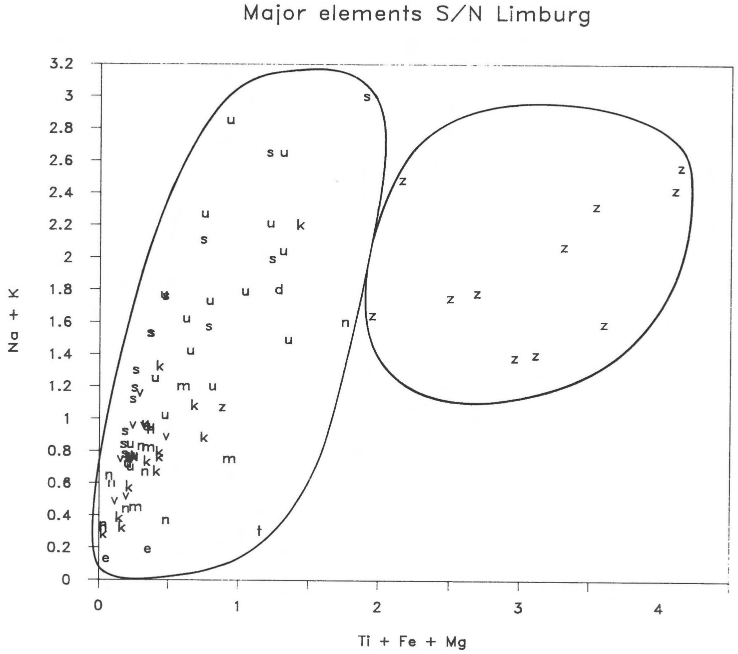

Fig. 3. **Individuality of South and North-Limburg samples according to K + Na/Ti + Mg + Fe plot (based on weight percentages of the oxides). Data points indicated by Formation letters: z = South-Limburg, s = Sterksel, u = Urk, k = Kreftenheije, n = Nuenen, v = Veghel, (e = Kedichem, m = Malden, samples not discussed in this paper).**

in Table 4. After varimax rotation, three factors together represent 82.1% of the total variance.

- Factor 1, which accounts for 65% of the total variance, is composed of the major elements Fe, Al, Mg and K and the trace elements As, Sc, Cs, Sm, Ce, Rb, La and Th, all with positive loadings. Si has a strongly negative loading within this factor.
- Factor 2 (13% of the total variance), is dominated by Na, Ca, Al, Mg, Th and Sr. As in factor 1, the element Si presents a negative loading.
- Factor 3 (7% of the total variance), explains most of the variance of Zr, Nb, Cr, Ti, V and Lu.

Factor analysis excluding Si gives similar results, indicating that high loadings of elements in factor 1 and 2 are not simply the result of dilution by quartz. Factor score plots of the individual samples, especially using F2 and F3, give a good separation into three clusters: a South Limburg group, a Sterksel-Urk Group and a Nuenen-Kreftenheye-Veghel group (Moura & Kroonenberg 1988b). Cluster analysis gave similar results.

Discussion

The fact that several elements show high correlations with each other, and occur together in the factors emerging from PCA, suggest that they occur together in one or more sand minerals.

The site of the elements in the minerals that constitute the studied sands can be determined in various ways: (1) by matching groups of highly correlated elements with published average chemical compositions of minerals known to occur in the sediments; (2) by statistical correlation of element analyses with mineral countings of the same samples; and (3) by separating individual mineral species, analysing them chemically and multiplying them with their abundance in the sands as determined by mineral countings; this is the most independent check and comes closest to normative compositions as used in igneous petrology. Our approach has been restricted up to now to alternative (1).

Published mineral countings show that next to quartz also feldspars, micas, from the heavy minerals especially garnet, epidote, hornblende, zircon, rutile, tourmaline, the Al_2O_5 silicates and staurolite, and also opaque minerals and rock fragments are common constituents of Meuse and Rhine sands (Edelman 1933, Van Baren 1934, Zonneveld 1947, Van Andel 1950, Riezebos 1971). The bulk percentages of these minerals in the sediment are usually unknown as the authors only state the composition of specific fractions (heavy, light etc.). Therefore, these data are only helpful to establish in a qualitative way which elements could be present.

Most elements are present in most minerals, but in very different proportions. Often certain elements show preference for specific minerals because of matching ionic radii and charge. This is of course not a result of fractionating processes in the sediment itself, but in the igneous or metamorphic source rocks from which the sands are derived. Nevertheless the preference of certain elements for specific minerals ('indicator elements') can be used to trace back the mineralogical composition from the geochemistry.

Si in quartz

The statistical analyses show that both Factor 1 and Factor 2 elements have a strong negative correlation with Si. This would be explained if one as-

Table 3. Chemical composition of sands from different formations in North-Limburg. n = number of analyses. Major elements in wt %, minor elements in mg/kg) L.O.I omitted

	Urk n = 24	Sterksel n = 14	Kreftenheije n = 13	Nuenen n = 13	Veghel n = 8
SiO_2	93.78	93.76	95.98	95.57	94.78
TiO_2	0.07	0.09	0.06	0.09	0.03
Al_2O_3	3.05	3.43	1.95	1.52	1.74
Fe_2O_3	0.39	0.34	0.28	0.22	0.14
MgO	0.16	0.17	0.10	0.08	0.08
CaO	0.09	0.08	0.10	0.02	0.01
Na_2O	0.28	0.27	0.32	0.11	0.05
K_2O	1.13	1.33	0.52	0.55	0.77
P_2O_5	0.02	0.02	0.01	0.01	0.01
V	23	21	22	27	19
Cr	11	10	10	10	10
Ni	3	5	3	3	2
Cu	3	3	3	3	3
Ga	4	5	4	4	3
Rb	20	28	10	4	10
Sr	45	52	36	30	33
Zr	29	28	80	183	34
Nb	7	7	8	13	7
La	6	7	7	6	6
Pb	10	9	8	8	9
INAA	(n = 13)	(n = 6)	(n = 5)	(n = 7)	(n = 3)
As	3.50	2.26	0.87	1.31	0.45
Cs	1.95	1.29	1.15	0.51	0.39
Sc	3.67	2.35	0.67	1.34	0.97
Th	3.31	2.19	1.98	1.31	1.67
REE (sum)	58	29	17	16	18

sumes that much variability is simply the result of mixing in varying proportions of quartz with a Factor 1 non-quartz mineral and a Factor 2 non-quartz mineral. However, it is unlikely that all Factor 1 elements occur in one single mineral species. Moreover, both the Na + K/Ti + Mg + Fe plot (Fig. 3) and PCA excluding quartz show that dilution by quartz can by no means explain all variability. Unraveling the relation between Factor 1 elements and mineralogy has largely proceeded by trial and error.

K, Rb and Cs in micas

Rb and Cs, and to a lesser extent also Ba can replace K in K-bearing minerals such as K-feldspar, muscovite, biotite and clay minerals (notably illite). This is obviously the reason for their joint occurrence in Factor 1. However, Rb and Cs are much more fractionated by micas (and clay minerals) than by any other K-bearing mineral (Wedepohl 1978). Furthermore they are not readily accommodated in other non-K minerals, so that Rb and Cs contents will strongly depend on the mica and clay content of the sediment. This was also demonstrated in our previous studies in France (Kroonenberg et al. 1988) and Colombia (Moura & Kroonenberg 1988a).

Table 4. Loadings of each variable in the first three principal factors. Loadings < 0.550 are not quoted

Factor 1	Factor 2	Factor 3
Fe (0.780)	Na (0.885)	Ti (0.666)
K (0.675)	Ca (0.853)	
Mg (0.635)	Al (0.696)	
Al (0.621)	Mg (0.653)	
	K (0.594)	
As (0.915)	Sr (0.813)	Nb (0.969)
Sc (0.860)	Th (0.652)	Zr (0.967)
Cs (0.810)		Cr (0.753)
Nd (0.794)		V (0.602)
Sm (0.741)		Lu (0.564)
Ce (0.732)		
La (0.728)		
Rb (0.713)		
Si (−0.573)	Si (−0.663)	

Micas, by their platy nature, settle much more slowly than spherical particles of similar density. Therefore, micas are often concentrated in the finer grain size fractions. This was the main reason for the increasing Rb content with decreasing grain size below 500 m in the Allier sands (Kroonenberg et al. 1988). In that case there was a statistically very significant negative correlation between median and Rb content. An attempt to show such correlations in the present data set was unsuccessful.

However, if median and Rb content are plotted for each formation separately (Fig. 4a–c) it appears that

1. South Limburg sands have the highest Rb contents, but because of the limited spread in median most data points cluster together. Moreover, there are two anomalous fine-grained samples with low Rb contents. Fractionated mineralogical analysis of three South Limburg terrace sands by Riezebos (1971, Fig. 3) indicate higher mica contents in the finer fractions.
2. Sterksel sands show an excellent negative correlation between Rb and median at an overall lower level than South Limburg sands.
3. Urk sands show a larger spread of data points, but remains a recognizable cluster at a generally still slightly lower level than the Sterksel sands.
4. Kreftenheije and Veghel sands are indistinguishable from each other as to their Rb/median ratios, but are generally poorer in Rb than the South Limburg, Sterksel and Urk sands.
5. The Nuenen sands do not contain enough Rb for statistical analysis (except for one highly anomalous loamy sample) and hence are virtually mica free. These are the only purely eolian sands that have been included into this study.

It appears, that Rb contents of individual samples of a specific grain size will not be tell-tale enough as a rule for assigning them to one formation or another, except in the case of South Limburg. The Rb contents of a series of samples of different grain sizes from a single lithological unit, however, can help to classify it in one or another formation, at least in the area now studied.

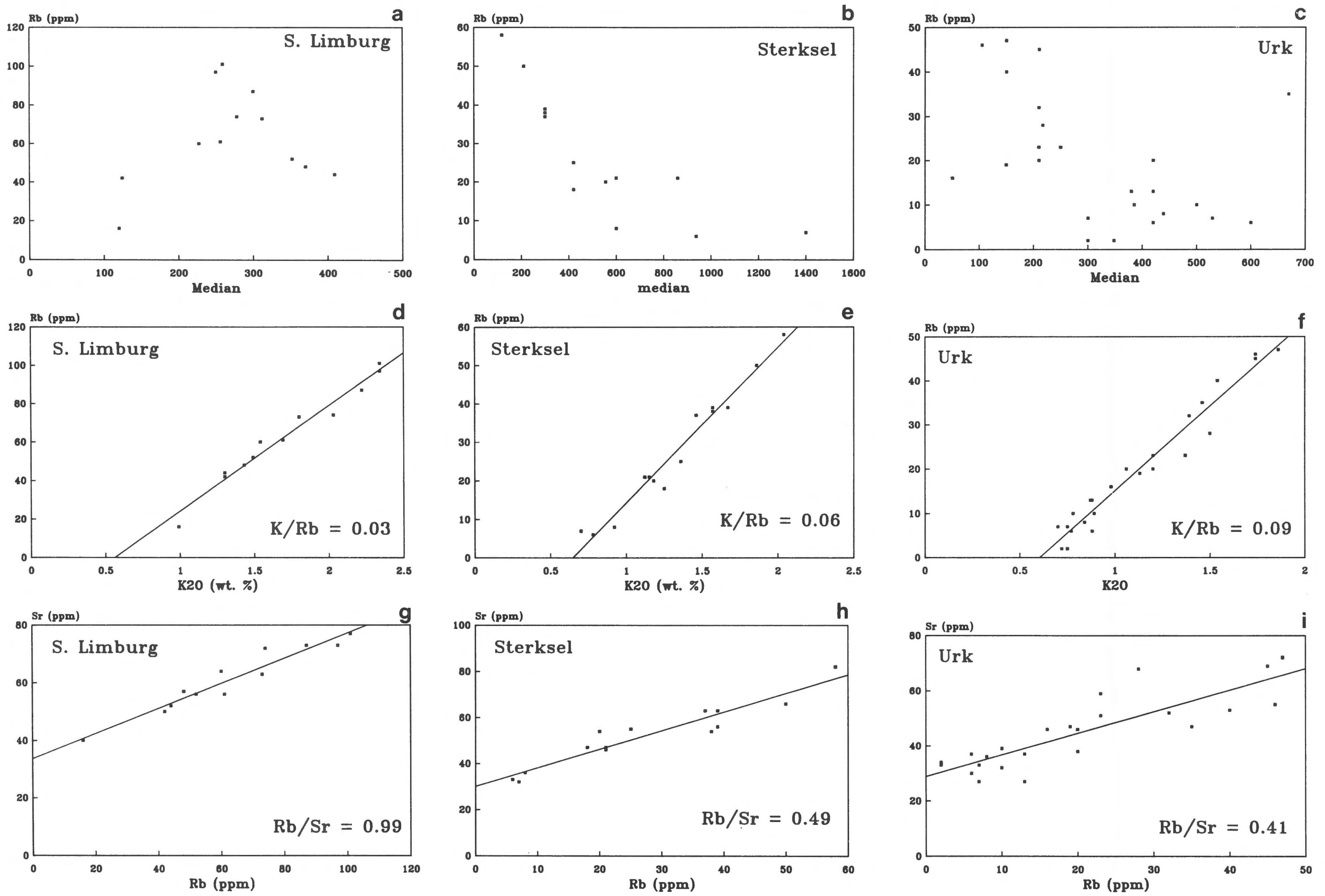

Fig. 4a–c. Rb-median plots, *d–f*: K/Rb plots and *g–i* Rb/Sr plots of South-Limburg, Sterksel and Urk sands. Note different scales! Other formations not plotted because of wide scatter or low values.

K, Na, Rb, Sr in feldspars

K is an important element both in K-feldspar and in micas. Because Rb is more strongly fractionated in micas than in K-feldspar, the K/Rb ratio (in weight percentages) can give clues whether important variations in K-feldspar/mica ratios exist. South Limburg sands have comparatively low K/Rb ratios suggesting high mica contents (Fig. 4d). In the other formations K/Rb is higher, suggesting higher K-feldspar/mica ratios than in the South Limburg sands. The Nuenen sands are virtually Rb-free; most K will be bound in K-feldspar here.

Albite (i.e. as the albite endmember in plagioclase) is the only Na-rich mineral known to occur in the sands of the southeastern Netherlands. Ca occurs in plagioclase, but also in the heavy mineral epidote. Sr generally replaces Ca. The joint occurrence of K, Na, Ca, Sr and Al in factor 2 suggests that this is essentially a feldspar factor. The presence of Mg and Th in this factor is less well explained (see below).

Also K/Na ratios show a crude linear correlation, though with a considerable spread of data points (Fig. 5a–c). K/Na data of Urk formation sands seem to show two populations: one Na (and Sr) rich population from the Fransche Kamp sandpit, and one Na and Sr poor population from the other sites sampled (Table 5). The Fransche Kamp samples apparently are richer in plagioclase. This might be a reflexion of volcanic influence in Rhine sediments, as these samples are also very augite-rich.

Fe and As in goethite

One of the obvious ways in which sediments can differ from each other is in the content of heavy minerals. For a limited number of samples the amount (by weight) of heavy minerals has been determined. South-Limburg samples had significantly higher amounts of heavy minerals, and show a positive linear correlation between heavy mineral content and especially Fe and As abundances (Fig. 5g), both elements showing high loadings in Factor 1.

Table 5. Element ratios (wt %) for different sands of the Urk Formation

Sand pit	K/Rb	Rb/Sr	K/Na	K/Sr	N
Driessen, Buijssen	438	0.67	5.51	292	9
Fransche Kamp	210	0.90	3.11	186	4

Riezebos (1971) and Bisdom et al. (1978) have shown that next to light and translucent heavy minerals, goethite (including lepidocrocite) is an important constituent in the middle terraces in South Limburg. Also in the low terraces and derivative eolian deposits in the middle stretch of the Meuse around Roermond goethite particles amount to about half the heavy fraction according to Riezebos et al. (1978). Ti-Fe oxides (rutile, ilmenite, leucoxene) were microscopically shown to occur intergrown with the goethite in most particles. The goethite particles were thought to have derived from Jurassic goethite bearing rocks (i.e. the Minette oölitic iron ore formation) in Lotharingen (Riezebos 1971, Riezebos et al. 1978).

We made a comparison between our data and geochemical data for two typical weathering products of such ores (Rasenerz and Bohnerz) in Luxemburg, presented by Riezebos et al. (1981) (Table 6). Both ore types are geochemically very similar. They contain between 24.6 and 61 weight % Fe averaging 46.8% Fe for Rasenerz and 43.0% Fe for Bohnerz. If the elements which show high correlation with iron occur in goethite particles as well, their ratio to Fe should be similar to those in the Rasenerz and Bohnerz.

As the As/0.01Fe ratio is of the same order of magnitude in the Limburg sands and in the goethite iron ores, most As in the sands may be considered to be bound in goethite particles. It is to be stressed that our data refer to individual goethite particles alone, as coatings and other forms of secondary iron were removed during the pretreatment of the samples. The element As is also known to occur in high concentrations in bog iron ore in the Netherlands (Edelman 1984, p. 41, Van Pruissen & Zuurdeeg 1988). However, goethite iron ores apparently do not fractionate the other elements indicated in Table 6. These elements occur in much higher concentrations in the sands than can be accounted for by the presence of goethite particles in the

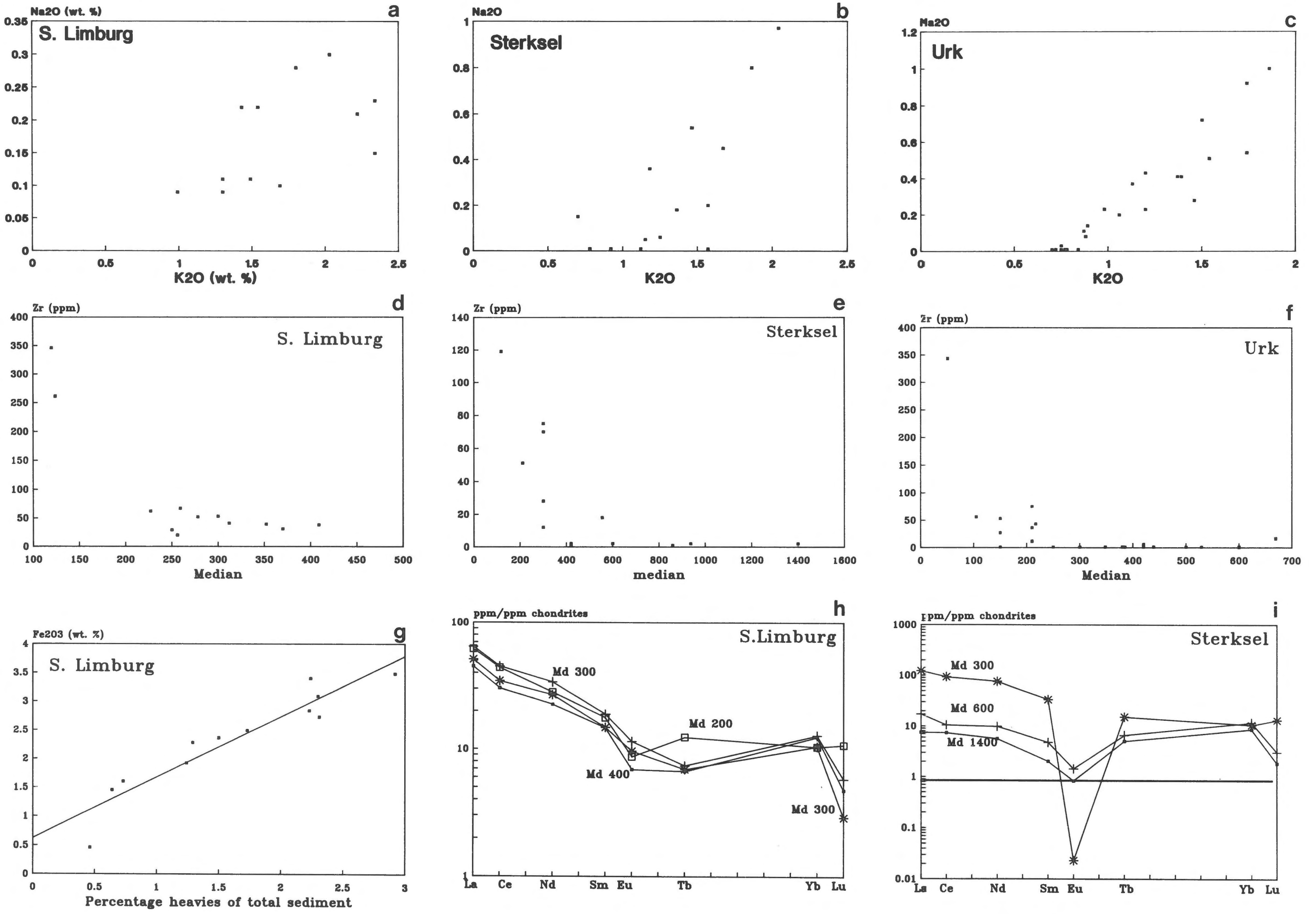

Fig. 5a–c. K/Na plots, *d–f* Zr-median plots for South Limburg, Sterksel and Urk sands; *g*: ratio Fe content/percentage of heavy minerals in South-Limburg sands; *h–i*: REE spectra South-Limburg and Sterksel sands. Md = median.

sediment. Therefore these elements must be bound to other minerals.

The fact that Fe and As, though occurring in a component of the heavy fraction, do not show up in PCA factor 3 determined mainly of minerals of the heavy fraction, may be explained by the fact that goethite particles unlike zircon etc. are not restricted to any particular grain size, and hence will be found in all grain size classes.

Ti, Cr, Zr, Nb in zircon, rutile, opaques

Factor 3 with high loadings for elements Ti, Cr, V, Zr, Nb and Lu probably comprises various minerals, mostly belonging to the heavy fraction, Zr in zircon as a separate mineral, Nb possibly replacing Ti in rutile, Cr, Ti and V possibly in opaques (see above). Concentration of heavy minerals by density sorting could explain their occurrence in a separate factor. Furthermore, many heavy minerals are supplied only in restricted grain sizes in the sediment. In the statistical analysis no element shows good correlations with median, but bivariate plots of Zr against median (Fig. 5d–f) show that Zr is concentrated in finer fractions, obviously because zircon is supplied only in small grains as a rule. Plots of Nb give similar results. The fact that this is not apparent from the statistics is due to the fact that the individual formations have greatly differing amounts of zircon. Zircon and rutile are both very stable minerals, which might explain the close association of Zr and Nb.

Table 6. Comparison of selected element ratios (wt %) of Limburg sands with Luxemburg goethite iron ores

	Limburg sands	Rasenerz*	Bohnerz*
Average As/0.01Fe	0.07	0.09	0.12
Average Cr/0.01Fe	0.55	0.03	0.03
Average La/0.01Fe	0.23	0.005	0.007
Average Ce/0.01Fe	0.41	0.012	0.015
Average Sc/0.01Fe	0.06	0.007	0.005
Average Th/0.01Fe	0.06	0.003	0.003

* Data calculated from Table II of Riezebos et al. (1981).

REE in micas and heavy minerals

It is customary to express REE contents not as absolute values, but as a ratio to REE contents of chondritic meteorites. The rationale for such a procedure does not need to detain us here, but is discussed extensively by Taylor & McLennan (1985). REE spectra for South Limburg sands and Sterksel sands are shown in Fig. 5h, i. Most samples of the Urk, Kreftenheije, Veghel and Nuenen sands have too low REE values for most analysed elements to make reliable spectra. The spectra show that both sample groups are strongly enriched (50–125 times for La) in the light rare earth elements (LREE) with respect to chondritic abundances, and slightly enriched (2–10 times) for the heavy rare earth elements (HREE). Some curves show a dip for Eu and/or higher Yb abundances. Fine-grained samples have higher REE abundances than coarser grained ones.

We will try to establish in which sand minerals the REE are concentrated using the REE spectra of common rock forming minerals and common heavy minerals published by Taylor & McLennan (1985, p. 36, 38). Quartz contains little REE, and feldspars are usually slightly depleted in REE with respect to chondritic abundance, except for Eu. Enrichment as noted in the sediments cannot be related to quartz or feldspar content, therefore. This is probably the reason why Edelman (1984) failed to show a correlation between REE contents and feldspar content in Dutch surface soils.

Hornblende and augite show also enrichment between 10 and 100 times chondritic levels and Eu-anomalies, but they are equally or slightly more enriched in HREE than in LREE. This holds even stronger for garnet and zircon. Our data show that in the statistical analysis the heavy rare earth element Lu is included into the same factor as Ti, V, Zr, and Nb (Table 4), suggesting some influence of heavy minerals. However, as Lu analysis with INAA may be unreliable, this conclusion should be taken with caution. The overall chondrite-normalized pattern of the sands is very different, however. The only heavy minerals which show comparable spectra to those of the sands (LREE > HREE) are epidote and tourmaline, though REE enrichment in tourmaline falls slightly below values for the sands. Epidote (and saussurite) comprise about 10–20% of the heavy fraction of Meuse sediments (cf. Riezebos 1971). As heavy mineral fraction of the sands themselves rarely surpasses 1–2%, epidote contents of the bulk sediment cannot be higher than 0.4%. Tourmaline contents may be higher, especially in somewhat coarser fractions (210–400 μm), up to 1.5%, but probably still too low to greatly contribute to REE of the sands.

It is more probable, that REE are concentrated in micas, especially muscovite, a common constituent in many Dutch sands. Muscovites are strongly enriched with respect to chondrite (>100 times for La, >10 times for HREE), and show a pronounced negative Eu-anomaly. Eu-levels are still higher than the average Eu abundances in feldspar, so there is little influence of the latter mineral on the REE spectra. At last muscovite has similar chondrite-normalized patterns and abundance levels as most clayey sediments (Taylor & McLennan 1985), which also consist of phyllosilicates predominantly. Other phyllosilicates such as biotite are probably of minor importance as biotite is a rare mineral in Dutch sands. The observed increase of REE contents with decreasing grain size is in harmony with the concentration of mica in the finer fractions due to sorting, as borne out by the Rb contents (see above).

Importance of rock fragments

Most elements discussed can be assigned to one or two specific minerals because they are fractionated more by one mineral than by another. Other elements not discussed so far, such as Mg, Ca and Al, are more cosmopolitan. Nevertheless, the analysis shows that elements contained in minerals with very different hydraulic behaviour, such as goethite and muscovite, are lumped together by Principal Component Analysis in a single factor 1.

A plausible explanation for this phenomenon is that many of these minerals do not occur singly, but together in rock fragments. Van Baren (1934) shows that shale fragments may occupy up to 25% of the total sediment in South Limburg terrace sands. North of Roermond the amount of shale particles suddenly drops sharply. Part of the 'composite particles' in the studies by Bisdom et al. (1978) and Riezebos et al. (1978) are also rock fragments, but as they studied only composite particles in the heavy fraction, they may have overlooked the importance of rock fragments in the light fraction. This fits very well into the large compositional differences found between these two regions. Chlorite, a common constituent of shales, may well explain the good correlation with Mg, although the presence of this mineral could not be proved as yet with the help of an indicator element. If this assumption is correct, than our conclusion should be that 60% of the variability of the geochemistry is due to a component not normally studied in routine sedimentary petrography.

Origin of the variability in sand geochemistry

The geochemical and mineralogical composition of sands is dependent upon provenance, sorting and wear during transport, and postdepositional weathering and diagenesis. The effect of the latter two processes has not been studied in this project. We will discuss the influence of sorting processes before proceeding to the importance of provenance and the usefulness of this method for stratigraphic purposes.

Fluvial and eolian sorting

Fluvial transport of sands can bring about sorting of different mineral grains because of differences in density and shape and differences in the size they are supplied to the sediment. Heavy minerals can be concentrated or depleted both because of their greater density and because they are usually restricted to the finer sand fractions. Micas, because of their platy shape settle slower than round grains of similar density, and are therefore also concentrated in finer fractions. The higher Rb, REE and Zr contents in the finer-grained samples due to concentration of muscovite and zircon have already been discussed above.

It is striking that the fluvial sands are much richer in Rb (mica) than the purely eolian Nuenen Group sands. It is conceivable that during deflation of fluvial sands micas are winnowed and transported in suspension, while equant sand grains are transported by saltation. In this way eolian sands are depleted in mica (cf. Pettijohn et al. 1972, p. 513). It is an old field rule among Dutch Quaternary geologists that eolian sands are poor in mica (Maarleveld, pers. comm. 1989). The complementary eolian sediments deposited from suspension, i.e. loesses, should be enriched accordingly. The Kreftenheije Formation sands, though of fluvial origin, may have reworked a lot of eolian sands that have been deposited from the Saalian glacial period onwards.

Provenance

The geochemical data and the interpretations presented here indicate that at least two fundamentally different populations of sand samples are present, a South-Limburg one and a North-Limburg one. Our data therefore confirm the individuality of the South-Limburg petrographical provinces distinguished by Edelman (1933). Doppert et al. (1975) included the deposits of Caberg and Rothem terraces of the Meuse in South-Limburg into the Veghel Formation and those of the Valkenburg terrace to the Sterksel Formation. From a geochemical point of view, however, the studied South-Limburg sands form a group of their own, and should be given a separate lithostratigraphical designation.

Our data suggest that the geochemical differences between South and North-Limburg are due mainly to differences in the content of shale fragments (cf. Van Baren 1934) and of goethite particles. The shale fragments reflect strong river incision in the hinterland due to Late Cenozoic uplift of the Ardennes massif (Van Baren 1934). The goethite particles may proceed from Jurassic oölitic iron ore in northern France (Riezebos 1971). Why South-Limburg sands are so much richer in these components than North-Limburg ones, remains to be investigated. We speculate that the Rhine deposits with which the Meuse sediments were mixed in North-Limburg are much richer in quartz, possibly proceeding from the vast expanses of Tertiary quartz sands in the lower course of the Rhine.

The South-Limburg sands are generally considered as a 'poor' mineral province, because of the predominance of stable heavy minerals in them. Our data show exactly the opposite: almost all elements are present in higher abundances in South-Limburg sands than in North-Limburg sands. The reason for this paradox is clear: shale fragments, muscovite and goethite are not normally analysed in routine sedimentary petrographical characterization of sands. As these components explain 60% of the geochemical variability of the bulk sediments, there is still a rich potential for this technique in provenance studies.

Conclusion

It appears to be possible on the basis of general knowledge on mineral composition to attribute specific element associations to specific minerals. Factor 1 probably records the admixture of muscovite- and goethite-rich shale fragments and goethite fragments with quartz, Factor 2 the admixture of feldspars, and Factor 3 the stable heavy minerals zircon, rutile, and Ti-bearing opaques. This shows that most variability is due to minerals and rock fragments not normally studied in routine sedimentary petrology. On the other hand, important heavy minerals consisting of major elements mainly, such as sillimanite, kyanite, andalusite, staurolite, garnet, epidote and hornblende, could not be singled out geochemically as yet. Therefore bulk geochemical analysis of sands is a useful technique complementary to heavy mineral analysis, but cannot replace it. Chemical studies of concentrates of mineral species from the studied sands are being carried out at present, in order to obtain a closer match between geochemistry and mineralogy.

The origin of the geochemical variability is due to (1) grain size effects, related to sorting of specific minerals such as micas and opaques and availability of specific minerals in restricted grain sizes such as zircon, (2) provenance, as shown by the significantly differing compositions of South and North-Limburg sands, and, to a lesser extent, to the composition of the different geological formations in North-Limburg. The former phenomenon is tentatively attributed to a greater admixture of quartz-rich Tertiary sands from the Lower Rhenish Embayment in North-Limburg sands. Differences between formations in North-Limburg are at least partly thought to be due to depletion of muscovite in eolian Nuenen Group sands and admixture of Saalian eolian sands in the Kreftenheije Formation.

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