



A geochemical record of Late Cenozoic sedimentation history in the southern Netherlands

D.J. Huisman¹ & P. Kiden²

¹ Wageningen Agricultural University, Department of Soil Science and Geology, P.O. Box 37, NL-6700 AA Wageningen, the Netherlands; present address: Netherlands Institute of Applied Geoscience TNO – National Geological Survey, P.O. Box 157, NL-2000 AD Haarlem, the Netherlands (e-mail: h.huisman@nitg.tno.nl);

² Netherlands Institute of Applied Geoscience TNO – National Geological Survey, District Zuid, P.O. Box 35, NL-5670 AA Nuenen, the Netherlands (p.kiden@nitg.tno.nl)

Received 21 March 1997; accepted in revised form 25 February 1998

Key words: clay mineralogy, geochemistry, heavy minerals, stratigraphy

Abstract

A sediment-geochemical study was performed on unconsolidated Upper Cenozoic siliclastic sediments from an area in the south of the Netherlands. Glauconite-rich sediments (Breda Fm) show high K contents and low Ba/K ratios. Major shifts in sediment composition as a result of changes in the Rhine system and of shifts between Rhine and Scheldt provenance, as known from heavy-mineral studies, are also recorded in changes in the grain-size-dependent variations between Al, Na and K. Pleistocene Rhine sediments (Tegelen Fm) show higher Na contents than Pliocene Rhine sediments (Oosterhout and Kiezeloöliet Fms) and Scheldt-derived material (Kedichem Fm), probably as a result of larger contents of sodic plagioclase. Scheldt-derived sediments show low K/Al ratios as a result of a smectite-dominated clay-mineralogical composition and low contents of micas, whereas Rhine-derived sediments have high K/Al ratios which reflect an illite-kaolinite-dominated clay mineralogy and higher contents of muscovite.

The presence of siderite causes high Fe contents in the Tegelen Fm in the east of the area, suggesting a freshwater depositional environment. Increased Mg contents in the siderite-bearing sections of the Tegelen Fm and in parts of the Oosterhout and Kiezeloöliet Fms are probably caused by the presence of minor amounts of dolomite. Localized high concentrations of (pyrite-) S are not only found in the marine Oosterhout Fm and the estuarine Tegelen Fm, but also in the fluvial Kiezeloöliet and Kedichem Fms, which indicates at least minor marine transgressions during their deposition.

Introduction

In 1993 a project was started for a nation-wide characterization of the geochemical variation in Dutch unconsolidated subsurface sediments. Geochemical data from these sediments are still scarce, but from two Dutch regional investigations (Moura & Kroonenberg 1990; Hakstege et al. 1993) and from several other larger-scale studies (Bhatia 1983; Roser & Korsch 1986; Kroonenberg 1992; Cox et al. 1995; Tebbens et al. 1996) we know that grain size, provenance-related variations in mineralogy, weathering and diagenetic processes are the major factors that determine the geo-

chemical composition of such sediments. As a start of our mapping project we wanted to determine to what extent and in which ways these factors influence the geochemical composition of the sediments, which mainly consist of mature siliclastic material. For this purpose, we sampled and analyzed 14 borings from the central-southern Netherlands (Table 1). Two borings, Reusel and Sprundel, were selected because they contain a more or less complete representative sequence of Late Cenozoic deposits, with major variations in provenance, grain-size, lithology and depositional environment. Other borings contain only Early Pleistocene deposits, and are especially rel-

Table 1. Investigated borings, codes of the Geological Survey of the Netherlands (RGD; presently NITG-TNO), X- and Y-coordinates, surface elevation, depth reached and number of samples. For locations see Figure 2, for stratigraphy see Appendix.

Boring	RGD-code	X (m)	Y (m)	Surface elevation (m)	Depth (m)	# Core samples	# Bailer samples
Gastel	49F423	91.450	397.540	3.00	11	43	
Rucphen 1	49F418	96.850	392.570	13.00	20	24	
Rucphen 2	49F424	98.480	396.520	3.60	11	50	
Sprundel	50A337	102.450	393.750	10.40	113	72	83
Rijsbergen	50A336	104.330	391.785	9.60	21	57	
Zundert	50A338	103.255	387.585	10.80	9	31	
Strijbeek	50B339	112.130	390.900	5.80	11	27	
Ulicoten 1	50D34	117.695	381.450	18.20	10	34	
Ulicoten 2	50D35	117.150	383.890	15.80	6	30	
Ulicoten 3	50D36	118.505	385.680	16.20	7	39	
Gilze Raakeind	50E368	121.175	395.320	12.10	22	55	
Alphen	50E367	126.120	388.005	22.00	21	56	
Baarle-Nassau	50G90	124.675	383.485	26.30	24	63	
Reusel	50H74	138.830	375.290	28.70	98	53	73
Total samples						634	156

evant for studying lateral variations in these deposits. In this paper we will study how these known variations are reflected in the bulk geochemical composition.

Establishing the relation between chemical composition and sedimentation history requires consideration of the relation between chemistry and mineralogy, and ways to portray these relations graphically. Provided that a sediment consists of only a limited number of monocrystalline mineral species, its mineralogical composition can be inferred from geochemical data alone by combining patterns that emerge in bivariate plots of major and trace-element concentrations without having to perform extensive mineralogical analyses (Argast & Donnelly 1987). Hypothetical mixtures consisting of varying proportions of two minerals plot on a straight line between the data points of the pure minerals (Figures 1a, b). Random mixtures of three minerals plot in a triangle with the chemical compositions of each pure mineral as corners (Figure 1c). In a situation where the sediment consists of three minerals which are preferentially sorted, this triangle will be only partially filled. A set of samples, derived by grain-size sorting from a mixture of coarse quartz, fine muscovite and clay (with 33% illite, 33% smectite and 33% kaolinite) would show mixing of predominantly quartz and muscovite in the coarse-grained samples, and of muscovite and clay in the finer-grained sam-

ples (Figure 1d). A Al_2O_3 diagram of mixtures of coarse quartz, medium-sized albite and fine clay minerals shows basically the same pattern (Figure 1e), but here Na_2O correlates negatively with Al_2O_3 in the fine samples as albite contents drop with higher contents of clay minerals. Grain-size-induced relations in element contents, like those in Figures 1d and e, can be used to deduce mineralogical properties of sedimentary units, provided the samples encompass sufficient variation in grain size. Variations in these inter-element relations indicate changes in overall mineralogical composition, effectively recording changes in provenance and degree of weathering.

In this study we will compare variations in these inter-element relations with stratigraphic data. The Dutch Pliocene-Pleistocene stratigraphy is based on a combination of lithology, heavy-mineral composition and palynology (Zagwijn & Van Staaldin 1975). In this stratigraphy, following Zagwijn (1985, 1989), the Plio-Pleistocene boundary is conventionally placed as early as 2.3 Ma. The heavy-mineral subdivision employs variations in the contents of the various sand-sized transparent heavy minerals that can be distinguished optically (polarizing microscope). A major distinction made is between associations of so-called stable and unstable minerals. Typical stable minerals are zircon and tourmaline, whereas typical

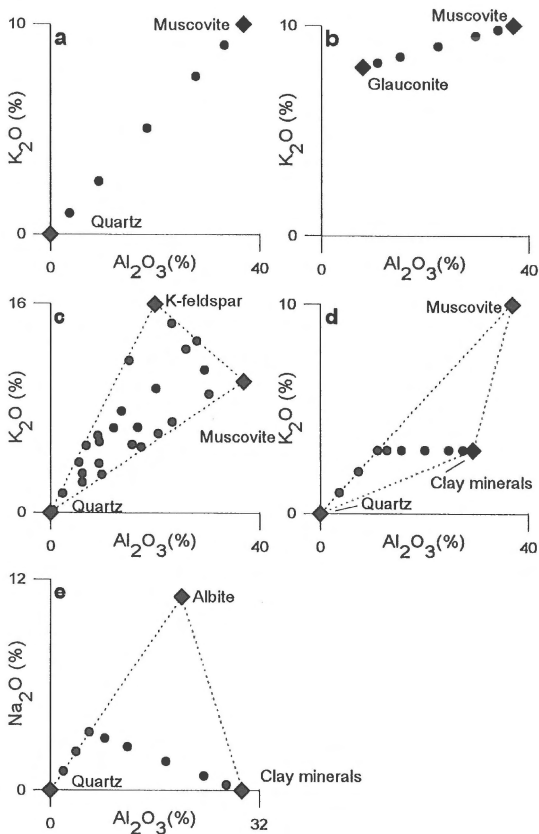


Figure 1. a–d. Theoretical mixing ranges of K and Al: a) theoretical contents of mixtures of quartz and muscovite, b) mixtures of glauconite and muscovite; c) and d) three-component models of mixtures of quartz, muscovite and K-feldspar or clay minerals; c) random mixtures, d) effects of grain-size sorting of mixtures of (coarse) quartz, (medium) muscovite and (fine) clay. e) Effects of grain-size sorting of mixtures of (coarse) quartz, (medium) albite and (fine) clay on the Na and Al contents.

unstable minerals include garnet, epidote, hornblende and alterite. Note that in this heavy-mineral stratigraphy the heavy minerals are defined only by their optical properties and that some, e.g. alterite, would not be distinguished on the basis of chemistry or crystallography (Van Aniel 1950, 1958). The only published research on light minerals in the Netherlands (Van Baren 1934) shows that in general high contents of unstable heavy minerals are associated with high contents of feldspars.

Geological setting

The study area is situated on the southern edge of the North Sea Basin, west of the Roer Valley Graben. Figure 2, Table 1 and the Appendix give an overview

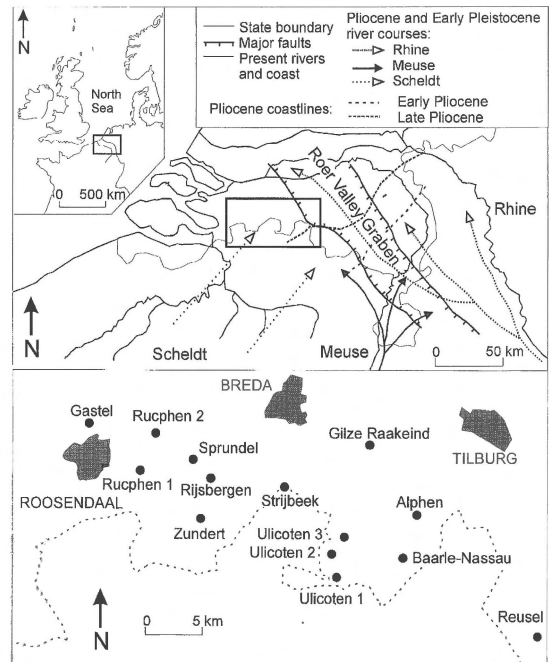


Figure 2. Study area and position of borings listed in Table 1.

of the borings investigated. The sedimentary record in this area shows a general regression with smaller-scale fluctuations during the Late Cenozoic, with sediment supplied alternately by the Rhine (Rijn), Meuse (Maas) and Scheldt (Schelde) river systems (Figure 3; Zagwijn & Van Staaldunin 1975; Kasse 1988).

The oldest sediments investigated belong to the Miocene marine Breda Formation (Fm), according to the stratigraphic nomenclature of Zagwijn & Van Staaldunin (1975). They were only recovered from the Reusel boring, where they consist of glauconiferous sands with phosphorite nodules. Glauconite is a K and Fe-rich mica of marine diagenetic origin (Deer et al. 1992; Porrenga 1967). In our samples, the glauconite is present as coarse black-green grains. The Pliocene Oosterhout Fm consists predominantly of shell-bearing sands with clayey intercalations and is locally glauconiferous. It records a general regression with some smaller oscillations, related to uplift south of the area studied in the Ardennes and the Brabant Massif, as well as to climatic cooling. The formation is distinguished from the Breda Fm by its higher content of shells and lower content of glauconite (Figure 3; Zagwijn 1960, 1989; Zagwijn & Doppert 1978). The Oosterhout Fm was recovered from the Reusel and Sprundel borings. In the Reusel boring it is overlain by the Kiezeloöliet Fm, which is its continental

Ma	Formations		Provenance (Heavy minerals)	Climate	Events
	East	West			
1.1					
1.7	Kedichem		Schelde (stable)	Glacial-Interglacial cycles	Rijn extends into Alps
	Tegelen		Rijn (unstable) and Schelde (stable)		
2.3	Maassluis			Warm temperate with cool periods	Increased tectonic uplift
		Kiezeloöliet	Rijn (unstable)		
5.0	Oosterhout		Rijn (stable)	Warm temperate	Sea level fluctuations
	Breda				
					Overall regression ↑

Figure 3. Summary of stratigraphy, heavy-mineral provenance and geological history of the Late Cenozoic in the study area.

equivalent and which is distinguished from it by the absence of marine shells. The Pliocene Oosterhout and Kiezeloöliet Fms are overlain by the Early Pleistocene Tegelen Fm. The base of the latter is typically marked by a transition from a stable (zircon, tourmaline) to an unstable (epidote, alterite, hornblende) heavy-mineral association (Boenigk 1970; Zagwijn & Van Staalduinen 1975). This break is interpreted as a change in sediment provenance from reworked regional weathered deposits to fresh Alpine sources caused by the headward extension of the Rhine system into the Alps, combined with the onset of the first glaciations (Figure 3; Gibbard 1988) and increased tectonic activity (Van den Berg 1996).

The Tegelen Fm in the area studied consists of micaceous sands and finely laminated clays which were deposited in a fresh to brackish tidal environment (Kasse 1988). It locally contains siderite and pyrite enrichments. Heavy-mineral counts show that most of the formation has a Rhine provenance, but locally Scheldt-derived material is found. Sediments with Scheldt provenance seem to be more frequent in the lowermost units (Merksplas Sands) and also to the west of the study area (Woensdrecht and Hoogerheide Members, Kasse 1988). The borings Reusel and Sprundel are the only ones which contain a complete Tegelen Fm. In the Sprundel boring the lowermost parts of this formation are calcareous and interfinger with sands of the Maassluis Fm which is characterized by the presence of abundant shells. In the Reusel bor-

ing the Maassluis Fm is lacking. In the other borings where the Tegelen Fm is reached, it consists of homogeneous or laminated clay which often is organic-rich near the top.

The Kedichem Fm overlying the Tegelen Fm consists of fluvial sands of Early Pleistocene (Menapien to Bavelien) age, with local clay and peat intercalations. Its low mica contents and higher sand contents are used to distinguish the Kedichem Fm from the Tegelen Fm. By virtue of their very stable heavy-mineral association, the sands seem to be derived from the Scheldt river system, which supplied reworked Paleocene and Eocene sediments, whereas its gravels suggest a Meuse provenance (Kasse 1988).

In the east of the study area, a thin cover of Middle Pleistocene fluvial gravel, belonging to the Sterksel Fm, occurs locally on top of the Kedichem Fm. Most profiles are overlain by Upper Pleistocene cover sands of the Nuenen Group. Neither the Sterksel Fm nor the Nuenen Group will be considered in this study.

Materials and methods

The borings were carried out within the framework of the completion of sheet 50 (Breda-Tilburg) of the 1:50 000 geological map by the Geological Survey of the Netherlands (presently NITG-TNO). Generally a core sampler with a diameter of 10 or 6 cm was used. The samples produced by this method are undisturbed cores, with a maximum length of 1 m. In loose material (sand and shells) in the Reusel and Sprundel borings the Bailer-bore method was used. This gives a composite sediment sample in which all material from an interval of 1 m is mixed.

The cores were sampled at least once per meter, and whenever there were visible changes in lithology, grain size or color of the deposits. Samples consisted of ca. 50 to 100 g taken over intervals of 2 to 20 cm, depending on the thickness of the homogeneous layers. In laminated deposits, with layers < 2 cm in thickness, samples comprised several layers. From each meter of Bailer-bore material one representative sample was taken.

Samples were dried at 60 °C, sieved through a copper or stainless steel 2-mm sieve and stored. Aggregated material was crushed by hand in a ceramic mortar before sieving. From all samples, subsamples were taken for X-ray fluorescence (XRF) analyses. Additional subsamples were taken from the Reusel and Sprundel samples for grain-size analyses. Fur-

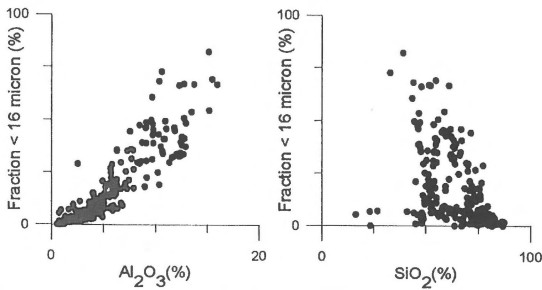


Figure 4. Scatterplots of Al_2O_3 and SiO_2 versus grain-size fraction < 16 μm . This fraction correlates positively with Al_2O_3 and negatively with SiO_2 . Borings Reusel and Sprundel, 284 samples.

thermore, subsamples were taken from a series of 57 samples from all of the 14 borings except Zundert and Srijbeek to determine the clay-mineralogical composition.

For the XRF analyses, samples from the Reusel and Sprundel boring were ground using an agate swing-mill, the other samples using a Tungsten-carbide mill. After grinding, pressed powder pellets were prepared and analyzed for major and trace elements by X-ray spectroscopy, using an ARL8410 spectrometer with a Rh tube, with full matrix correction for major elements (SiO_2 , TiO_2 , Al_2O_3 , Fe_2O_3 , MnO , MgO , CaO , Na_2O , K_2O , P_2O_5 , S), and the Compton scatter method for trace elements (As, Co, Cr, Cu, Ni, Pb, V, Zn, Ba, Ga, Nb, Rb, Sr, Y, Zr). The XRF was calibrated using approximately 100 certified geological reference samples. Three reference samples were added to each batch of 50 samples to determine the precision (0.5–1% relative standard deviation) and accuracy (1–5% relative standard deviation). No Fe-speciation was determined, so all Fe is reported as Fe_2O_3 .

The grain-size distribution was determined using a Malvern-X laser grain sizer for samples from the Reusel and Sprundel borings. No grain-size analyses were done for samples from the other borings.

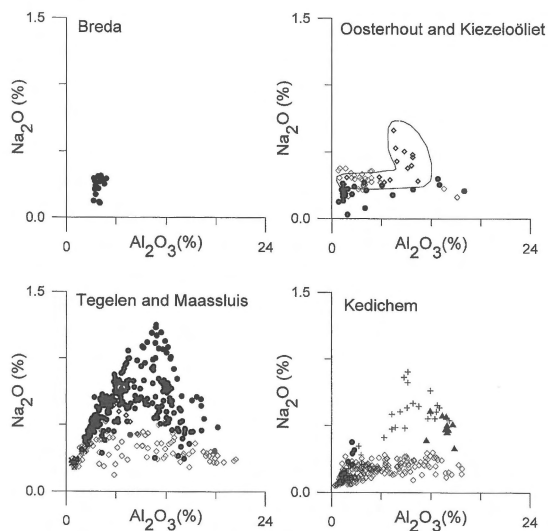
The samples for clay-mineralogical analyses were treated with Na-acetate, H_2O_2 and Na-dithionite to remove carbonates, organic matter and Fe and Mn (hydr)oxides. The clay fraction was separated by pipetting after settling, and X-ray diffractograms (XRD) were made of orientated samples. The diffractograms were digitized by hand. Some subsamples were taken to make powder-X-ray diffractograms.

Heavy-mineral counts were performed for some additional samples from boring Rucphen 2.

Results

Effects of grain-size and specific mineralogy

In order to study the expected relations of Al_2O_3 and SiO_2 with the fine grain-size fractions, bivariate plots of both oxides versus the percentage of the fraction < 16 μm were made. In these plots, Al_2O_3 shows a clear positive correlation with this fraction, while SiO_2 shows a negative correlation (Figure 4). Therefore either of these oxides can be used as a general proxy for grain size, but Al_2O_3 seems much better suited. The variability of SiO_2 is mainly related to the quartz content which correlates negatively with the contents of clays and carbonates. Most detrital variability between sediments, however, is related to varying contents of feldspars, micas and clay minerals, in which the ratio between Al_2O_3 and other oxides such as K_2O and Na_2O plays a major role (Bhatia 1983; Roser & Korsch 1986; Argast & Donnelly 1987; Moura & Kroonenberg 1990; Hakstege et al. 1993; Cox et al. 1995). From the total of bivariate plots made for all element combinations, the Ba/ K_2O plot was the best to discriminate for the presence of the macroscopically visible coarse-grained glauconite. Most of the other measured elements (Ti, Co, Cr, Cu, Ni, Pb, V, Zn, Ga, Nb, Rb and Y) show linear relations with the Al_2O_3 content in all formations as they occur in clay minerals and micas in constant ratios to Al_2O_3 (Huisman et al. 1997). As these elements do not show clear differences between the formations, they cannot be used for classification. Strontium shows a strong linear correlation with CaO content, as does Mn with Fe_2O_3 . Since Fe_2O_3 , CaO, MgO and S do not only occur in clays and micas but also in oxides, carbonates, sulfides and sulfates, we made plots and depth profiles of these elements or oxides versus Al_2O_3 to study possible diagenetic controls on the bulk geochemical composition. In order to study the detrital and diagenetic chemistry, we plotted the geochemical variation separately for each of the four main (groups of) formations: Breda, Oosterhout and Kiezeloöliet, Tegelen and Maassluis, and Kedichem. To facilitate the discussion a further division was made, based on the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ diagrams. This division is presented in the next paragraph, and used in the subsequent paragraphs where the major geochemical variations in our dataset are presented. A mineralogical and sedimentological interpretation of these geochemical variations follows in the 'Discussion'.



Legend for Figures 5–9 (in brackets: number of samples):

Oosterhout and Kiezeloöliet Fms:
 ● Kiezeloöliet (16)
 ◇ Top Oosterhout section Sprundel (14)
 ◇ Rest Oosterhout (26)

Tegelen and Maassluis Fms:
 ◇ Tegelen between Maassluis and Oosterhout (10)
 ◇ Lower Tegelen sections Reusel (43) and Sprundel (20), Tegelen sections Ulicoten 2 (10) and Ulicoten 3 (10), Top Tegelen sections Gilze (10) and Gastel (10)

Kedichem Fm:
 ▲ Top Kedichem section Gilze (10)
 ● Top Kedichem section Rijsbergen (8)
 + Lower Kedichem section Rucphen 2 (9)
 ◇ Rest Kedichem (237)

● Rest Tegelen (231)
 × Maassluis (10)

Figure 5. Scatterplots of Na_2O versus Al_2O_3 for all samples, per formation investigated. The samples can be grouped in a high-Na and a low-Na group. This division roughly follows the stratigraphic subdivision, with high Na values in the Tegelen Fm and low Na values in the other formations; exceptions are indicated. Samples with high Na_2O contents probably contain abundant sodic plagioclase, which mineral is absent in low-Na samples.

The $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ diagrams

In bivariate $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ diagrams of the Breda, Kiezeloöliet and Oosterhout Fms the data points show a wide scatter around 0.25% Na_2O , irrespective of Al_2O_3 content (Figure 5). Only a few samples from the top part of the Oosterhout Fm in boring Sprundel show elevated Na_2O contents. Sediments from the Tegelen Fm tend to show a steeply increasing Na_2O content with increasing Al_2O_3 content until about 10% Al_2O_3 . At higher Al_2O_3 contents, Na_2O drops again. The Kedichem Fm generally shows a scatter in low Na_2O contents without a relation to Al_2O_3 , similar to the Breda and Oosterhout Fms.

In both the Tegelen and Kedichem Fms exceptions to the general $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ trends occur. The samples from the lower halves of the Tegelen sections in the Reusel and Sprundel borings show a scatter between 0.25 and 0.5% Na_2O , irrespective of Al_2O_3 . The same is true for the Tegelen Fm in borings Ulicoten 2 and 3 and in the upper few meters of the Tegelen Fm in borings Gastel and Gilze. The section of Tegelen

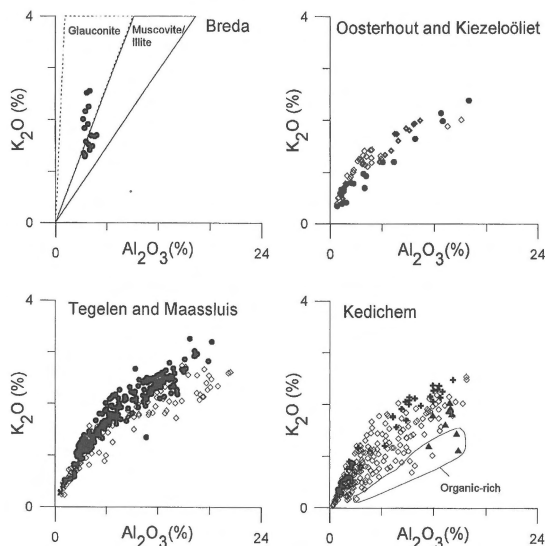


Figure 6. Scatterplots of K_2O versus Al_2O_3 . For the Breda Fm a range of literature values of $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios for muscovite/illite (solid lines) and glauconite (dashed lines) are plotted (Newman & Brown 1987). The high K_2O contents in the Breda Fm can be attributed to abundant glauconite. In the other formations, variations in the relation K_2O to Al_2O_3 can be attributed to variations in muscovite and illite contents. The Kedichem Fm includes organic-rich samples with low $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios that are probably due to *in situ* weathering. Legend in Figure 5.

Fm intercalated between the Maassluis and Oosterhout Fms in the Sprundel boring shows elevated Na_2O contents which are in the same range as those of the directly underlying top part of the Oosterhout Fm. The upper few meters of Kedichem Fm in the Gilze and Rijsbergen borings, and the lower half of this formation in Rucphen 2 show higher Na_2O contents than the rest of the formation.

Further on in this paper, we will use a subdivision based on these $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ trends (Figure 5). We distinguish within the Oosterhout Fm the high-Na group in the formation's top part in the Sprundel boring from the low-Na rest of the formation. Within the Tegelen Fm we distinguish the low-Na sections in the Ulicoten 2 and 3, Gilze and Gastel borings, and in the lower parts of the Reusel and Sprundel borings from the high-Na parts of the other Tegelen sections. In addition we distinguish the section of Tegelen Fm with intermediate Na_2O contents between the Maassluis and Oosterhout Fms in the Sprundel boring. In the low-Na Kedichem Fm we plot the high-Na sections of Gilze, Rijsbergen and Rucphen 2 separately.

The K_2O/Al_2O_3 diagrams

Bivariate K_2O/Al_2O_3 diagrams show that the samples from the Breda Fm are strikingly different from those of the other formations. The Breda samples show a scatter around 4% Al_2O_3 , while K_2O contents vary between 1 and 3% (Figure 6). The K_2O/Al_2O_3 ratios of the samples with low K_2O contents fall in the range of published values for muscovite, while they approach the K_2O/Al_2O_3 ratio of glauconite in the high- K_2O samples (Newman & Brown 1987).

The other formations show in general a positive correlation between K_2O and Al_2O_3 . In the Oosterhout Fm, K_2O shows a steep increase with increasing Al_2O_3 in the range from 0 to 4%, and a less steep increase above 4% Al_2O_3 . The K_2O/Al_2O_3 ratio in the high- Al_2O_3 range varies considerably. The Kiezeloöliet Fm has a constant slope of the mixing line with K_2O/Al_2O_3 ratios comparable to the lowest ratios from the Oosterhout Fm. The Tegelen Fm shows a similar pattern as the Oosterhout Fm, i.e. a high K_2O/Al_2O_3 ratio between 0 and 4% Al_2O_3 which decreases above 4% Al_2O_3 . The absolute K_2O/Al_2O_3 ratios, however, reach higher values. In the Kedichem Fm, the K_2O/Al_2O_3 ratio shows considerably more scatter, and is often lower than in the other formations. In organic-rich layers in the Kedichem and Tegelen Fms, a drop in the K_2O/Al_2O_3 ratio can often be observed. The samples with lowest K_2O/Al_2O_3 ratios in the Kedichem Fm are all organic-rich, as indicated in Figure 6. A similar drop can furthermore only be observed in the Ba/Al_2O_3 ratio, but not in any of the other ratios of elements or oxides to Al_2O_3 .

The samples from the Tegelen Fm that show low Na_2O contents in the Na_2O/Al_2O_3 diagrams also have slightly lower K_2O/Al_2O_3 ratios (Figures 5, 6). In the Kedichem Fm, the high- Na samples show no clear distinction in K_2O/Al_2O_3 ratio.

The Ba/K_2O diagrams

The Ba/K_2O diagrams show a decrease in Ba content with increasing K_2O for the glauconiferous Breda Fm, whereas the Ba contents increase with increasing K_2O in the Oosterhout, Tegelen and Kedichem Fms (Figure 7). The Ba/K_2O ratios are lower in the Oosterhout Fm than in the Kiezeloöliet Fm. The Ba/K_2O ratios of the Tegelen and Kedichem Fms fall in the same range as those of the Kiezeloöliet Fm.

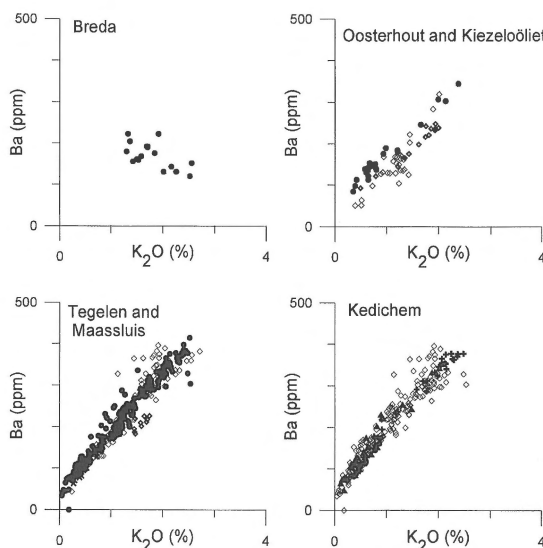


Figure 7. Scatterplots of Ba versus K_2O . Note the relatively low Ba/K_2O ratio in the Breda Fm, which is attributed to abundant glauconite. The variation in Ba/K_2O in the Oosterhout Fm suggests local glauconite presence. Legend in Figure 5.

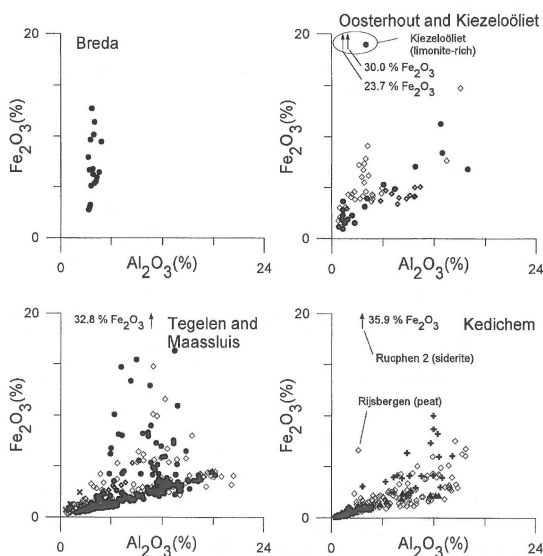


Figure 8. Scatterplots of Fe_2O_3 versus Al_2O_3 . There appears to be a background with an Fe_2O_3/Al_2O_3 ratio of 1/4. Higher Fe_2O_3 contents are related to glauconite (Breda Fm), siderite, Fe-(hydr)oxides and pyrite. Legend in Figure 5.

The Fe_2O_3/Al_2O_3 diagrams

In all formations with the exception of the Breda Fm, there is a basic linear correlation, with an Fe_2O_3/Al_2O_3 ratio of approximately 0.25, with groups of high- Fe_2O_3 outliers rising up to 35% (Figure 8). Note that all Fe, including $FeCO_3$ is reported

as Fe_2O_3 . The group of three high outliers in the Kiezeloöliet Fm are from limonite-crusts at the boundary with the Oosterhout Fm. In the Tegelen Fm, the high- Fe_2O_3 group ($> 0.25 \times \text{Al}_2\text{O}_3\%$) does not relate to the subdivision based on $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ diagrams, but is restricted to borings Gilze, Alphen and Reusel in the east of the study area. In the Kedichem Fm, the sample with ca. 35% Fe_2O_3 is from a 2-cm-thick siderite layer in the Kedichem clay in Rucphen 2. Other high- Fe_2O_3 outliers in this formation are from a peat layer in Rijsbergen, and from the lower half of Rucphen 2.

The $\text{MgO}/\text{Al}_2\text{O}_3$ diagrams

In the $\text{MgO}/\text{Al}_2\text{O}_3$ diagrams of the Oosterhout and Kiezeloöliet Fms, two groups can be distinguished which both show a linear correlation between MgO and Al_2O_3 (Figure 9). One group, consisting of parts of the Kiezeloöliet and Oosterhout Fms has $\text{MgO}/\text{Al}_2\text{O}_3$ ratios of ca. 1 : 4. The other samples have a ratio of ca. 1 : 10 or less. In the Tegelen Fm, a similar distinction can be made, but here the high- $\text{MgO}/\text{Al}_2\text{O}_3$ group shows more variation. There is no correlation between the subdivision in high and low- $\text{MgO}/\text{Al}_2\text{O}_3$ groups and in high and low- Na_2O groups. The high- $\text{MgO}/\text{Al}_2\text{O}_3$ group however is only found in the high- Fe_2O_3 sections of the borings Gilze, Alphen and Reusel (Figure 10), and in the calcareous Tegelen deposits between the Oosterhout and Maassluis Fms in the Sprundel boring. The $\text{MgO}/\text{Al}_2\text{O}_3$ contents of all the samples from the Kedichem Fm are comparable to those of the 1 : 10 groups in the Tegelen, Oosterhout and Kiezeloöliet Fms.

The sulfur contents

In all formations the sulfur (S) content is low ($< 0.5\%$) with sporadic isolated peaks (Figures 11a, b). These are often but not exclusively related to organic-rich layers. Taking the Reusel and Sprundel borings together, these S peaks are highest in the Oosterhout, the Kiezeloöliet and the lower half of the Tegelen Fm (9000–12 000 ppm). They decrease upwards in the upper parts of the Tegelen Fm and in the Kedichem Fm. In boring Rucphen 2, however, the lower half of the Kedichem Fm shows increased S contents up to 15 000 ppm (Figure 11c), and in the peat layer from the Kedichem Fm in boring Rijsbergen the highest S content of the study area is found: 49 000 ppm. All of these S peaks coincide with increases in As content (Huisman et al. 1997).

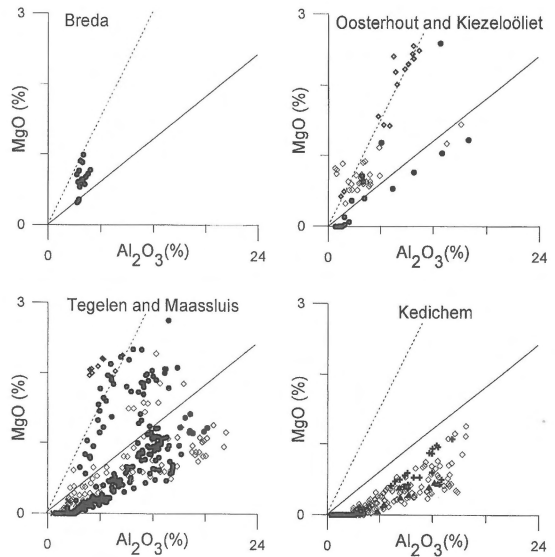


Figure 9. Scatterplots of MgO versus Al_2O_3 . There appears to be a background with an $\text{MgO}/\text{Al}_2\text{O}_3$ ratio $\leq 1/10$ (solid lines indicate 1/10 ratio). MgO contents that exceed this ratio can be linked to glauconite (Breda Fm) and dolomite. In the Oosterhout and Kiezeloöliet Fms, samples with elevated MgO contents appear to have an $\text{MgO}/\text{Al}_2\text{O}_3$ ratio around 1/4 (dashed lines). Legend in Figure 5.

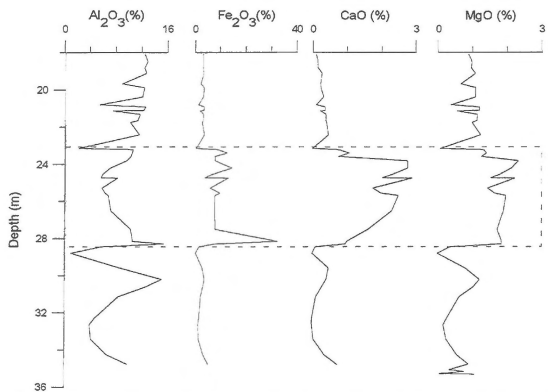


Figure 10. Boring Reusel, Tegelen Fm section 18–36 m. Depth profiles of Al_2O_3 , Fe_2O_3 , CaO and MgO . The dashed lines mark a section with increased Fe_2O_3 , CaO and MgO contents as a result of the presence of siderite, calcite and dolomite.

A comparison of the S profiles with the Fe_2O_3 profiles shows that most of the Fe_2O_3 peaks do not show elevated S contents and vice versa (Figure 11a–c).

Clay mineralogy

The samples for clay-mineral analyses were chosen so that enough representative analyses were obtained from the Oosterhout, Kiezeloöliet, Tegelen and Kedichem Fms (no clay-rich samples were recovered

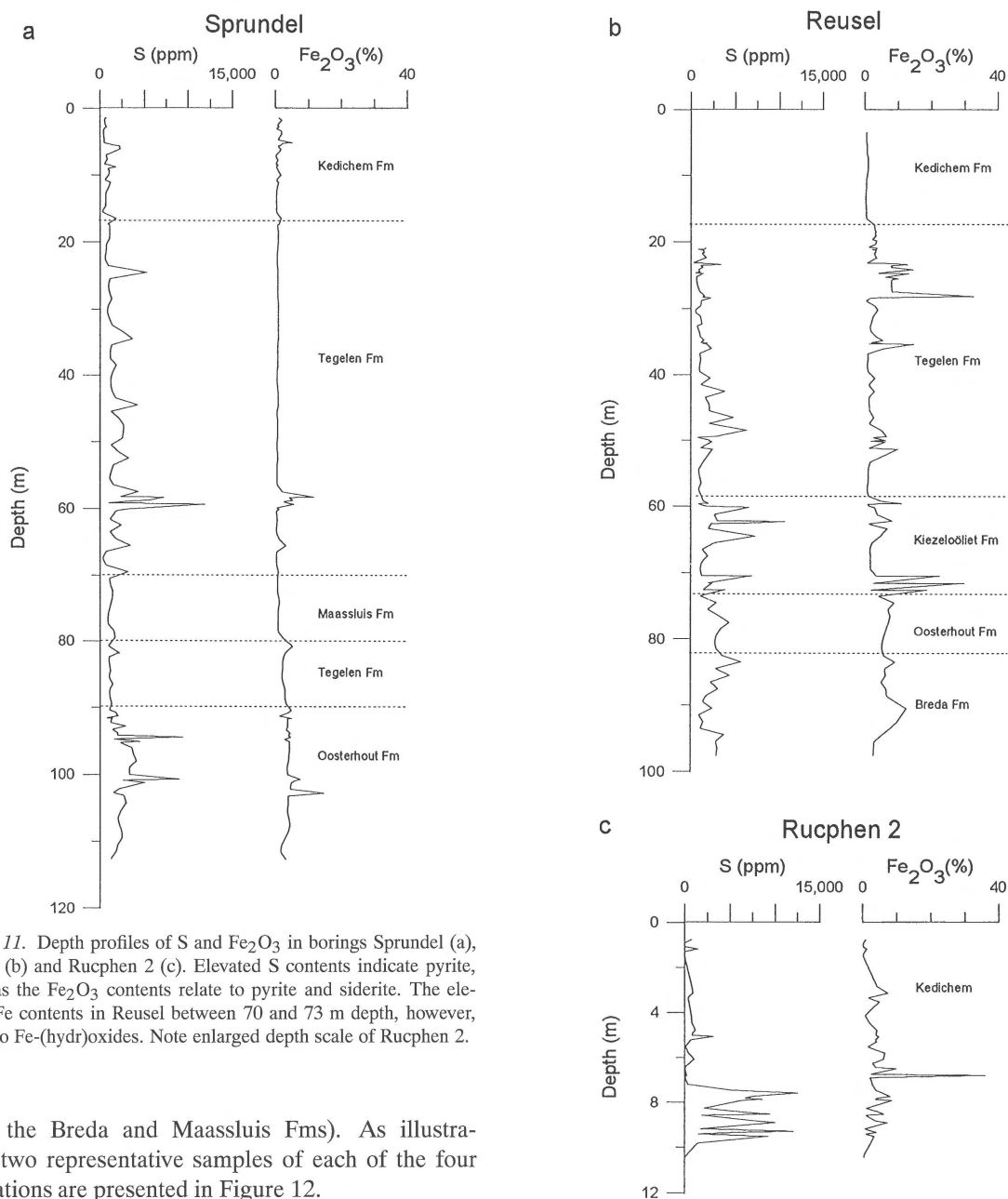


Figure 11. Depth profiles of S and Fe₂O₃ in borings Sprundel (a), Reusel (b) and Rucphen 2 (c). Elevated S contents indicate pyrite, whereas the Fe₂O₃ contents relate to pyrite and siderite. The elevated Fe contents in Reusel between 70 and 73 m depth, however, relate to Fe-(hydr)oxides. Note enlarged depth scale of Rucphen 2.

from the Breda and Maassluis Fms). As illustration, two representative samples of each of the four formations are presented in Figure 12.

The Kiezeloöliet and the Oosterhout Fms are characterized by a mixture of moderately-well-crystallized smectite, with illite and kaolinite (Figures 12a, b). The kaolinite content varies greatly. In the lower units of the Tegelen Fm, the clay composition is dominated by well-crystallized smectite with illite and kaolinite. In the upper units of the formation, such as at 20.32 m in Rucphen 1, the clay is dominated by illite and kaolinite (Figure 12c). The smectite contents in these units are low and variable and the smectite itself is poorly crystallized. In organic-rich layers, the illite content

tends to decrease whereas that of smectite is higher. The clays of the Kedichem Fm in general show high contents of well-crystallized smectite with some additional kaolinite (Figure 12d), but locally they are illite-kaolinite-dominated with low contents of poorly crystallized smectite.

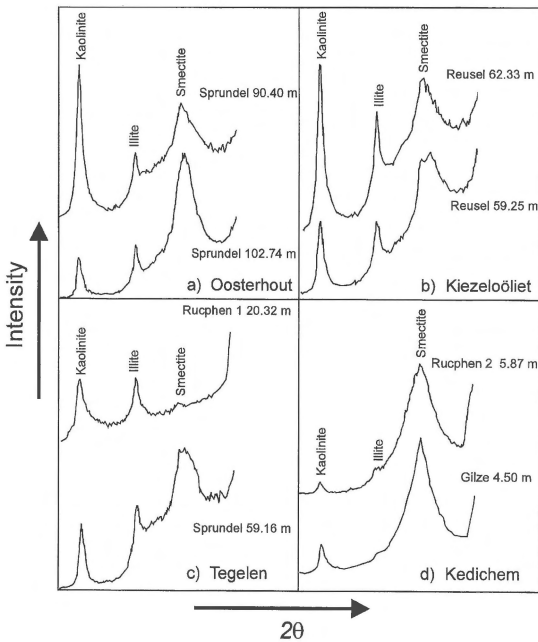


Figure 12. X-ray diffractograms of samples with clay mineralogy typical for the Oosterhout (a), Kiezeloöliet (b), Tegelen (c) and Kedichem (d) Fms. 'Kaolinite', 'Illite' and 'Smectite' at respectively 7, 10 and 14 Å.

Heavy minerals

The heavy-mineral profile of boring Rucphen 2 was studied to assess whether the variations in geochemistry ($\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$) and clay mineralogy which do not coincide with a formation boundary could be linked to a provenance-change. The heavy-mineral profile of the Kedichem Fm in this boring (Figure 13) shows an upper unit with an extremely stable composition, whereas the lower unit has a mixed heavy-mineral composition (cf. Kasse 1988; Woensdrecht and Hoogerheide Members of Tegelen Fm). This change is consistent with the above-mentioned change in the $\text{Na}_2\text{O}_3/\text{Al}_2\text{O}_3$ trend. A few decimeters below the change in $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ trend, the clay-mineralogical composition changes from smectite-dominated to an illite-kaolinite-smectite mixture.

Discussion

Interpretation of $\text{Na}_2\text{O}_3/\text{Al}_2\text{O}_3$ diagrams

The relation between Na_2O and Al_2O_3 seems to be controlled by mineralogical properties. The samples with low Al_2O_3 contents are generally coarse-grained

because of the abundance of quartz in the coarse fractions, whereas samples high in Al_2O_3 are clay-rich (Figure 4). The characteristic peak of the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ trend in the upper layers of the Tegelen Fm (Figure 5, 'Rest Tegelen') falls around 10% Al_2O_3 . Samples with these percentages of Al_2O_3 are silts and very fine sands. As sodic plagioclase is the only major Na-bearing mineral in Cenozoic Dutch sediments (Van Baren 1934), this suggests that sodic plagioclase is common in the silt and very fine sand fraction of these layers. The positive correlation in the low- Al_2O_3 range reflects a mixing range of relatively fine-grained sodic plagioclase with coarse quartz. In this range, increasing Na_2O content is caused by increasing contents of sodic plagioclase. The fact that the $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ ratio is much lower than that of a pure albite/quartz mixing line (Figure 1) is probably caused by the presence of additional Al_2O_3 in the micas in the fine sand fraction (see below). As the CaO content does not show increased values in the fine sandy and silty samples it is unlikely that significant amounts of Ca-rich, Na-poor plagioclase are present. The negative correlation in the high- Al_2O_3 range corresponds with dilution of sodic plagioclase with Na-poor clay in the very fine grain-size classes.

The elevated but lower Na_2O contents in the top part of the Oosterhout Fm in boring Sprundel suggest that these sediments also contain sodic plagioclase in the fine sand fraction in abundancies comparable to those of the Tegelen sediments intercalated between the Maassluis and Oosterhout Fms in the same boring. The low Na_2O contents in the Kedichem Fm indicate that sodic feldspar is absent or rare. The sporadic occurrences of elevated Na_2O contents point to localized sodic-plagioclase-rich sediments.

Interpretation of $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ diagrams

On the basis of the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ diagrams, the sediments can be subdivided into a number of groups: one (1) with a positive correlation between K_2O and Al_2O_3 and a characteristic change in $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio around 4% Al_2O_3 (Tegelen and Oosterhout Fms), one (2) with a lower $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio and lacking the characteristic knickpoint at 4% Al_2O_3 (Kiezeloöliet Fm), one (3) with a large spread in $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios but still with a positive K/Al correlation and also a knickpoint at 4% Al_2O_3 (Kedichem Fm), and one (4) with high K_2O contents and no correlation with Al_2O_3 (Breda Fm; Figure 6).

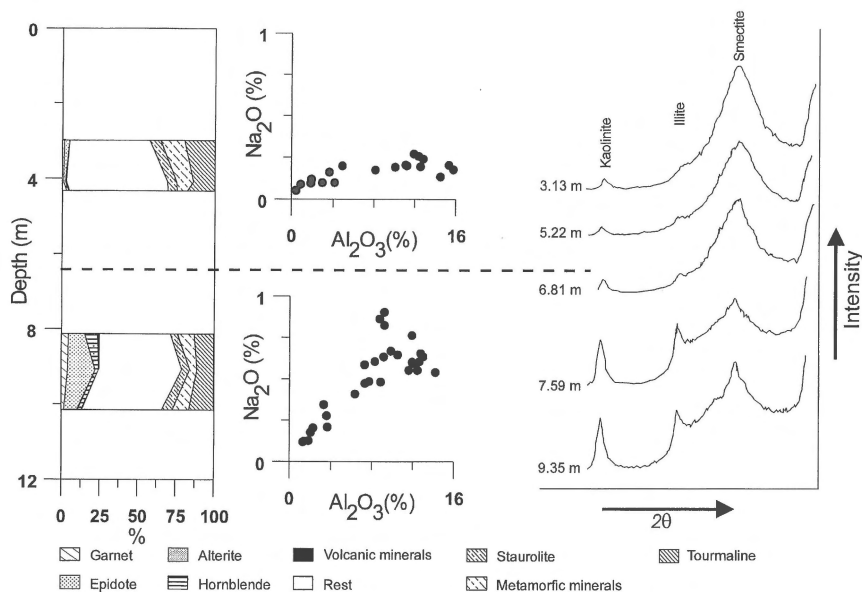


Figure 13. Heavy minerals, Na/Al relation and clay minerals of Kedichem Fm in boring Rucphen 2. Interval 4.90–8.00 m is clay. Dashed line indicates boundary between high and low Na_2O contents. Note that shift from kaolinite-illite-dominated to smectite-dominated clay mineralogy is somewhat below this boundary.

The characteristic change in $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio around 4% Al_2O_3 in the Kedichem, Tegelen and Oosterhout Fms can be explained by grain-size related variations in the mineralogy. Between 0 and 4% Al_2O_3 , the sediment is coarse-grained and the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio falls in the range of quartz-muscovite mixtures. Above 4% Al_2O_3 the material is finer and contains more clay, consisting of mixtures of illite, kaolinite and smectite, resulting in a lower $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio.

The variation in $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios in the Oosterhout Fm can probably be attributed to variations in the kaolinite content (cf. Figure 12a). It is not clear however why a similar difference in kaolinite content in the Kiezeloëliet Fm does not seem to affect the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio. The lack of the bend at 4% Al_2O_3 in the Kiezeloëliet Fm may be attributed to lower contents of micas in the sand fraction when compared to the Oosterhout Fm.

The high $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio in the Tegelen Fm if compared to the Oosterhout and Kedichem Fm can be linked to the macroscopic observations of relatively large amounts of micas, and to the dominance of illite in the clay fraction (Figure 12). There are two groups of occurrences of relatively lower $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios in the Tegelen Fm. In the first group these ratios coincide with lower Na_2O contents (Reusel, Sprundel, Gastel, Gilze and Ulicoten 2 and 3). This group shows increased contents of well-crystallized smec-

tite which apparently lowered the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio through dilution. As this indicates major mineralogical changes in both the sand and the clay fraction, it suggests a change in sediment provenance. The second group consists of localized drops in $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio in organic-rich layers. Usually, these drops are accompanied by an increase in the contents of poorly crystallized smectite and a decrease in illite content (Figure 14). This indicates that in these organic-rich layers illite is weathered to smectite, probably as a result of attack by organic acids, resulting in a net loss of K_2O from the clay fraction.

The, in general, lower $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios in the Kedichem Fm can be attributed to the high contents of smectite, although also here local decreases in $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio occur in organic-rich layers. Typical Kedichem clays with high contents of well-crystallized smectite have a $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratio of ca. 1 : 12. The samples with the highest $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios have higher illite and kaolinite contents. The samples distinguished by their high Na_2O contents are not significantly different from the rest of the Kedichem Fm, but high Na_2O contents in general correlate with high $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios, which strengthens the argument for mineralogical change.

The trend in the Breda Fm is not comparable to those in the Oosterhout, Tegelen and Kedichem Fms because Al_2O_3 is constant, but K_2O varies consider-

ably. The variations in K_2O content can be linked to the macroscopically observed variations in glauconite content.

Interpretation of Ba/K₂O diagrams

In general, Ba and K_2O show a linear correlation, indicating that Ba substitutes for K in most K-bearing minerals. However, if K-bearing minerals are formed in an environment where no Ba is available, no Ba will substitute for K_2O . Of the sediments under consideration, all formations show a linear correlation between Ba and K_2O with the exception of the Breda Fm in which Ba is negatively correlated with K_2O (Figure 7). This indicates that the major K-bearing mineral in this formation (viz. glauconite) was formed in a Ba-poor environment. Glauconite is formed by biological activity in a marine depositional environment (Hillier 1995), where Ba is unavailable as a result of scavenging by microorganisms and subsequent immobilization by the formation of barite ($BaSO_4$; Van Santvoort & De Lange 1996; Deer et al. 1992). The lack of substitution of Ba for K therefore can be attributed to the unavailability of Ba during the formation of glauconite. This also suggests that generally the Ba/ K_2O relation indicates the presence of glauconite. Therefore the relatively low Ba contents in relation to K_2O in part of the Oosterhout Fm could indicate the presence of glauconite, which is indeed not uncommon in the Oosterhout Fm (Zagwijn & Van Staaldunin 1975).

Interpretation of the Fe₂O₃/Al₂O₃ and S diagrams

The background Fe_2O_3/Al_2O_3 ratio of approximately 0.25 lies close to the ratio generally regarded as normal for detrital siliclastic sediments, and represents the Fe content of phyllosilicates (Dellwig et al. 1996). The Fe contents in the Breda Fm exceed this background as a result of the relative abundance of glauconite. In the other formations, Fe contents can exceed the 0.25 Fe_2O_3/Al_2O_3 ratio as a result of diagenetic processes which led to neoformation of secondary minerals.

The presence of peaks of S and associated As as recorded in the Oosterhout, Kiezeloöliet, Tegelen and Kedichem Fms indicates the presence of pyrite (Huisman et al. 1997). This is confirmed by a series of XRD and micromorphological observations (Huisman 1998). On the whole there is a lack of correlation between S and Fe_2O_3 peaks (Figure 11) because the vast variation in carbonate and oxide-derived Fe_2O_3 dwarfs the pyrite-Fe content. This shows that most of

the Fe is present in non-sulfidic Fe minerals. XRD and micromorphological observations show that in the Tegelen Fm most of the Fe enrichments are in the form of siderite ($FeCO_3$). In the Kiezeloöliet Fm, the major part of the Fe is present as (hydr)oxides. The localized high S values in the Kedichem Fm (Rucphen 2, Figure 11c, and the Rijsbergen peat) are probably pyritic, but in the latter case the XRD analyses show that gypsum is present also.

Interpretation of MgO/Al₂O₃ diagrams

In the Tegelen Fm, the striking division in high- MgO/Al_2O_3 and low- MgO/Al_2O_3 can be linked to the presence of carbonates. All siderite-rich sections show elevated MgO/Al_2O_3 ratios, as does the calcareous Tegelen section between the Oosterhout and Maassluis Fms in the Sprundel boring. The Mg could be partly present as minor substituent for Ca and Fe in calcite and siderite respectively, but XRD measurements and scanning electron microscope (SEM) analyses (Huisman 1998) show also the presence of minor amounts of dolomite in some of the samples from siderite-rich sections. Therefore it is likely that the division in high- MgO/Al_2O_3 and low- MgO/Al_2O_3 sections in the Tegelen Fm is in fact a division in relatively dolomite-rich and dolomite-poor sediments. The presence of high and low- MgO/Al_2O_3 sections in the Oosterhout and Kiezeloöliet Fms suggests that here also dolomite-bearing sections occur.

Geochemistry and sedimentation history

The geochemistry and the sedimentation history of the Late Cenozoic in the study area are summarized in Figure 15. The marine character of the Breda Fm is clearly illustrated by the combination of high contents of K_2O , MgO and Fe_2O_3 and low Ba/ K_2O ratios, which characterizes the presence of glauconite.

The marine depositional environment of the Oosterhout Fm is reflected by the presence of shells or shell debris, causing high CaO contents. Apart from that, the relatively low Ba/ K_2O ratio in part of the Oosterhout sediments probably indicates glauconite formed in a marine environment. The differences in Ba/ K_2O ratio that occur in the clays of the Oosterhout Fm indicate that glauconite formation did not occur uniformly throughout the formation. As in modern deltas this K_2O -enrichment increases with increasing distance from the river mouth (Porrenga 1967), the lack of diagenetic enrichment of K_2O could suggest a more littoral depositional environment locally in

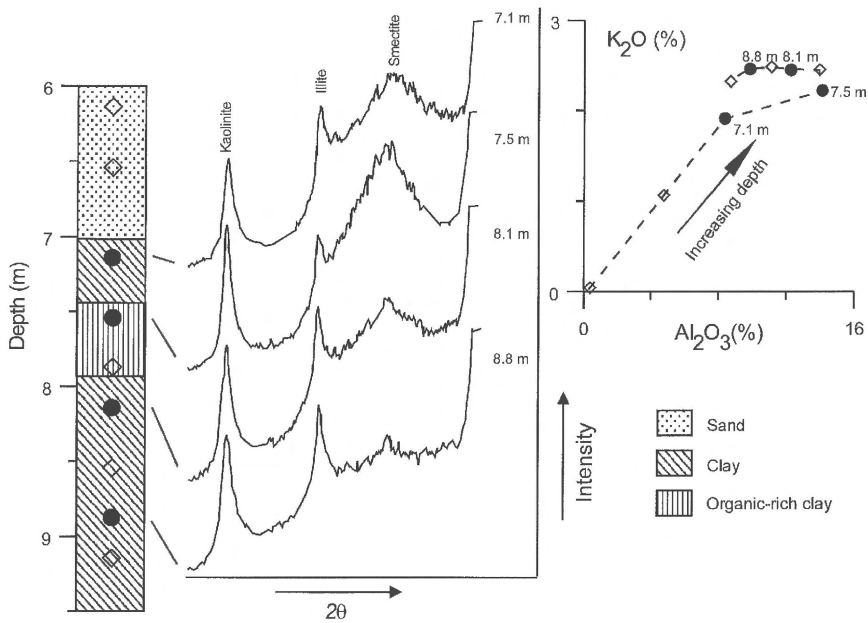


Figure 14. K/Al relation and clay mineralogy around an organic-rich clay layer (Tegelen Fm) in boring Rijsbergen. The ratio K_2O/Al_2O_3 decreases in this layer. \diamond and \bullet mark samples for orientation purposes.

Ma	Formations		Provenance (Heavy minerals)	Climate	Events	Na/Al ¹		K/Al ²	Clay minerals ³	Ba/K	S-content	Fe/Al ⁴		Mg/Al ⁵	
	East	West				East	West					East	West	East	West
Pleistocene	Kedichem		Schelde (stable)	Glacial-Interglacial cycles	Rijn extends into Alps	Low	Low to high	Sm.	Positive correlation Ba-K	Sporadic high peaks	Local lower peaks	Low with sporadic high peaks		Low	
	Tegelen		Rijn (unstable) and Schelde (stable)			High	Increasing slightly ↑					Ill./Ka.	High sections and local peaks	Alternating high and low	
	Maas-sluis		Rijn (unstable) and Schelde (stable)			Low	High ¹	Ill./Ka./Sm.							
Pliocene	Kiezeloëliet		Rijn (unstable)	Warm temperate with cool periods	Increased tectonic uplift	High ¹	High	Ill./Sm.; Ka. variable	Local high peaks	Decreasing peak height ↑	Low		Low		
	Oosterhout		Rijn (stable)			Low	Low				Local high peaks	Low			
Miocene	Breda			Subtropical	Sea level fluctuations	Very high	Very high	?	Negative correlation Ba-K		Variable	Variable		Variable	

¹Low: Na₂O = 0 - 0.4 % High: Na₂O = 0 - 1.2 %
²Low: K₂O/Al₂O₃ = 0.33 - 0.06 High: K₂O/Al₂O₃ = 0.33 - 0.11 Very high: K₂O/Al₂O₃ = 0.67 - 0.33
³Ill. = Illite Sm. = Smectite Kaol. = Kaolinite
⁴Low: Fe₂O₃/Al₂O₃ = 0.2 - 0.3 High: Fe₂O₃/Al₂O₃ > 0.3
⁵Low: MgO/Al₂O₃ ≤ 1:10 High: MgO/Al₂O₃ ≥ 1:10

Figure 15. Correlation of geological history with geochemistry and clay mineralogy of the Late Cenozoic in the study area.

the Oosterhout Fm. The shifts between deeper marine and more littoral environments in the Oosterhout Fm can be interpreted as an expression of one of the many regressional and transgressional cycles during the Pliocene (Van den Berg 1996). The overall large-scale regression or delta progradation is reflected in the sequence from the marine sediments of the Oost-

erhout Fm to the littoral or continental Kiezeloëliet deposits in the Reusel boring.

The stratigraphically deepest occurrences of Na₂O-rich sediment in the studied sections are in the top part of the Oosterhout Fm and in the overlying Tegelen Fm, indicating a transition from plagioclase-poor to plagioclase-rich deposits. The shift to-

wards plagioclase-rich sediments coincides with the change from stable to unstable heavy minerals around the Pliocene-Pleistocene boundary which marks the change in the provenance of Rhine sediments from regional to Alpine. As sodic plagioclase is easily weathered, its presence in sedimentary deposits indicates that the material is relatively fresh. The lack of sodic plagioclase in the Breda, Oosterhout and Kiezeloöliet Fms, as deduced from the low Na contents, is consistent with prolonged weathering in the warm, humid climate during the Miocene and Pliocene (Zagwijn 1960; Buurman 1972). The increase in Na content thus reflects the input of fresh sediment by the headward extension of the Rhine into the Alps, the onset of glaciations and increased tectonic activity during the Plio-Pleistocene transition.

The $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ diagrams of the Pleistocene deposits show an overall succession from plagioclase-poor (lower sections Tegelen Fm) to plagioclase-rich (upper sections Tegelen Fm) to plagioclase-poor (Kedichem Fm). Similar successions can be observed in the $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ diagrams and the clay mineralogy. The $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios rise somewhat from the lower to the upper half of the Tegelen Fm and subsequently decrease and become more variable in the Kedichem Fm. The clay mineralogy shifts from illite-kaolinite-smectite to illite-kaolinite to smectite-dominated. This reflects the succession in the sand provenance from Scheldt (Merksplas Sands) to Rhine (Turnhout and Rijkvorsel Members) and back to Scheldt (Gilze Member) as described on the basis of heavy minerals by Kasse (1988). Apparently sediments of Scheldt provenance have low Na_2O contents, relatively low $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios and a clay mineralogy dominated by well-crystallized smectite, whereas Rhine sediments have high Na_2O contents, high $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios and a clay mineralogy dominated by illite and kaolinite.

Low Na_2O contents, low $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$ ratios and smectite-rich clays in the Tegelen Fm in the borings Ulicoten 2 and 3 and in the top parts of the borings Gilze and Gastel, and elevated Na_2O contents in the lower section of the Kedichem Fm in Rucphen 2 (Figure 13) indicate that the transition from Rhine to Scheldt provenance locally does not coincide with the lithological and sedimentological formation boundary between the Tegelen and Kedichem Fms. This could be due to localized sediment supply or reworking of Scheldt material during deposition of the Tegelen Fm, and of Rhine material during deposition of the Kedichem Fm. The elevated Na_2O contents in the top

part of the Kedichem Fm in Gilze and Rijsbergen can be due either to reworking of Tegelen material or to increased Rhine influence.

It is striking that the siderite-rich sections in the Tegelen Fm are concentrated in the east of the study area (Gilze, Alphen, Reusel; cf. Figure 10). Siderite can only be formed in a reducing environment without sulfate, as the presence of (sea-water) sulfate would cause the formation of pyrite (e.g. Postma 1982). Therefore the occurrence of localized S peaks in siderite-rich sections in the Oosterhout, Kiezeloöliet and especially the Tegelen Fm could indicate a fresh-water depositional environment with small marine incursions. The concentration of siderite-rich sections in the east of the area suggests a decreasing marine influence from west to east. In the easternmost area there was not sufficient S to form a major pyritic phase, and instead siderite was formed (cf. Postma 1982). Kasse (1988) interpreted the presence of siderite underneath a pyrite-bearing peat in quarry Ravels, south of Baarle-Nassau, as an indicator for a transition from a fresh-water to a brackish or saline depositional environment in the top part of the Tegelen Fm. Pyrite formation, however, depends not only on the Fe- and sulfate availability but also on sedimentation rates, biological activity and the availability and degradability of organic matter. Several cases have been described recently where siderite was formed along with pyrite in marine coast-near settings (Aller & Michalopoulos 1996; Haese et al. 1997). Moreover, the siderite in the Tegelen sediments is formed after deposition through interaction with groundwater (Huisman 1998). Therefore the presence of siderite or the absence of pyrite on their own are not diagnostic for continental depositional environments.

The presence of considerable amounts of S in the Kiezeloöliet Fm and locally in the Kedichem Fm of Rucphen 2 and in the peat of the same formation in Rijsbergen are indications for at least localized marine influences during deposition, and can be interpreted as resulting from minor marine transgressions over coast-near fluvial deposits.

Conclusion

The observations and interpretations in the foregoing 'Discussion' as summarized in Figure 15 show that grain-size-related variations in concentrations and ratios of Al_2O_3 , K_2O , Na_2O and Ba in scatter diagrams, provide information about the con-

tents of light minerals like muscovite, glauconite and sodic plagioclase, and about the clay-mineralogical composition in a sedimentary unit. This information correlates well with macroscopical observations and XRD-measurements and indirectly with heavy-mineral counts. The scatter diagrams therefore can be used to determine boundaries between sedimentary units with provenance-related mineralogical differences. Diagenetic processes which are indicative for depositional environments can be identified by using scatter diagrams and depth profiles of Al, Fe, Ca, Mg and S. In this way, sediment geochemistry combined with a few representative mineralogical analyses can be used to trace transgressions and regressions, major shifts in provenance and the impact of weathering.

Acknowledgements

This research is part of the GEOBON project, which is funded by the Geological Survey of the Netherlands (RGD, presently NITG-TNO), the Wageningen Agricultural University (WAU) and the Institute for Environmental Protection and Public Health (RIVM). Thanks are due to F. Vermeulen and J. Baker for the XRF, and to J. van Doesburg for the XRD analyses, to A. Burger for counting heavy minerals and to H. van der Wiel, R. Lantman, B. Aarts and A. Steegs for technical support during coring. This paper benefited from comments by S.B. Kroonenberg, A. Veldkamp, J.J. van Dijke and L. Tebbens and by the journal's reviewers G.Th. Klaver and S.P. Vriend.

Appendix

Summary stratigraphy of borings investigated (Table 1). Depths in meters below surface.

Gastel	0 – 1.35	Twente Fm (not studied)
	1.35 – 8.55	Kedichem Fm
	8.55 – 9.90	Tegelen Fm
Rucphen 1	0 – 3.80	Twente Fm (not studied)
	3.80 – 18.35	Kedichem Fm
	18.35 – 20.40	Tegelen Fm
Rucphen 2	0 – 2.10	Twente Fm (not studied)
	2.10 – 10.60	Kedichem Fm
Sprundel	0 – 1.28	Twente Fm (not studied)
	1.28 – 17.90	Kedichem Fm
	17.90 – 70.00	Tegelen Fm
	70.00 – 80.00	Maassluis Fm
	80.00 – 90.00	Tegelen Fm
Rijsbergen	90.00 – 113.00	Oosterhout Fm
	0 – 1.30	Twente Fm (not studied)
	1.30 – 7.30	Kedichem Fm
	7.30 – 21.15	Tegelen Fm
Zundert	0 – 6.27	Twente Fm (not studied)
	6.27 – 6.88	Kedichem Fm
	6.88 – 8.60	Tegelen Fm
Strijbeek	0 – 2.20	Twente Fm
	2.20 – 11.00	Tegelen Fm
Ulicoten 1	0 – 9.60	Kedichem Fm
Ulicoten 2	0 – 1.24	Twente Fm (not studied)
	1.24 – 3.22	Kedichem Fm
	3.22 – 5.60	Tegelen Fm
Ulicoten 3	0 – 5.53	Kedichem Fm
	5.53 – 6.60	Tegelen Fm
Gilze Raakeind	0 – 2.00	Twente Fm (not studied)
	2.00 – 8.92	Kedichem Fm
	8.92 – 21.85	Tegelen Fm
Alphen	0 – 3.63	Twente Fm
	3.63 – 14.38	Kedichem Fm
	14.38 – 20.75	Tegelen Fm
Baarle-Nassau	0 – 9.40	Twente Fm (not studied)
	9.40 – 13.38	Kedichem Fm
	13.38 – 23.95	Tegelen Fm
Reusel	0 – 4.00	Twente Fm (not studied)
	4.00 – 18.00	Kedichem Fm
	18.00 – 59.00	Tegelen Fm
	59.00 – 73.00	Kiezeloöliet Fm
	73.00 – 83.00	Oosterhout Fm
	83.00 – 98.00	Breda Fm

References

- Aller, R. & P. Michalopoulos 1996 Controls on Fe diagenesis and authigenic mineral formation in terrigenous, nearshore environments. In: S.H. Bottrell (ed.): Proc. 4th Internat. Sympos. Geochem. Earth's Surface, 22–28 July 1996, University of Leeds: 15–18
- Argast, S.A. & T.W. Donnelly 1987 The chemical discrimination of clastic sedimentary components – *J. Sed. Petrology* 57: 813–823
- Bhatia, M.R. 1983 Plate tectonics and geochemical composition of sandstones – *J. Geol.* 91: 611–627
- Boenigk, W. 1970 Zur Kenntnis des Altquartärs bei Brügg. Geol. Instit. Universität Köln, 143 pp
- Buurman, P. 1972 Paleopedology and stratigraphy on the Condrusian peneplain (Belgium). PhD thesis, Wageningen, Pudoc, 67 pp
- Cox, R., D.R. Lowe & R.L. Cullers 1995 The influence of sediment recycling on evolution of mudrock chemistry in the south-western United States – *Geochim. Cosmochim. Acta* 59: 2919–2940
- Deer, W.A., R.A. Howie & J. Zussman 1992 An introduction to the rock-forming minerals, 2nd edition. Longman, Harlow, 696 pp
- Dellwig, O., H.J. Brumsack & M. Böttcher 1996 Geochemical characterisation of a Holocene sedimentary sequence from the NW German coastal area. In: S.H. Bottrell (ed.): Proc. 4th Internat. Sympos. Geochem. Earth's Surface, 22–28 July 1996, University of Leeds: 43–46
- Gibbard, P.L. 1988 The history of the great Northwest European rivers during the past three million years – *Phil. Trans. R. Soc. Lond. B* 318: 559–602
- Haese, R.R., K. Wallman, A. Dahmke, U. Kretzman, P.J. Müller & H.D. Schulz 1997 Iron species determination to investigate early diagenetic reactivity in marine sediments – *Geochim. Cosmochim. Acta* 61: 63–72
- Hakstege, A.L., S.B. Kroonenberg & H. Van Wijck 1993 Geochemistry of Holocene clays of the Rhine and Meuse rivers in the central-eastern Netherlands – *Geol. Mijnbouw* 71: 301–315
- Hillier, S. 1995 Erosion, sedimentation and sedimentary origin of clays. In: B. Velde (Ed.): *Origin and Mineralogy of Clays*. Springer, Berlin: 162–219
- Huisman, D.J. 1998 Geochemical Characterization of subsurface sediments in the Netherlands. PhD thesis, University of Wageningen, 175 pp
- Huisman, D.J., F.J.H. Vermeulen, J. Baker, A. Veldkamp, S.B. Kroonenberg & G.Th. Klaver 1997 A geological interpretation of heavy metal concentrations in soils and sediments in the southern Netherlands – *J. Geochem. Explor.* 59: 163–174
- Kasse, C. 1988 Early-Pleistocene Tidal and Fluvial Environments in the Southern Netherlands and Northern Belgium. PhD thesis. Amsterdam, Free University Press, 190 pp
- Kroonenberg, S.B. 1992 Effect of provenance, sorting and weathering on the geochemistry of fluvial sands from different tectonic and climatic environments. In: Proc. 29th Internat. Geol. Congr., Kyoto, Japan, Part A: 69–81
- Moura, M.L. & S.B. Kroonenberg 1990 Geochemistry of fluvial and eolian sediments in the south-eastern Netherlands – *Geol. Mijnbouw* 69: 359–373
- Newman, A.C.D. & G. Brown 1987 The chemical constitution of clays. In: Newman, A.C.D. (ed.): *Chemistry of clays and clay minerals*. Longman, Harlow: 1–129
- Porrenga, D.H. 1967 Clay mineralogy and geochemistry of recent marine sediments in tropical areas. PhD thesis, University of Amsterdam, 145 pp
- Postma, D. 1982 Pyrite and siderite formation in brackish and freshwater swamp sediment – *Amer. J. Sci.* 82: 1151–1183
- Roser, B.P. & R.J. Korsch 1986 Determination of tectonic setting of sandstone-mudstone suites using SiO₂ content and K₂O/Na₂O ratio – *J. Geol.* 94: 635–650
- Tebbens, L.A., A. Veldkamp & S.B. Kroonenberg 1996 The onset of postglacial soil formation recorded in Late Weichselian and Early Holocene Meuse river sediments (The Netherlands). In: S.H. Bottrell (ed.): Proc. 4th Internat. Sympos. Geochem. Earth's Surface, 22–28 July 1996, University of Leeds: 225–228
- Van Aniel, Tj.H. 1950 Provenance, transport and deposition of Rhine sediments. PhD thesis. Wageningen, Veenman, 130 pp
- Van Aniel, Tj.H. 1958 A defense of the term Alterite (Discussion) – *J. Sed. Petrol.* 28: 234–235
- Van Baren, F.A. 1934 Het voorkomen en de betekenis van kalihoudende mineralen in Nederlandse gronden. PhD thesis, Wageningen, Veenman, 118 pp
- Van den Berg, M.W. 1996 Fluvial sequences of the Maas. PhD thesis. University Wageningen, 181 pp
- Van Santvoort, P.J.M. & G.J. de Lange 1996 The process of oxidation of sapropels in eastern Mediterranean sediments, and its implications for paleoclimatic interpretations. In: 3e Nederlands Aardwetensch. Congres, 2, 3 May 1996, Veldhoven, Abstracts 1: 90
- Zagwijn, W.H. 1960 Aspects of the Pliocene and Early Pleistocene vegetation in the Netherlands. PhD thesis, Leiden. Meded. Geol. Stichting, Serie C–III–1, 6, 78 pp
- Zagwijn, W.H. 1985 An outline of the Quarternary stratigraphy of the Netherlands – *Geol. Mijnbouw* 64: 17–24
- Zagwijn, W.H. 1989 The Netherlands during the Tertiary and the Quarternary: a case history of coastal lowland evolution – *Geol. Mijnbouw* 68: 107–120
- Zagwijn, W.H. & J.W.C. Doppert 1978 Upper Cenozoic of the southern North Sea Basin: palaeoclimatic and palaeogeographic evolution – *Geol. Mijnbouw* 57: 577–588
- Zagwijn, W.H. & C.J. Van Staaldunin 1975 Toelichting bij geologische overzichtskaarten van Nederland. Haarlem, Rijks Geol. Dienst, 134 pp