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Sediment mineralogy and geochemistry

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ABSTRACT

Insight in the mineralogical and the geochemical composition of Dutch geological sediments is needed for environmental management of the subsurface. A comprehensive overview of these compositions is given in this chapter. The first part of this chapter deals with the mineralogy of the Paleozoic and Mesozoic sedimentary rocks where properties of the rocks are discussed per stratigraphic period. The information presented is mainly based on studies that had a commercial interest in exploring and exploiting the associated natural resources, which gives some indication of what has been studied. The detrital versus diagenetic origin of minerals is considered as fully as possible. The second part covers the Cenozoic, unconsolidated sediments where both the mineralogical and the geochemical compositions are considered. The studies that are summarized were diverse in scope and dealt with the soil and deeper Cenozoic sediments. The sediment geochemical composition is first considered based on results of factor analysis, which has frequently been applied in sediment-geochemical studies. Next, individual elemental relationships are presented for several minor elements. Then the mineralogy is briefly considered for quartz, feldspars, heavy minerals, clay minerals and carbonates, whereby notable differences as well as similarities are discussed. Finally, four specific features are discussed that are worth to be summarized from an environmental perspective: bog iron ores, trace elements in pyrite, sulphur in peat, and lead and its isotopes in soils.

<< A freshly excavated clay deposit (1 m ruler for scale) with redox layering (Tegelen Member, Maalbeek quarry, southeast Netherlands). Photo: Jasper Griffioen.

DOI: 10.5117/9789463728362_ch13

Introduction

The objective of this chapter is to present a comprehensive overview of the mineralogical and geochemical properties of Dutch geological sediments, where geochemical refers to the elemental composition. Staring (1856) and contemporaries already paid attention to the mineralogical and geochemical composition of Dutch sediments and soils. The occurrences of shells, bog iron ore and reactive Fe minerals were frequently addressed in his monograph on Dutch soils. Since then, mineralogical and geochemical analysis of Dutch geological sediments, soils and rocks has been performed to characterize these solid geo-materials for a broad range of purposes. Examples refer to: provenance and geological stratigraphy (Baak, 1936; Schuttenhelm & Laban, 2005), properties of oil and gas (and geothermal) reservoirs (Gaupp & Okkerman, 2011), soil genesis and biogeochemical cycling (Zuur, 1936; Kooistra, 1978; Mol et al., 2003), background composition and the natural range of variation (Tebbens et al., 2000; Van der Veer, 2006), anthropogenic enrichment and impact of land use (Spijker et al., 2005; Van Gaans et al., 2007), weathering rates in relation to critical acid loads (Van der Salm, 2001), the geo-availability and reactive transport of trace elements (Van der Grift & Griffioen, 2008; Zhang & Oliver, 2009), production of drinking water (Saaltink et al., 2003; Antoniou et al., 2013), subsurface disposal of radioactive waste (Koenen & Griffioen, 2016; Hoving et al., 2017, 2020), geo-scientific mapping in general (Huisman et al., 2000; Goldberg et al., 2021).

Overviews on the geochemistry and mineralogy of Dutch sediments are limitedly present. The geochemical soil atlas of the Netherlands was presented as a national reference by Mol et al. (2012) and primarily addresses the elemental composition of shallow soils. Griffioen et al. (2016) recently wrote an extensive review of the mineralogical composition of Cenozoic sediments in which fresh sediments and suspended matter in marine, riverine and limnological environments were also addressed. To date, there are no overviews for the geochemical composition of Cenozoic, Mesozoic and Paleozoic sediments.

The full range from Paleozoic to Cenozoic sediments is addressed in this chapter. The set-up of the overview for the Paleozoic and Mesozoic sediments differs from that for the Cenozoic sediments. For the first, qualitative, summarising descriptions of the mineralogy are presented per geological unit for the entire Dutch subsurface; both on- and offshore. For the Cenozoic, quantitative descriptions of the geochemical and mineralogical properties of the different types of sediments are provided supported with statistical or other quantitative data. Here, focus is on the deposits on land, which have been studied much more intensively than in the offshore. Some attention is also paid to anthropogenic contamination of soils and sediments with trace metals. Four specific, geochemical topics are highlighted that are relevant from an environmental perspective and have not been summarized before: bog iron ores, trace elements in pyrite, sulphur speciation in peat and isotope geochemistry of lead.

Approach

For this overview, existing literature was consulted and original data were used. The mineralogy and petrography of the Paleozoic and Mesozoic sedimentary rocks were mainly studied with thin section petrography for quantitative and descriptive analyses of the components, including their mineralogy, texture and paragenesis. In addition, XRD was applied for the minerology of the bulk rock and, in particular, the clay fraction. Thin section petrography and SEM analysis have the advantage that the detrital and authigenic minerals and components can be distinguished and their spatial and temporal relationship can be determined. Moreover, the effects of diagenesis, including changes in the mineralogy and texture, on the sediment and the reservoir-aquifer quality can be reconstructed. This is done by the interpretation of the spatial relationships of grains, cementing minerals and pores. Open, geochemical data from Paleozoic and Mesozoic sedimentary rocks are only limitedly available for the Dutch subsurface. Most geochemical data are company confidential data, which could therefore not be included in this review.

The most common methods used in studying the mineralogical composition of the Quaternary sediments have been optical microscopy and X-ray diffraction (XRD). The first was traditional in the past and has become uncommon in the last decades. It especially refers to analysis of heavy minerals for stratigraphic and provenance studies. XRD-analysis has transformed into a quantitative approach in more recent years, including XRD-analysis of clay assemblages (e.g. Zeelmaekers, 2011). About 300 XRD-analyses of geological sediment and soil samples were available from recent research projects and literature as old as Favejee (1951). As applied to Dutch sediments, the most common methods used to study the bulk geochemical composition have been X-ray fluorescence analysis (XRF) and ICP analysis following aqua regia destruction. Other methods that have been used intensively are thermographimetric analysis and CS-elemental analysis, especially to characterize the organic matter and carbonate contents. Various other methods have been applied, including various selective and sequential extraction techniques. More than 15,000 geochemical analyses were available from research projects over the past 30 years. Most of these projects were performed by TNO –

Geological Survey of the Netherlands and its predecessors, while several were performed by research institute KWR (or its predecessor KIWA) for drinking water companies, and others by PhD students.

The mineralogical and geochemical compositions of sediments are strongly interlinked but cannot be set equal to each other as the chemical elements may be distributed among various minerals major or not. The mineralogical composition of Dutch, Quaternary sediments has frequently been deduced from geochemical analysis using chemometric methods (e.g. Van Gaans et al., 2011; Griffioen et al., 2012). When translating the geochemical composition to the mineralogical composition of sediments, one should bear in mind that such approaches are based on assumptions. One such assumption is that carbonates are found as calcite and aragonite, which neglects the occurrence of dolomite, siderite and also ankerite. However, other studies have shown that these carbonates are also present in Dutch sediments (e.g. Salomons, 1975; Huisman & Kiden, 1998). Another major assumption is that sulphur in Cenozoic sediments is predominantly found as pyrite, which may not always be true. Some studies showed that gypsum and jarosite are present in the soil of reclaimed marine polders (Van Dam & Pons, 1972; Miedema et al., 1973).

Sediment mineralogy of Paleozoic and Mesozoic sedimentary rocks

Introduction

The Dutch Paleozoic and Mesozoic subsurface demonstrates a complex geological history and contains siliciclastic, carbonate and evaporite deposits (De Jager et al., 2025, this volume). Lithologies often occur in separate stratigraphic intervals and in a framework of permeable (mostly sandstones but also carbonates) and impermeable (shales and evaporites) lithologies. The present-day mineralogical composition and petrophysical properties of sediments in general are the result of provenance, depositional processes and early to late diagenetic processes. The burial history, and resulting factors such as maximum burial depth, temperature and effective pressure reached, residence time at depth and uplift and depressurising, are external factors influencing burial diagenesis. Internal factors are the initial mineralogical composition of the clastic as well as carbonate sediments in combination with their texture. As a consequence, the mineralogical composition can always be expected to be highly variable and the rocks in the Dutch subsurface are indeed no exception.

The main petrophysical properties relevant for both hydrocarbon and geothermal reservoirs are porosity and permeability, which affect their storage and flow capacity. The roughness of pore surfaces and wettability play an important role and are governed by the mineralogical composition of detrital grains and diagenetic cements. The mineralogical composition is of great importance for geothermal exploitation since induced fluid flow or induced temperature changes will cause fluid-rock interactions that will change the chemistry of the pore fluids, which may have adverse consequences. The sedimentary and also diagenetic components may dissolve as a consequence of induced physical-chemical changes, such as changes due to CO_2 sequestration (e.g. Laenen et al., 2004), which may cause precipitation of minerals along the fluid flow either within the sediments or in the technical installations. In addition, dissolved minerals may be nutrients to bacterial growth. The mineralogical composition of shales has an effect on their ductility, which may be relevant for their sealing capacity. Some other examples of the importance of understanding mineralogical and textural properties of the subsurface on hydrocarbon exploitation and geothermal production are the presence of quartz and carbonate cements preventing sand production, formation damage caused by authigenic clay minerals and the presence of minerals reactive to introduced fluids such as feldspars and clay minerals.

Mineralogical studies of Paleozoic and Mesozoic sediments in the Netherlands have virtually only been carried out where the mineralogy (rock salt) and rock properties (hydrocarbon and geothermal reservoirs) are of commercial interest. In the Netherlands and neighbouring countries, Permian and to a lesser degree Triassic sandstones have been most intensively studied petrographically and petrophysically (e.g. Glennie et al., 1978; Hancock, 1978; Gaupp & Okkerman, 2011; Olivarius et al., 2015), because they contain most of the economic gas and oil reservoirs. Relatively recently, interest in Triassic sandstones rose because they form potential geothermal reservoirs in parts of the onshore. Less is known about upper Carboniferous (Namurian-Stephanian) sandstones, simply because they contain less hydrocarbons. Carboniferous sandstones are often rather tight and low permeable, with a few exceptions of the Coevorden field (Kombrink et al., 2007) and in the Dutch-British border area (Huis in ’t Veld et al., 2020). Carbonates have locally been the subject of studies where they form reservoirs in the lower Carboniferous (Gökdag, 1982), Zechstein (Clark, 1986; Reijers, 2012), Muschelkalk (Pöppelreiter et al., 2004, 2005; Borkhataria et al., 2005, 2006) and Late Cretaceous chalk (Scholle, 1977; Taylor & Lapré, 1987; Hjuler, 2007). Evaporites and shales were of interest when forming regional seals and/or source rocks (Wei & Swennen, 2022; Remmelts et al., 2025, this volume). Rocksalt deposits have only rarely been cored and described petrographically (e.g. wells Barradeel Salt-1; Pieterburen-1; see www.nlog.nl for information on deep oil, gas and geothermal wells), partly because of their mechanical and chemical instability. In parts of the Netherlands, sufficient petrographic research has been published for some of these mentioned economic stratigraphic units to provide a robust overview. This includes the West Netherlands Basin, The Roer Valley Graben, Groningen and Friesland, and offshore areas south from the E and F quadrants. Summary maps of areas with hydrocarbon interest of the individual formations can be found in Remmelts et al. (2025, this volume). Very little is known for other areas, including the upper Carboniferous coal-bearing sediments in the Limburg area, as there was apparently a lack of interest in the mineralogy of their inorganic components, and as mines were closed already before 1975. For areas without sufficient data only basic descriptions based on the general literature and models can be given and observations from adjacent areas such as the Carboniferous in the Campine Basin in Belgium (e.g. Bertier et al., 2008). Most studies that form the basis of this chapter are single-well industry studies published on the NLOG website (www.nlog.nl/datacenter/brh-overview).

Detrital composition and clastic source areas

The supply of siliciclastic detritus or its absence determines whether clastic sediments or carbonates and evaporites were deposited. Hybrid deposits are rarely present in the Dutch subsurface; one of them is the Triassic Rogenstein (Palermo et al., 2008; McKie & Kilhams, 2025, this volume). Carbonates (Tournaisian-Visean, Triassic Muschelkalk, Zechstein, Cretaceous chalk) and evaporites (Zechstein, Middle Triassic, locally Jurassic and Cretaceous) formed or precipitated only when there was little or no siliciclastic sand and/or clay influx. Carbonates and evaporites formed in situ, biogenically or chemically respectively, but were also locally eroded and reworked.

The provenance, also influenced by climatic and tectonic activity, determines the initial mineralogical composition of the sediment. The main clastic source areas were the London Brabant Massif in the southwest, the Rhenish Massif in the southeast, the Vindelician-Bohemian Massif in the far southeast, the Mid North Sea High (MNH) in the northwest, and the Ringkøbing-Fyn High (RFH) area in the northeast (De Jager et al., 2025, this volume). Detrital input from the Fennoscandian Massif is uncertain for the Dutch subsurface. These areas remained the main source areas during the Devonian until the Late Triassic at least. The Carboniferous Variscan orogeny formed a main tectonic activity phase and in front of the deforming Variscan Mountains, a late Carboniferous foreland basin was filled with a thick succession of molasse-type clastic deposits. After the Variscan orogeny, the source areas became increasingly denuded and as a consequence were less prolific clastic source areas. Related to these key changes in the source areas, also the detrital composition changed accordingly (Fig. 13.1 and discussions in next sections).

Not only the overall paleogeographic setting, but also local factors were of influence on the detrital composition and depositional processes. Permo-Carboniferous volcanism provided a local source of detritus (Van Bergen et al., 2025, this volume), while diapiric movements of Zechstein evaporites caused both local uplift and deformation of overlying younger deposits and also created accommodation space (De Jager et al., 2025, this volume). Rifting periods and associated block faulting determined the location of depocentres, and local erosion of intrabasinal older deposits provided an additional source of sediments (Verreussel et al., 2025, this volume). Rapid lateral variations in the amount of subsidence and uplift played an important role in the inverted West Netherlands and Broad Fourteens basins and in the Dutch Central Graben, making prediction of reservoir properties difficult. Maximum (paleo-)burial depths, and thus the effects of diagenesis, can change quickly laterally, and consequently the mineralogical composition and petrophysical properties are difficult to extrapolate. Not only sediment input from the hinterland but also reworking of older deposits within the basin are important for understanding the primary mineralogy and lateral changes of clastic sediments in the Netherlands. In places, changes in accommodation space and local uplift caused synsedimentary diagenesis resulting in hardgrounds, for instance in the Upper Cretaceous Chalk Group (Molenaar & Zijlstra, 1997).

Diagenesis

Grey paleosols in the Namurian-lower Westphalian are often related to vegetated paleosurfaces and coal beds, and red aridisols in the upper Westphalian-Stephanian reflect a gradual aridization of the paleoclimate. In fluvial and eolian deposits of the Upper Rotliegend Group and the Lower Germanic Trias Group, early diagenesis started with clay infiltration and clay grain coating development, nodular calcrete and dolocrete development in calcareous paleosols, and anhydrite and possibly gypsum crystal growth in fine-grained floodplain-playa deposits. Early marine or terrestrial diagenesis was important in several stratigraphic units. Early marine diagenesis comprises marine hardground development by carbonate cementation, phosphate accumulation and glauconite development in Jurassic deposits and the formation of marine hardgrounds by calcite cementation in chalk. Such hardgrounds are often linked to local diapiric uplift.

The present-day burial depths of the stratigraphic units relevant for hydrocarbon and geothermal exploration and exploitation vary quite significantly. For the Cretaceous, the maximum burial depth ranges from 750 m in

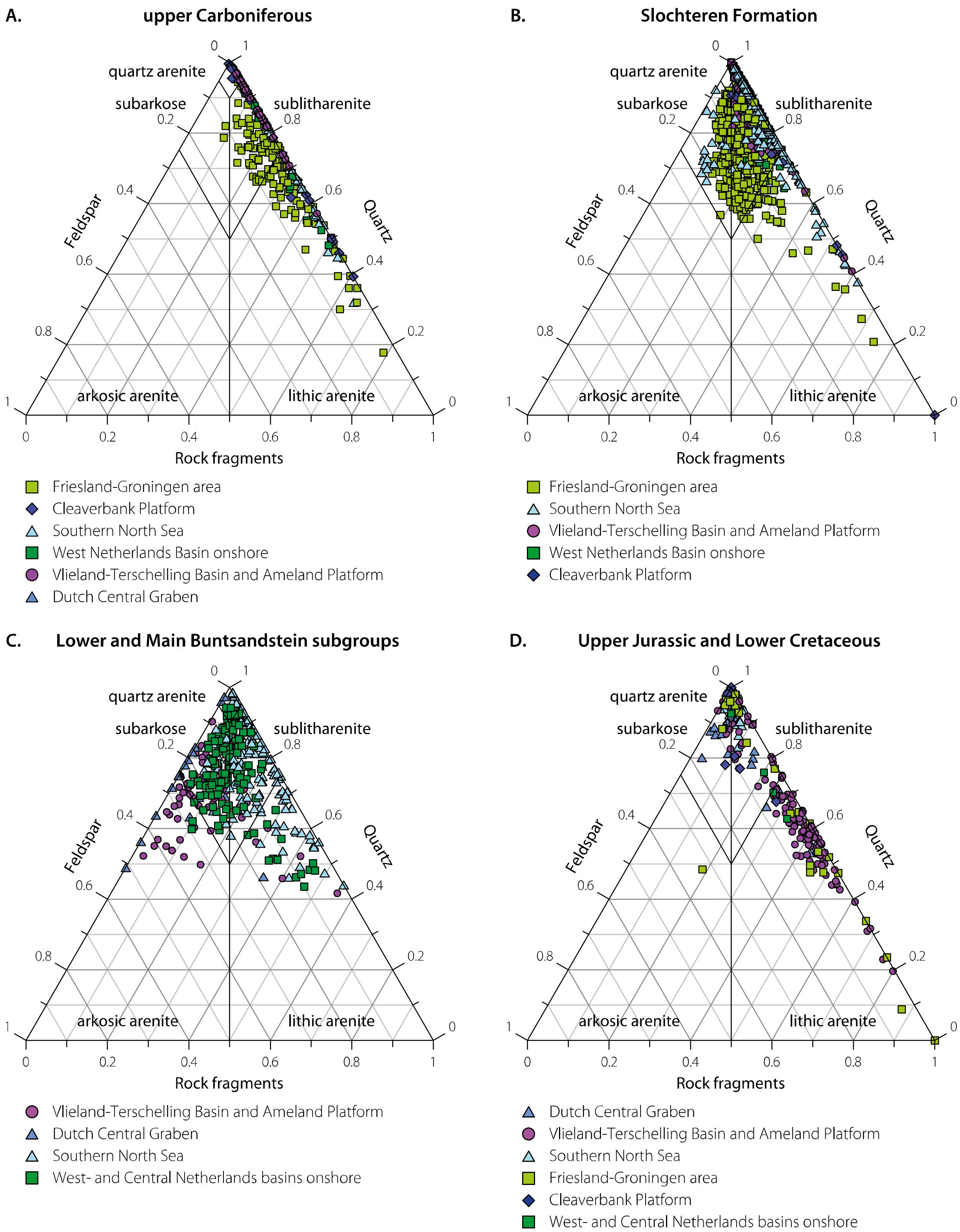


Figure 13.1. Detrital composition of arenites and wackestones for four different sandstone units in the Dutch subsurface. a) Upper Carboniferous. b) Slochteren Formation. c) Lower and Main Buntsandstein subgroups. d) Upper Jurassic and Lower Cretaceous. Detrital quartz is monocrystalline and polycrystalline quartz; feldspars comprise orthoclase, albite and minor microcline; rock fragments comprise extrabasinal fragments from magmatic and metamorphic rocks, Permo-Carboniferous volcanic rock fragments and intrabasinal sedimentary grains, including clay-shale and glauconite grains. See main text for discussion.

the southern part of the Netherlands to more than 2750 m in parts of the offshore K- and L-quadrants (Duin et al., 2006). Upper Permian and Triassic sandstones have been buried from about 2000 m down to more than 5000 m in the Dutch Central Graben (Duin et al., 2006). The burial depth of upper Carboniferous sandstones is in most places between 3000 to far more than 6000 m depth.

Burial diagenesis modified the original composition and texture of sandstones, carbonates, evaporites and clays. The more reactive minerals they contained originally, the more the mineralogy and also the texture changed due to diagenesis. A main and usually first process in sandstones is mechanical compaction which reduces the initial intergranular porosity and permeability (Paxton et al., 2002).

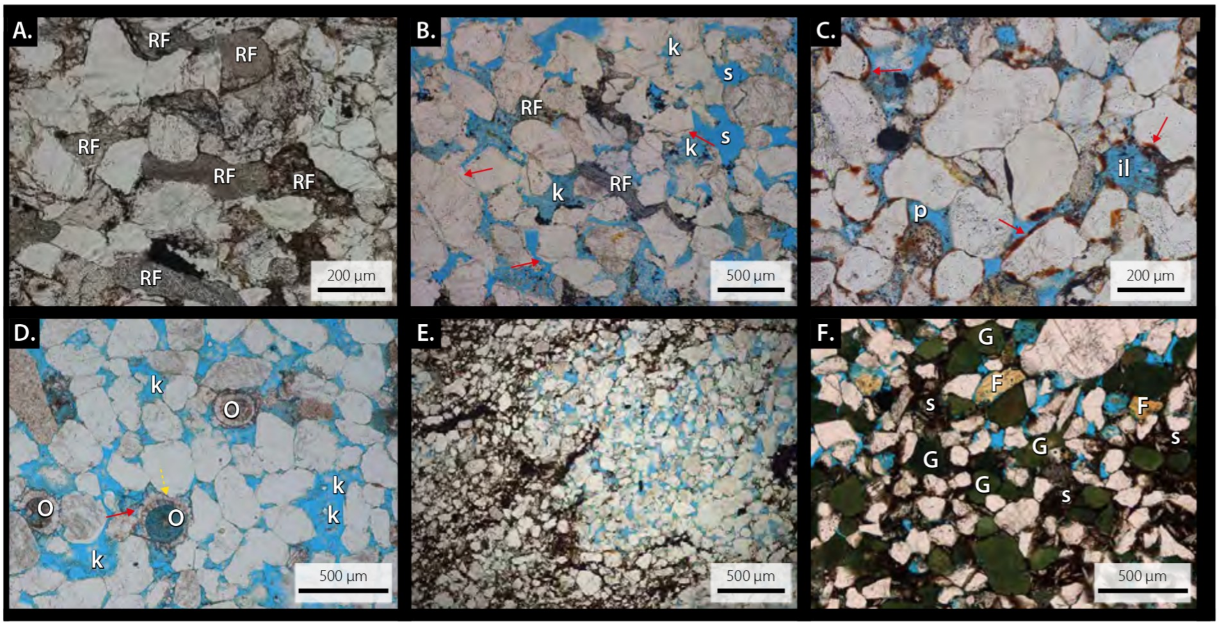


Figure 13.2 *Thin sections of sandstone units in the Dutch subsurface (blue resin shows porosity). Note that a) and b) illustrate two endmembers (see Fig. 13.1) of the range in detrital compositions (respectively lithic and quartz arenites) and the effect on diagenesis and final petrophysical properties of upper Carboniferous sandstones. a) In this lithic arenite, ductile rock fragments (RF) are abundant, most of which were deformed during burial compaction that significantly reduced the intergranular pores. Sample from the Bolsovian (WF-C), Lower Saxony Basin. b) Quartz arenite in which the amount of rock fragments was limited and the degree of compaction was therefore also limited. The dispersed rock fragments (RF) were nevertheless deformed by compaction. Dissolution of detrital feldspars caused precipitation of authigenic kaolinite (k) in the secondary pores. Some other detrital grains dissolved completely leaving oversized secondary pores (s). In parts of the sandstones with clean quartz grains, quartz cement overgrowths (red arrows) developed. Sample from the Asturian (WF-D), Cleaverbank Platform. c) Typical example of Permian Slochteren Formation sandstone (North Sea). Most of the detrital quartz grains are partly covered with hematite-stained red clay cutans (red arrows). Some feldspar grains dissolved leaving authigenic kaolinite and illite (il) clay minerals and authigenic feldspars in the secondary pores. The sandstone was compacted but ample intergranular pores (p) remained open. d) Example of a sandstone from the Triassic Volpriehausen Formation with dominant quartz grains and dispersed carbonate ooids (o). The quartz grains have thin and often incomplete quartz overgrowths (white arrows) whereas the ooids have rims of dolomite cement which precipitated in multiple phases (yellow and red arrows). Authigenic kaolinite (k) occurs in oversized pores after dissolution of detrital feldspar. The kaolinite formed loosely stacked booklets randomly oriented. e) Example of marine sandstone (Alblasserdam Member, Lower Cretaceous) with intense bioturbation. Some of the burrows have a sand infill that is slightly larger grained, better sorted and without a clayey matrix but with ample intergranular pores, whereas the adjacent bioturbated sandstone is matrix rich and poorly sorted. Bioturbation increased the heterogeneity of sandstones. Note that the quartz grains have virtually no quartz overgrowths, probably because the burial depth was insufficient here. f) Jurassic Greensand (Scruff Greensand Formation, Dutch Central Graben), characteristic of many Upper Jurassic and Lower Cretaceous greensands. The green grains (G), consisting mainly of the mineral glauconite, were deformed by compaction, depending on the mechanical stability of the surrounding grains. Some intrabasinal glauconite-quartz silt fragments and clay grains occur with euhedral siderite crystals (s) in the clay matrix. Authigenic siderite crystals also occur in the dispersed clay matrix. The greensand was bioturbated, leaving parts with clayey matrix and other parts with little or no matrix and with intergranular pores. Some phosphate grains with intragranular pores occur, derived from marine hardgrounds. Some other grain types largely dissolved leaving secondary pores.*

Thereafter, carbonate, quartz and clay mineral cementation further reduce the porosity and lithify the sandstones. In particular clay mineral cements reduce the permeability. Locally, anhydrite and halite partly fill remaining pores. In the process, pore fluids were either expelled and/or became overpressured. Precipitation of diagenetic minerals and dissolution of components are impacted by the composition of the pore fluids which continuously changed through rock-fluid interactions, and on the availability of nucleation sites for precipitation (e.g. Ajdukiewicz & Larese, 2012; Molenaar & Felder, 2018).

In the following sections, the detrital mineralogical composition and the post-depositional mineralogical and textural changes of the main commercially interesting sediments in the Netherlands are briefly summarized.

Carboniferous

In the south of the Netherlands, the lower Carboniferous Dinantian (Tournaisian-Visean) is composed of shallow-marine fossiliferous limestones, dolostones and shales (e.g. wells S02-02, Q18-01, Californie-GT-1). Their basic lithology is discussed in Huis in 't Veld & Den Hartog Jager (2025, this volume) and Vis et al. (2025, this volume). Generally, these carbonates are tightly calcite cemented or dolomitized (e.g. Reijmer et al., 2017) and have low porosity and permeability. Recently, these carbonates became of increased interest as deep geothermal reservoirs, because of exposure-related karstic porosity (Van Hulten, 2012; Jaarsma et al., 2013, 2018; Mozafari et al., 2019), fracture permeability (Van Oversteeg et al., 2014) or their interaction (e.g. Californië geothermal wells, published on NLOG). In the transition to the terrestrial Namurian deposits, organic-rich shales of lower Namurian Geverik Member of the Epen Formation, have shale gas potential (Wei et al., 2021).

Namurian and lower Westphalian clastic deposits were deposited under humid climate conditions, while during the late Westphalian and Stephanian the climate became more arid (Peyser & Poulsen, 2008; Tabor & Poulsen, 2008). The sandstones are fluvial to deltaic channel-fill deposits (e.g. Kombrink et al., 2007, 2008), whereas the shales and coals are paralic to floodplain related and locally marine (Dreesen et al., 1995; Huis in 't Veld & Den Hartog Jager, 2025, this volume). The detrital composition is highly variable ranging from lithic arenites and arkosic arenites to quartz arenites, with low feldspar contents. These are partly regional variations due to minor provenance differences, but also within each region the composition is highly variable, in particular with respect to the amount of rock fragments (Fig. 13.1a). The sandstones in the Lower Saxony Basin and Friesland-Groningen area contain more feldspars and more metamorphic rock fragments, including schist and phyllite rock fragments than other areas (Becker et al., 2017). Volcanic rock fragments are rare. The detrital feldspar content is predominantly below 5 vol%. In some wells a significant fraction of detrital feldspars is replaced by kaolinite (well Deurningen-1), indicating that the feldspar content at the time of deposition was higher. Mica is another common minor detrital component in the upper Carboniferous sandstones. The detritus was derived from the, partly synsedimentary evolving, Variscan Mountains and from reworking of the foreland molasse in the south (Remmelts et al., 2025, this volume). However, also quartz arenites occur, mainly in the Cleaverbank Platform, with clastic supply from the north.

Depositional environment-related early diagenetic cement in the upper Carboniferous sandstones is siderite in lacustrine and paralic environments and pyrite in marine beds and in intervals with plant remains, such as coals. Locally in upper Westphalian and Stephanian sandstones, hematite-stained dolomite rhombohedra occur, which are thought to represent partly dissolved and oxidized former iron-rich dolomites related to surface exposure and weathering below the Base-Permian Unconformity (e.g. Besly et al., 1993).

Schist and phyllite rock fragments as well as mica grains became ductile during burial, resulting in a high degree of mechanical compaction or even complete framework collapse (Fig. 13.2a). In sandstones with common ductile lithic grains and mica, the degree of compaction is therefore high, with very high deformation of lithic grains leading in some cases to pseudomatrix development. The high degree of compaction explains the low porosity and permeability of most of the sublitharenites and lithic arenites (e.g. Bertier et al., 2008).

The main post-compactional cements are quartz and carbonates, both in highly variable amounts in each stratigraphic unit (Fig. 13.3). In sandstones with very small amounts of ductile lithic grains, the long period of burial below 2 km depth has not caused more quartz cementation. For instance, the high reservoir quality sandstones in the Cleaverbank Platform area have quartz cement contents below 8 vol% (e.g. wells D12-05, D15-FA-101, E18-3, Fig. 13.2b). Higher contents only occur in very few individual wells, such as K18-9. Overall, the range of quartz cement and carbonate contents overlaps in all regions and stratigraphic units in the Dutch subsurface.

Kaolinite and illite are the dominant clay minerals in sandstones (Fig. 13.4) and in shales interbedded in the sandstones, with variable amounts of illite/smectite and minor chlorite. Smectite is rare to virtually absent due to burial illitization (e.g. Lanson et al., 1996; Molenaar and Felder, 2018). Both, thin section point-count data and XRD clay fraction data (Fig. 13.4) show no indication of a systematic increase or decrease of any clay mineral rel-

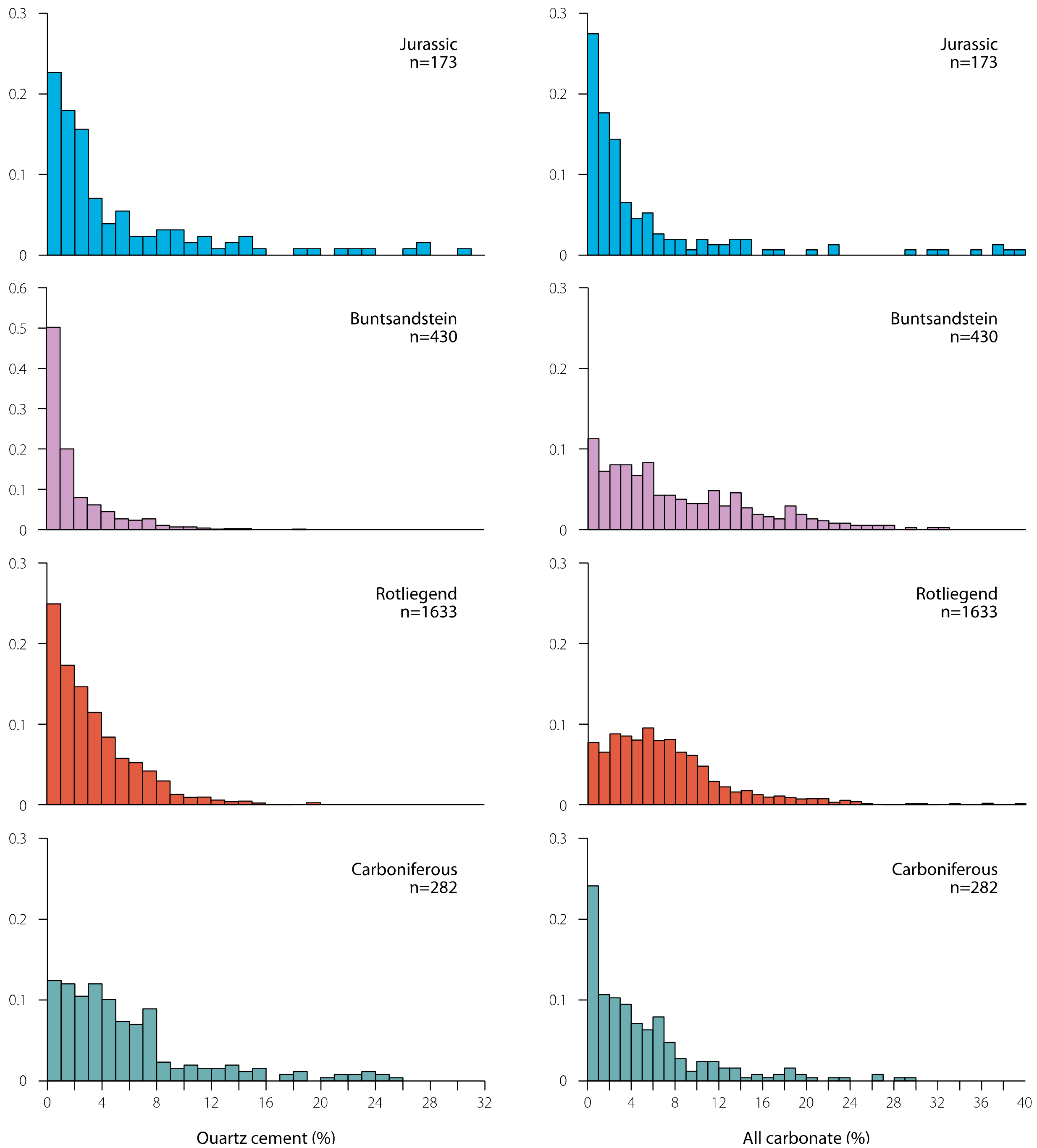


Figure 13.3. Left: Frequency of point-counted quartz cement content in vol% for the sandstone units. Right: Frequency of the content in vol% of all carbonates. Note that the total carbonate content is displayed, because grains and cements were often not distinguished in the point counts.

ative to younger stratigraphic units. This reflects similar provenance areas through time. Some stratigraphic levels in the Upper Rotliegend Group have higher chlorite contents, mainly as authigenic chlorite rim cement, whereas Jurassic deposits have high amounts of illite/smectite.

Permian

The Permian Upper Rotliegend Group (including the Slochteren Formation with Lower and Upper Slochteren members) is mainly composed of fluvial and eolian sandstones with interbedded playa shales, all deposited under hot, arid desert conditions (Grötsch & Gaupp, 2011). The sandstones are mainly sublitharenites and minor subarkoses, lithic arenites and quartz arenites (Fig. 13.1b). The main source of the siliciclastic detritus in the Permian deposits were the Variscan Mountains towards the south, and the eastern part of the Southern Permian Basin from which eolian deposits were mainly derived (Gaupp & Okkerman, 2011; Grötsch & Gaupp, 2011). Frequent local reworking is proven by common intrabasinal clay grains, which range from clay to granule size, dolomite grains (Molenaar & Felder, 2019) and occasional anhydrite grains (Henares et al., 2014). These intrabasinal grains can be the dominant type of rock fragments and had significant effect on diagenesis, more so than extrabasinal rock fragments, which include metamorphic and magmatic rock fragments. The latter were derived from the Variscan Mountains in the hinterland. Volcanic rock fragments occur especially in the northeast of the Netherlands in the Friesland-Groningen area and the adjacent offshore area (well Zeerijp-3A; NAM, 2017) as well as in northwest Germany (Hancock, 1978; Gaupp & Okkerman, 2011). These volcanic rock fragments are most likely derived from Carboniferous to lower Permian volcanic rocks from the Ems Graben area and in Germany (Hancock, 1978; Van Bergen et al., 2025, this volume). The feldspar content and composition (orthoclase and albite, rare microcline) show a regional change in the Slochteren Formation. The feldspar content is generally higher in the Friesland-Groningen area and the adjacent offshore area than in the North Sea towards the west (Fig. 13.1b), where K-feldspar is the dominant feldspar (e.g. wells L16-16A, K12-17). Both plagioclase and K-feldspar occur in the Groningen area (e.g. well Zeerijp-3A).

The Slochteren Formation sandstones are mostly orange to red, and are similar to sand in many modern deserts. Due to the hot, arid paleoclimate during the Permian, chemical weathering at the surface was minimal during times of low net deposition. Instead, dust and detrital clay particles with some iron oxides, now hematite, could infiltrate and settle in the sediment and cover detrital grains, whereby the eolian and fluvial sands obtained the typical red to orange colour (Fig. 13.2c; Seemann, 1982; Pye & Tsoar, 1987; Molenaar & Felder, 2018). Such hematite-stained clay-coated siliciclastic grains occur in large parts of the Slochteren sandstones and are similar to sand deposits in many modern deserts.

The main intergranular cements in the Slochteren Formation sandstones are dolomite and quartz, which are both wide-spread. Locally anhydrite and rarely halite form the cement. Clay mineral cements (illite and chlorite) are also common. All of these cements precipitated after mechanical compaction. Compaction was enhanced by the presence of clay grains, shale clasts and carbonate grains. Dolomite has a distinct negative impact on the reservoir quality by filling intergranular pores and obstructing pore connectivity. Usually, non-ferroan dolomite predates ferroan dolomite, ankerite and siderite (Pye & Krinsley, 1986; Vincent et al., 2018; Molenaar & Felder, 2019; Miocic et al., 2020). Dolomite is commonly dispersed throughout sandstone and also occurs in thick amalgamated sandstone intervals and is not related with shale intervals or shale interbeds.

The origin of dolomite has lately been discussed (Vincent et al., 2018; Molenaar & Felder, 2019; Miocic et al., 2020). That faulting and influx of Zechstein fluids as postulated by Vincent et al. (2018) causing dolomite cementation is considered unlikely, because dolomite is also the dominant carbonate cement in areas with few or no faults. Dolomite is even dominant in the Lower Slochteren Member sandstones, where hundreds of metres of shales from the Silverpit Formation separate the Rotliegend from the Zechstein, and in areas without Zechstein salt.

Dolomite has been interpreted as cement in sandstones that formed during early diagenesis due to evaporation (Amthor & Okkerman, 1998). Some authors consider that the dolomite finds its origin as cement in fluids expelled from adjacent shales (Miocic et al., 2020). Dolomite occurs as an authigenic early diagenetic-pedogenic component in fine-grained playa deposits, which were reworked during subsequent fluvial and eolian activity (Molenaar & Felder, 2019). In most sandstones, part of the dolomite present comprises detrital grains, reworked from the fine-grained playa deposits, and only part is cement. The cement occurs as syntaxial overgrowths on the detrital carbonate grains and formed after compaction (Molenaar & Felder, 2019). Dolomite grains became pressure dissolved at grain contacts yielding carbonate for local dolomite cementation as overgrowths on detrital dolomite grains, thereby obscuring the original grain shape. Other carbonate grains dissolved completely leaving secondary pores.

Quartz cement can locally be abundant in the Slochteren Formation sandstones, but usually is present with less than 5-9 vol% (Fig. 13.3). In most cases, it can be clearly linked to the well-established model of clay-induced siliciclastic grain dissolution (i.e. chemical compaction) as silica source (Sibley & Blatt, 1976; Walderhaug & Bjørkum, 2003; Čyžienė et al., 2006) in combination with the need of nucleation sites for quartz cement precipitation (Pittman et al., 1992; Ajdukiewicz & Larese, 2012). In the Slochteren Formation, grain rims of illite and chlorite cements retarded or even inhibited quartz cementation (Busch et al., 2020).

Illite is an important diagenetic mineral in the sandstones (Gaupp et al., 1993; Gaupp & Okkerman, 2011; Molenaar & Felder, 2019). A few percent of illite cement can already have a significant negative effect on the reservoir quality. How much depends on the origin and texture of the illite. Some authigenic illite occurs in secondary pores after partial or complete dissolution of detrital K-feldspar grains, which has little if any effect on porosity and permeability (Molenaar & Felder, 2019). In some stratigraphic levels, illite cement forms rims around detrital grains with crystals oriented perpendicular-oblique to

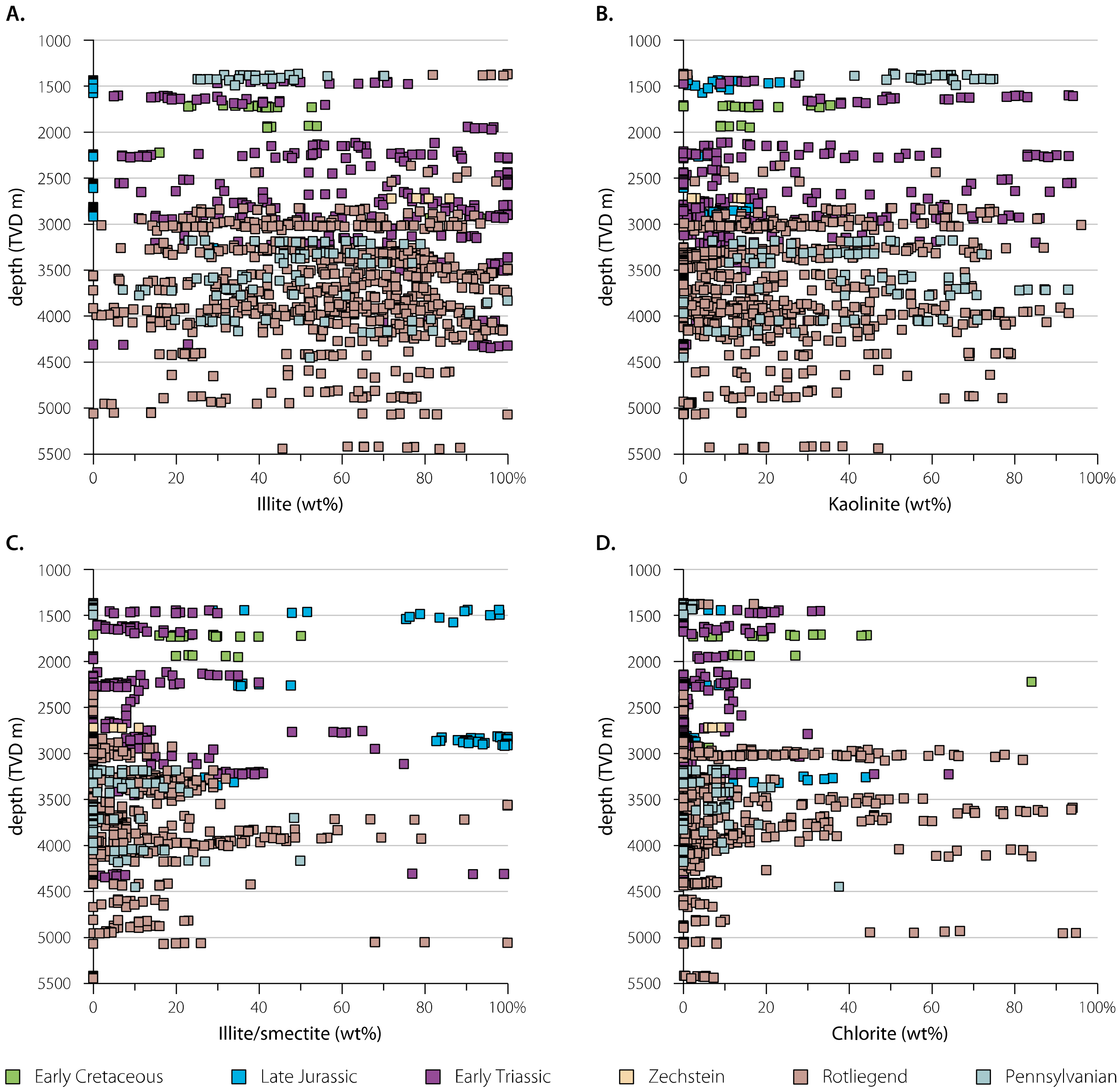


Figure 13.4. Clay fraction XRD results versus core depths, showing clay mineral percentages, mainly from sandstones but also from interbedded shales. Note that the maximum burial depth may have been larger than at present, but insufficient information is available to use it for the individual datasets in this plot. The mineral contents are given in weight%. Note the clay mineral contents show a wide range. a) Illite. b) Kaolinite. c) Illite-smectite. d) Chlorite (mostly clinochlore).

grain surfaces and may even bridge and fill pores completely. This authigenic illite cement significantly decreases the permeability (Gaupp & Okkerman, 2011; Molenaar & Felder, 2018; Busch et al., 2020). The bladed, and in particular fibrous, illite crystals are friable and could cause formation damage when dislodged by induced fluid flow. The origin of the illite rim cement was formerly considered to be linked to fluid flow along open faults derived from the Zechstein or Carboniferous and to illitization of kaolinite (Pye & Krinsley, 1986; Gaupp et al., 1993; Lanson et al., 1996). More likely, a local origin is associated with diagenesis of the detrital clay coatings around siliciclastic grains, causing precipitation of illite during burial after compaction (Seemann, 1982; Molenaar & Felder, 2019). Geochemical work done by Platt (1994) supports the view that the Zechstein derived formation waters only played a role in some horst blocks, where the Zechstein is juxtaposed to sandstones of the Upper Rotliegend Group. However, this is contradicted by the wide-spread regional occurrence of the illite cement.

Kaolinite is another common diagenetic mineral in the Slochteren Formation sandstones (Pye & Krinsley, 1986; Gaupp et al., 1993; Gaupp & Okkerman, 2011), but is absent in some areas, such as in well P02-07. It usually occurs with up to 10 vol% as randomly oriented thin booklets of crystals in grain-shaped secondary pores after dissolution of plagioclase feldspars (Fig. 13.2c), and rarely as larger clusters. The detrital clay assemblage in both sandstones and shales of the Slochteren Formation shows variable amounts of illite, kaolinite, chlorite and minor illite/smectite, similar to the detrital clay minerals found in Carboniferous and Triassic sandstones (Fig. 13.4). Smectite is usually not preserved in the Permian deposits. Increased chlorite contents can clearly be linked to the volcanic province in the east of the Netherlands (see also Gaupp & Okkerman, 2011).

The shales of the Silverpit Formation, overlying and partly laterally equivalent to the Slochteren Formation, are composed of silty-sandy shales and shaly silt- and sandstones with intervals of anhydrite and halite (Glennie et al., 1978; McKie, 2011; Bouroullec & Geel, 2025, this volume). The shale is mainly composed of illite and kaolinite. The silt- to sand-sized fractions contain quartz, dolomite, anhydrite and feldspar.

In the biggest part of the Southern Permian Basin, the Zechstein succession is dominated by evaporites, mainly anhydrite, halite and sylvite, and carbonates. It forms the impermeable seal for hydrocarbons in the underlying sandstones of the Slochteren Formation (Remmelts et al., 2025, this volume). Sandstones occur along the southern margin of the basin (Bouroullec & Geel, 2025, this volume) with similar mineralogy as sandstones in the underlying Slochteren Formation. Zechstein carbonates include oolithic- and calcimicrobial limestones and dolostones. The dolostones, usually with anhydrite, are either of synsedimentary early diagenetic origin (Peryt & Scholle, 1996) or may have formed primarily in an arid setting without calcium carbonate precursors under the influence of bacteria or as evaporitic precipitate (e.g. Bouroullec & Geel, 2025, this volume). The anhydrite could be a primary in situ precipitate formed by dehydration of primary gypsum near the paleosurface or at elevated temperature during burial. The topmost part of the Zechstein Group and Lower Germanic Trias Group are composed of shales of which the mineralogy is largely unknown.

Triassic

The sandy oolitic limestones (grainstones) and oolitic sandstones of the Rogenstein Formation (Lower Buntsandstein Subgroup) have been discussed and described in detail by Palermo et al. (2008). The ooids are mostly calcite and the sandstone is calcite cemented. Similar calcite ooids and calcite cemented ooid grainstone fragments also occur in the younger siliciclastic sandstones of the Main Buntsandstein Subgroup, e.g. in the Volpriehausen Formation and in the lower Detfurth Sandstone Member (e.g. well Q01-27, Fig. 13.2d). They were probably not eroded from the underlying Rogenstein Member but from laterally existing ephemeral lakes with ooids, analogue to the situation in the German Basin (Roman, 2004). Dolomitic ooids and partly dissolved ooids indicate replacement or dissolution of originally calcite ooids during diagenesis in some areas. In the Lower Germanic Trias sandstones, the ooids are usually slightly deformed and have pressure-dissolved contacts, yielding carbonate for carbonate cementation after or during late phases of compaction (Fig. 13.2d).

In many aspects, the mineralogical composition of the detrital and authigenic sandstone of the Main Buntsandstein Subgroup, Solling and Röt formations is similar to that of the Slochteren Formation sandstones. Differences are the low content of lithic grains derived from outside the Southern Permian Basin, the high feldspar content (Fig. 13.1c) and a higher total carbonate content in the sandstones of the Lower and Upper Germanic Trias Group. The detrital composition shows regional differences with enhanced feldspar contents in areas such as the West Netherlands Basin and Roer Valley Graben, the Dutch Central Graben and the Schill Grund High due to regional differences in provenance (Fig. 13.1c). The Broad Fourteens Basin and Friesland Platform have the lowest feldspar content and exhibit a wide range in the content of lithic components. The sandstones are mainly subarkoses, sublitharenites and minor arkosic arenites and lithic arenites with intraclasts and some quartz arenites. Intraclasts include calcite and dolomite ooids and intrabasinal dolomite grains and shale clasts, some with dolomite derived from eroded fine-grained playa deposits.

Sandstones are variably cemented by quartz, dolomite, kaolinite, anhydrite, halite and locally illite (see also Füchtbauer, 1967; Olivarius et al., 2015). The cementation and clay mineral composition are similar to the Slochteren Formation sandstones (Figs 13.3, 13.4), but anhydrite and halite are more abundant in sandstones of the Main Buntsandstein Subgroup, whereas illite is less common. The composition of the clay fraction shows the same variation as in the Slochteren Formation. Halite cement is only common in some areas. Most of the halite and anhydrite cements occur in compacted fabrics (e.g. wells M01-04 and L05-12; Füchtbauer, 1967) and thus formed after burial compaction, and not early as published by Purvis & Okkerman (1996). Halite cementation is probably related to local salt doming, lateral flow of halite supersaturated formation fluids and cooling of these brines (Dronkert & Remmelts, 1996). This preferentially cemented the coarser grained laminae. Authigenic feldspar (orthoclase and albite) is a minor but common cement that, apart from a few exceptions is largely absent in the Slochteren Formation sandstones. This probably reflects minor differences in provenance. The authigenic feldspar forms thin overgrowths on detrital feldspar grains.

The main carbonate interval of the Triassic is the Muschelkalk Formation, comprising shallow-marine limestones, dolostones and marls (Borkhataria et al., 2005, 2006; McKie & Kilhams, 2025, this volume) with intercalated evaporites. Evaporites also occur in the overlying Keuper Formation, indicating prevailing hot arid paleoclimate conditions (McKie & Kilhams, 2025, this volume). Dolomitization of limestones occurred during early diagenesis where meteoric water or more likely, evaporitic brines periodically flushed the sediment (Pöppelreiter et al., 2004; Borkhataria et al., 2006).

Jurassic and Lower Cretaceous

The Jurassic and Lower Cretaceous deposits are very similar with respect to their depositional setting (Herngreen et al., 2003; Trabucho Alexandre & Wong, 2025, this volume; Verreussel et al., 2025, this volume), detrital composition and diagenetic mineralogy. The Lower Jurassic and younger shale intervals are mainly marine deposits. Some shale intervals are organic rich and are important source rocks (notably the Toarcian Posidonia Shale Formation). In the Jurassic there are no significant carbonates (Trabucho Alexandre & Wong, 2025, this volume). The main early diagenetic mineralogical changes in shales and sandstones are represented by the formation of pyrite and siderite (well G16-A-01-S1; Drost & Korenromp, 2009). The pyrite is mostly bound to plant remains or other organic matter. Illite, illite/smectite and glauconite are the main detrital clay minerals in the clay fraction of sandstones and in the shales. Kaolinite and chlorite are often absent or form minor detrital components (less than 1-2 vol%), except in some sandstones in the Schieland Group which contain up to 15 vol% kaolinite.

During Jurassic and Cretaceous times, the relief in the hinterland was low. Clastic sediment input mainly came from the south and southeast, and from local tectonic highs or highs created by salt diapirism. This resulted in a low content of extrabasinal metamorphic and magmatic rock fragments. The depositional environments of the sandstones range from fluvial, coastal, to shallow marine. Sandstone intervals occur in the Upper Jurassic Aerdenhout Member and the Scruff Group, (including the Terschelling Sandstone, the Scruff Spiculite, the Scruff Greensand and the Schill Grund members), and also in the Lower Cretaceous Vlieland Subgroup. The main compositional difference of these sandstones is the highly variable glauconite grain content. Some of the sandstones have a high content of detrital matrix through bioturbation. The sandstone composition ranges from quartz arenites and quartz wackes (Vlieland Sandstone Formation, Aerdenhout Member), to sublitharenites (Fig. 13.1d) and wackestones (Fig. 13.2e), to glauconitic sandstones, i.e. so-called greensands (Fig. 13.2f). The content of detrital feldspar is commonly very low (e.g. in the Scruff Group, and Vlieland Subgroup). The amount of extrabasinal rock fragments derived from the hinterland is usually less than ~3%, but intrabasinal rock fragments and grains can be abundant. The reservoir quality of the coastal, paralic and marine sandstones is strongly related to the depositional facies.

The fluvial and coastal shallow-marine sandstones are quartz rich, and represent sublitharenites to quartz arenites that have little or no detrital matrix except where they were modified by pedogenesis and bioturbation (Fig. 13.2e). The marine sandstones are often bioturbated and contain detrital clay matrix, turning arenites into wackes (e.g. well Tietjerksteradeel-901, K18-Kotter-14). Locally, the sandstones contain intrabasinal shale clasts and carbonate grains, including fossil fragments (e.g. wells G16-06-S1, K18-Kotter-14). Most sandstones typically contain variable amounts of glauconite (e.g. well L06-02). These so-called greensands are often bioturbated to a variable degree and therefore contain detrital clay matrix. Feldspar- and extrabasinal rock fragment contents are very low.

The greensands are shallow-marine deposits and the intrabasinal grains are of marine origin, many of which are reworked material from sediments deposited during periods of low net sedimentation and hardground development. Greensands occur in the Scruff Group (the Scruff Spiculite, the Scruff Greensand and the Schill Grund members). They are composed of a mixture of detrital grains including quartz, feldspar, carbonate, fossil shells, and glauconite, phosphate bone fragments and phosphate intraclasts from reworked phosphatic marine hardgrounds (Gallois & Owen, 2017). Shell fragments are locally replaced by phosphate and/or by chert. Grains from local diapirically uplifted areas and from evaporites eroded at the sea floor are common and sometimes dominant. For instance, sandstones of the Scruff Group contain euhedral shaped detrital quartz grains with abundant anhydrite inclusions (well G16-06A). These quartz grains are locally the dominant detrital grain type. Occasionally carbonate breccias (dolostone and limestone clasts, e.g. well G16-A-01-S1) are intercalated in the sandstone, derived from diapiric caprocks. Spiculites are part of the Scruff Greensand Formation in the Dutch Central Graben (Herngreen et al., 2003; Abbink et al., 2006). They are also associated with diapiric highs and occur at the top of these structures.

The dominant diagenetic process in Jurassic sandstones is mechanical compaction resulting in grain deformation during burial, which affected the texture and petrophysical properties. The amount of glauconite grains is thereby crucial. During burial, glauconite grains deform plastically, which results in an enhanced mechanical compaction (Fig. 13.2f). Consequently, high glauconite contents significantly decrease porosity and permeability. Some glauconite-rich sandstones also have intergranular siderite cement, and euhedral siderite crystals and crystal clusters occur dispersed in the bioturbated detrital matrix. Besides siderite, also calcite and Fe-dolomite cements, and early diagenetic pyrite occur in the detrital matrix. Quartz overgrowth cement is restricted to matrix-free and matrix-poor sandstones. In particular, the quartz arenites are quartz cemented but also in matrix-free parts of wackestones. These quartz-rich arenites were less compacted because of the rigid quartz grains. Carbonate cements and locally also quartz cement is present in sandstones or parts of the sandstone with low glauconite content. Anhydrite cement is rare and only occurs in de Aerdenhout and Terschelling Sandstone members (e.g. well K18-Kotter-14). Halite cement is absent. Because of the dependency of these cements on the bioturbated texture, the sandstones are often highly heterogeneous with respect to cements and mineralogy.

Besides the common high content of glauconite grains, the clay mineralogy of the Jurassic and Lower Cretaceous sandstones stands out because these sandstones contain much more illite/smectite, which is often the dominant clay mineral, and far less illite than the older strata (Figs 13.4a,b). The kaolinite content is very low in Jurassic sandstones.

Upper Cretaceous

At the transition to the Late Cretaceous, the sediments became marlier and eventually fine-grained pelagic limestones were deposited (the Chalk Group; Van Lochem et al., 2025, this volume) often with nodular chert beds (Zijlstra, 1987). These Upper Cretaceous carbonates predominantly consist of chalk composed of low-Mg calcite. The more proximal coastal chalk onshore the Netherlands is composed of coarser grained skeletal debris whereas the more distal chalk is composed of pelagic carbonate mud (Molenaar & Zijlstra, 1997; Van Lochem et al., 2025, this volume). The chalk is composed of micritic limestone derived from microfossils and microfossil debris (mainly coccolith tests) and fine crystalline calcite cement which precipitated partly as overgrowths on the microfossils (Hjuler, 2007). Porosity declines rapidly even with shallow burial depths because chalk typically has high rates of compaction (Scholle, 1977). With increasing burial, low-Mg calcite coccoliths became unstable (e.g. Neugebauer, 1974; Hjuler, 2007) because of the small size of the composing skeletal parts. Aragonite and high-Mg calcite skeletal debris, which are more common in shallower paleo-coastal areas, dissolved resulting in secondary micropores and calcite cementation. Precipitation of low-Mg calcite cement mainly occurred as overgrowths on still stable low-Mg calcite fossil debris or on cement fringes of coarser grained fossil debris (e.g. Mapstone, 1975; Hjuler, 2007). In addition, pervasive stylolites developed in and along marlier interbeds, starting already at burial depths of several hundreds of metres (Egeberg & Saigal, 1991; Lind, 1993). Part of the microfossils, e.g. diatoms and radiolaria, was composed of metastable opal-A, the dissolution of which led to the development of layers of nodular chert. The silica precipitated often along burrows and/or filling burrows, probably influenced by microbial activity. Burial diagenesis thus resulted in increasing crystal grain size (Lind, 1993) and modification of the original carbonates into low-Mg calcite, mainly by local mass conservation.

Typically, marine hardgrounds developed during periods of non-deposition due to early marine cementation of the chalk layers at or closely below the paleo seafloor (Molenaar & Zijlstra, 1997). Such well-cemented hardgrounds form low-porous and low-permeable interbeds in the Chalk Group succession.

Comparison of Cretaceous and older stratigraphic units

Most remarkable in the studied Paleozoic and Mesozoic sandstone intervals is the similarity of detrital compositions, which resulted in similar diagenetic features and authigenic minerals that formed during burial. Nevertheless, subtle regional differences in composition in upper Carboniferous, Permian and Lower Triassic sandstones reflect input from different source areas in the south and in the southeast. Gradual unroofing of the southern source area explains the differences in contents of metamorphic rock fragments between Carboniferous and younger deposits. Also differences in the intensity and frequency of intrabasinal reworking affected the detrital composition and influenced diagenesis locally and regionally.

Compositional variation at local scales is related to different sedimentary processes and selective deposition of grain types, which tend to occur within narrow size fractions. The latter resulted in slight differences in detrital composition at the scale of laminae, beds and depositional cycles. Variations within stratigraphic intervals are mainly the result of changes in types and amounts of intrabasinal detritus. Intrabasinal grains are carbonate, shale, anhydrite clasts, and siliciclastic grains with clay coatings, the latter in Permian-Triassic fluvial-eolian sandstones. In Jurassic-Cretaceous deposits another type of intrabasinal grains is locally important comprising glauconite, phosphate and carbonate from eroded marine hardgrounds and euhedral quartz grains with evaporite inclusions from eroded evaporites. The content of these grains depends on the presence and erosion of paleosols, ephemeral lakes, and fine-grained playa deposits, as well as on the activity of the fluvial channel belts and lateral changes of these belts. In marine Jurassic deposits this depends on local uplift related to diapiric activity.

The clay mineral assemblages are similar throughout the stratigraphy and show no depth trends. Still the quantities of individual clay minerals vary widely even within a single stratigraphic interval. The same can be stated for the cement mineralogy. The overlapping assemblages of detrital and diagenetic minerals and properties clearly reflect the result of a multivariate controlled diagenesis. As example for the multitude of factors that influence cementation, quartz cement can be mentioned. Quartz cement mainly precipitated as overgrowths on quartz grains when clean quartz surfaces were available and when the temperature was sufficient. The amount and distribution of detrital clay matrix, clay grains, clay grain coatings, and other cements that formed earlier than quartz cement can therefore inhibit quartz cement precipitation partly or completely, and locally or pervasively. Changes in the detrital composition of a few percent can thereby have a significant effect on the amount of quartz cement. The intrabasinal clay grains and clay grain coatings in sandstones of the Slochteren Formation and Lower Germanic Trias Group vary stratigraphically and locally. This indicates that the tectonic setting did not play a significant role for quartz cementation. The presence of quartz cement inhibited further compaction, mainly chemical, thereby preserving porosity.

This complex interplay of regional and local parameters implies that the prediction of the composition (and thus also the petrophysical properties) of sandstones from extrapolation of known cases, as would be desirable for hydrocarbon and geothermal purposes, is difficult.

Geochemistry and mineralogy of Cenozoic sediments

Introduction

The Cenozoic formations consist of clastic sediments as well as peat layers. The Paleogene formations are dominated by marine clays while the Neogene formations are mainly composed of marine sands and clays (Munsterman et al., 2025, this volume). The Quaternary formations mostly contain fluvial sands but significant marine and glacial clayey to sandy deposits are present in parts of the Netherlands (Busschers et al., 2025, this volume). Eolian and limnological deposits are also present but mostly at smaller scales and so are peat layers. In terms of terrestrial provenances, two major systems must be recognized: the Eridanos system from the east and the Rhine system from the south (Table 13.1). The deposits of the Eridanos system originated from the Baltic area and have been assigned to the Lower Pleistocene Peize Formation (Overeem & Kroonenberg, 2002). The sediments of the Middle Pleistocene Appelscha Formation also have an eastern provenance, but they originate from northern Germany and the Central German Uplands (i.e. Mittelgebirge in Central Germany). The provenance area of the Rhine system grew kind of abruptly towards the Alps at the onset of the Pleistocene. This had important effects on the sediment mineralogy, in particular the heavy minerals (Westerhoff, 2009). The Meuse River system is a much smaller system as the river discharge has been considerably smaller and frequently it was part of the Rhine system. Its importance for the southern Netherlands is, however, large. The Scheldt system plays a role in the SW Netherlands, and local Belgian rivers leading to the Stramproy Formation played a role during the Middle Pleistocene (Busschers et al., 2025, this volume).

It is important to realize that considerable amounts of Quaternary sediments originate from the reworking of older sediments. Parts of the glacial deposits consist of locally eroded sediments that may have been fluvial or glacial themselves. For example, some of the periglacial sediments at the foot of the ice-pushed ridges originate from glacial ridges. Mineralogically, they are highly comparable, although sorting processes have resulted in some differences. Sediments from the Boxtel Formation frequently have a local origin as well. Another example is that sandy sediments from the Kreftenheije Formation in the provinces of North and South Holland partly consist of reworked sediments from the marine Eem Formation (Busschers et al., 2007), resulting in high carbonate contents. Syn- and post-depositional diagenetic processes and weathering altered the geochemical and mineralogical composition of Cenozoic sediments, although they have

Table 13.1. *Provenance areas of the Dutch fluvial Cenozoic formations.*

Provenance area	Lithostratigraphic formation
Rhine	Echteld, Kreftenheye, Urk, Sterksel, Waalre
Meuse	Beegden
Belgian rivers, including Scheldt	Kreekrak, Koewacht, Stramproy
Eastern – northern Germany and Mittelgebirge	Appelscha
Eastern – Eridanos (Baltic)	Peize
Pre-Alpine Rhine	Kieseloolite, Inden

not been as intensive as for the Paleozoic and Mesozoic sediments largely for reasons of time and burial depth. Ultimately, this has led to a situation where the mineralogical and geochemical composition of individual Cenozoic geological units is not unique.

The geochemical and mineralogical characteristics of the Cenozoic formations have not been surveyed at a national scale as systematically as their geological characteristics. Consequently, systematic descriptions at the level of geological formations cannot be made. The TopIntegraal project of TNO – Geological Survey of the Netherlands has systematically collected geochemical data for the first 30-40 m below surface for about half the Netherlands until 2024. In the overview below, these new results are combined with previous results.

Sediment geochemistry

Factor analysis

Factor analysis (FA) or principal component analysis has frequently been applied to Dutch sediment geochemical data sets (Hakstege et al., 1993; Huisman, 1998; Tebbens et al., 1998; Mol, 2002; Spijker, 2005; Van Helvoort et al., 2005; Heerdink & Griffioen, 2007, 2012; Vermooten et al., 2011; Klein et al., 2015). It provides insight into a) the minerals that are dominantly present and b) the association of trace elements with main elements. Table 13.2 summarizes the findings of studies that characterize individual geological units based on total element analysis extended with some element contents according to aqua regia destruction (Spijker, 2005) and 0.43 M HNO_3 extraction (Mol, 2002). The factor analysis performed was not carried out in the same manner for all studies and this may affect the detailed results. Despite this, the number of factors needed to describe the geochemical variability within the data sets in adequate detail lies between 2-5 with an average of 3.46 ± 1.24. Only twice, more than 5 factors are required. The total explained variance varied between 0.66 and 0.97 with an average of 0.85 ± 0.06. When a small number of factors was present, one factor (or two) typically consist of a combination of two factors also observed in the models having 3-5 factors.

The most prominent factor identified in many (25 of 37) of the FA models, and which then usually explained most of the variance, is the Al-factor. In all but one of the other FA models, the factor explaining most of the variance is akin to this first one, being defined by both Al and Ca or both Al and S. The first features 8 times in total and the last 6 times. Another major factor is a Ca-factor. This factor features 21 times in total, always in combination with the first Al or Al-S factor. In 6 additional models, Na is a co-defining variable on the Ca-factor. Two further factors that emerged frequently in the 37 FA models are an S-dominated factor (occurring 20 times) and a factor defined by Na and/or K (occurring 13 times). Finally, the heavy minerals and trace metals factor types emerged more than four times. The geochemical compositions of the various Cenozoic geological formations are thus characterized by a small number of factor types. They are discussed below based on their defining variables and geological parentage. First, the four, major factor types are discussed that have a singular explanation. Subsequently, three major factor types are discussed that are intrinsically composed of two or three of these factor types. Finally, some minor factor types are briefly mentioned.

Al-factor

The variable defining this factor is Al; in addition, K is frequently present as co-defining variable with 24 scores out of 25. Other variables that contribute in more than half of the cases are the clay and silt contents, the major elements Ti, Fe, Mg, and the trace elements Ba, Cr, Ni, Pb, Zn, Nb, Rb, V and Y. Ca-loadings on this factor are always below 0.6. The Al-factor is found for both carbonate-poor and carbonate-rich, sandy to clayey formations from various sedimentary origins. This factor most likely represents the variability in the content of Al-silicates as an overall group. Iron may be excluded from this factor or not depending on the presence of reactive Fe minerals in addition to association of Fe with Al-silicate minerals. The prominence of K points in particular to illite, muscovite and/or K-feldspar, where the first is associated with the clay fraction and the last two with the sand and silt fractions (Boggs, 2009). Also Pb, when not present in ore minerals, is known to be mainly hosted by K-aluminosilicates, specifically K-feldspar, where the content ranges between 25-100 mg kg^{-1} (Heier & Taylor, 1959; Heinrichs et al., 1980; Herron & Matteson, 1993), while the average Pb content in the upper continental crust is 17 mg kg^{-1} (e.g. McLennan, 2001; Rudnick & Gao, 2014). Barium is typically an accessory element in K-feldspar (Deer et al., 2013), further illustrating the dominance of sedimentary Ba in aluminosilicates that define this factor.

Ca-factor

The Ca-factor is frequently, but not always, co-defined by Sr and Mn, where the factor loadings are usually higher for the first than for the last. High loadings of Al, Na, K and Pb are never observed on this factor; Fe, Mg, P and As appear as co-variables in about one third of the cases, other variables just a few times. The Ca-factor factor plays a role in data sets for both carbonate-rich formations such as present in the Holocene part of the Netherlands, as well as in carbonate-poor formations in the Pleistocene part. This factor clearly represents carbonate content as controlling factor for the related element variability. Several important observations can be made on some specific element

Table 13.2. Factors as deduced from factor analysis or principal component analyses applied to 37 data sets of single geological units or soils. Note that the Kedichem Formation is now part of the Waalre Formation. The Schoorl, Walcheren and Wormer members are part of the Naaldwijk Formation, the Singraven Member is part of the Boxtel Formation. Factors that were found three times or less are not included.

Factor (n observed)	Variance explained	Elements typically associated (loading mostly >0.6)	Minerals represented	Distinguished in geological units (formations and members)
Al (25)	0.20-0.55	Al, Fe, K, Ti, Ba, Cr, Ni, Pb, Nb, Rb, V, Y, Zn, Ga, (Mg)	Clay minerals, mica	Echteld, Pleistocene fluvial, Boxtel, Drente, Oosterhout, Naaldwijk, Walcheren Member, Holocene Beegden, acid sandy soils, Holocene marine soils
Al (25)	0.07-0.40	Ca, Mn, Sr, (Fe, Mg, P)	Ca-carbonates	Waalre (before: Kedichem), Holocene Beegden, Singraven Member, buried Boxtel, Sterksel, Stramproy, Waalre, Kreftenheye, Drente, Eem, Naaldwijk, Holocene marine soils
S (20)	0.07-0.21	S, org. matter, As	(Fe-)sulphides, (atmospheric S binding to soil org. matter)	Boxtel, Sterksel, Stramproy, Waalre, Kreften-heye, Drente, Oosterhout, Naaldwijk, Echteld, Waalre (before: Kedichem), acid sandy soils
Na (13)	0.02-0.28	Na, Ba, (K)	Na(,K)-feldspar	Waalre (before: Kedichem), Sterksel, Waalre, Urk, Peelo, Eem, Naaldwijk, Holocene Beegden, Holocene marine soils
Al/Ca + Na (4) + S (4)	0.33-0.64	Al, Fe, Mn, Ca, Mg, K, P, Cr, Ni, Pb, Sr, Zn	Clay minerals, mica, Ca-carbonates	Boxtel, Drachten, Urk, Peelo, Naaldwijk
Al/S (6)	0.31-0.71	Al, Fe, Mn, Mg, K, Ti, P, S, As, Cr, Ni, Pb, Zn	Clay minerals, mica, Fe-sulphides	Echteld, Eem, Wormer Member, Naaldwijk
Ca/Na (8)	0.17-0.38	Ca, Sr, Na	Ca-carbonate, Na-feldspar	Echteld, Urk, Drente, Oosterhout, Walcheren Member
Heavy minerals (8)	0.04-0.14	Ti, Fe, Cr, Nb, Zr, Y	Heavy minerals	Boxtel, Oosterhout, Drente, Schoorl Member, Echteld, Waalre (before: Kedichem), acid sandy soils
Trace metals (5)	0.13-0.20	Cu, Ni, Zn, Th	Anthropogenic contamination?	Boxtel, Singraven Member, Drachten, Stramproy, Echteld

associations relating to carbonate content, diagenesis and weathering:

1. Sr is absent for four, sandy, carbonate-poor formations but present in the rest, including many carbonate-rich marine formations (except the calcareous Urk Formation in the northern Netherlands). This difference may be due to lack of dominance of detrital carbonates for the first cases.
2. When Mn is absent, the factor is present in the Holocene Naaldwijk Formation and its members where Ca-carbonate contents (including shell fragments) are highest in both clayey and sandy sediments. This may indicate a difference between dominance of detrital Ca carbonates versus more diagenetic carbonates incorporating Mn under reduced conditions as commonly present in the Dutch subsurface (Griffioen et al., 2013).
3. Fe and P show parallel behaviour while As is also frequently present with or without S. This may refer to diagenetic precipitation of siderite, vivianite and pyrite (Postma, 1982; Huisman, 1998; Hartog et al., 2005). High factor loadings for these elements are observed for all four types of sedimentary environments. In the Netherlands, shallow groundwater is frequently saturated for siderite, rhodochrosite and vivianite (Griffioen, 1994; Griffioen et al., 2013) suggesting that secondary precipitation of these minerals is probable across the country.
4. The relevance of this factor for Mg may be controlled by secondary enrichment of dolomite relative to calcite and aragonite following leaching of the last two under paleohydrological conditions (Griffioen et al., 2013, 2016).

The differences in elemental associations among the different data sets point to a sedimentological, detrital signal (as more often observed for the marine formations) versus a post-sedimentary diagenetic or leaching signal (as is more often observed for the periglacial, glacial and also fluvial formations) for the Ca-carbonate factor.

S-factor

This factor is often co-defined by organic matter and As and is found in fluvial and marine units as well as in the

Drente and Boxtel formations. It is notable that this factor occurs at a lower frequency in marine formations for which it appears as a Al/S factor instead (see below). The S-factor is complemented with some of the following variables in one or two data sets out of the 20 in which this factor is found: Fe, Mn, Ca, Mg, P, Ti, or clay, and the trace elements Cr, Cu, Pb, Zn, U, or V. Sulphur is presumably present as pyrite since presence of gypsum is negligible in the shallow subsurface of the Netherlands (Griffioen et al., 2013, 2016). The strong association with organic matter (as reductant) and with As (as impurity in sulphides) also points to diagenetic sulphides as controlling minerals. The general absence of Fe as co-defining variable for this factor implies that sulphides are of minor importance for explaining the variability in Fe, probably because in the formations studied Fe is for the greater part associated with other minerals like Al-silicates, heavy minerals and Fe-bearing carbonates (as indicated earlier). Most of the associated trace elements are well scavenged by sulphides but their limited presence in this factor indicate that this is not the major control for these trace elements.

The emergence of the S-factor in the FA models for data sets from the Pleistocene part of the Netherlands is peculiar as the formations concerned have not been subject to marine conditions after deposition (with the exception of the Pliocene Oosterhout Formation). Therefore, the source of S cannot be seawater-SO_4 but must have been fresh river water on a geological time scale and/or recent atmospheric deposition and agricultural activities (cf. Griffioen et al., 2008).

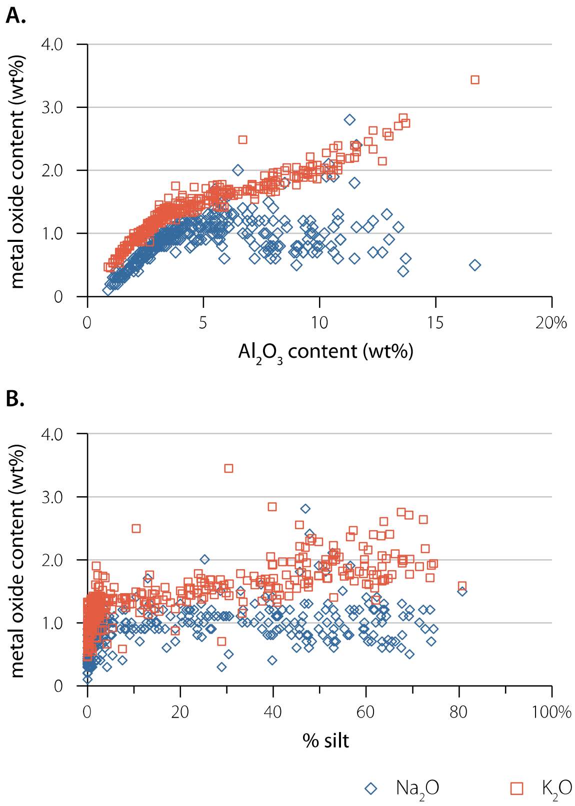


Figure 13.5. The differences in correlation between the total content of Na_2O or K_2O with that of Al_2O_3 (a) and the silt content (b) for samples from the Naaldwijk Formation in the western Netherlands illustrating the presence of an independent Na-factor.

Na- (and K-) factor

The Na factor shows up 13 times independently from an Al-bearing factor. Frequently, K and Ba are associated with this factor and a comparable factor that contains K and Ba without Na is found just once. When Ba appears as significant contributor to this factor, it is not strongly correlated to the Al-factor or vice versa. Feldspars are usually the most dominant mineralogical hosts for Na in sediments or rock. Barium is a typical accessory in K-feldspars (Deer et al., 2013). This factor thus specifically refers to Na and K-feldspars as far as their content varies independently of that of the overall group of Al silicates. Silt or clay are only once predominant, which implies that the relationship with grain size is weak. Figure 13.5 illustrates that there is a linear relationship between Na or K with Al_2O_3 up to 5% Al_2O_3 indicating that these elements are associated with Al-silicates. A second linear relationship with lower slope is found for K above 5% but not for Na. No relationship with the silt fraction is found for Na, and only a weak one for K, which indicates the independence of especially Na to grain size. Some other elements appear as co-definers once (Zn, Sr, Rb, Nb, Y) or twice (Zr) making this a rather unimportant factor for the trace elements as well. This factor is found within about half the data sets of the fluvial and marine formations and not for the data sets of the Boxtel Formation.

Al/Ca-factor

This factor is mostly found in data sets that generated a 2-factor model. The Al/Ca-factor is then co-defined by many of the other variables considered, which accounts for the high explained variances by this factor. Sodium is notably present in half of the data sets while S is present in the other half. This factor type thus combines three of the above factor types. Iron and Mn are always present as co-defining variables. Other co-defining variables that appear in nearly all models are silt, Mg, K, P, Cr, Ni, Pb and Sr. Many main and trace elements are thus present in this factor.

Mostly, this factor emerges in FA models for calcareous-poor, sandy formations with low contents of pyrite and other reactive Fe-minerals, as well as in the model for the Naaldwijk Formation in Zeeland, which is characterized by being rich in all reactive compounds. This factor presumably represents the main dichotomy between 'sterile' quartz-rich sand deposits on the one hand and deposits rich in Al-silicates and reactive minerals that all correlate together on the other hand. For the first, this factor can be viewed as describing variability due to the 'impurity' of the sand, whereas it describes the 'dilution' by quartz sand for the Naaldwijk Formation as the second. At both extremes, the need (in terms of explained variance) and opportunity (in terms of available resolution) to have a larger number of factors that recognize independent variability among the various non-quartz fractions appears to be absent.

Al/S factor

This elemental association especially co-defines factor models for the marine Eem and Naaldwijk formations and the buried Echteld Formation just once. Iron, Mg, P, Cr, Ni and Pb are always associated with this factor and K, As, Zn, clay and silt almost always. The depositional or postdepositional marine environment for this factor type indicates the presence of seawater-SO_4 for the reduction to pyrite or other reduced S minerals. For these data sets, organic matter is also often incorporated in this Al/S-factor with high explained variances, probably due to a grain-size effect where solids other than quartz increase with decreasing grain size together with a strong association between clay minerals and sedimentary organic matter.

Ca/Na-factor

This factor is defined by Ca, Na and also Sr with loadings for Al, Fe, clay and silt always below 0.6. Manganese occurs as co-defining element in this factor in half of the factor models. Magnesium, Fe and P, which frequently co-define the Ca-factor, are usually irrelevant in this factor. Potassium, As, Ba and Zn co-define once and Cu is also noted once. This makes this factor type unimportant for the trace elements. The Ca/Na factor is only found in data sets where the separate Ca- and Na/K-factors are absent while the Al-factor is present. It mostly emerges for calcareous formations of fluvial, glacial and marine origin. This factor is thought to describe the parallel variability in carbonate as well as feldspar content. Since the elements Mg, P and Fe are not strongly associated with this factor, diagenetic carbonates are not reflected in this factor, whereas detrital Ca-carbonate is.

Other factors

A few additional factors appear in the factor models, and always more than once. One such factor is defined by Zn and some other trace elements (Cu, Pb, Cr, Ba, Ni, Th, Y). It may be related to anthropogenic contamination as it occurs in formations close to the surface with acid to neutral groundwater pH or young floodplain sediments, i.e. vulnerable to anthropogenic contamination and soil leaching of trace metals (Schröder et al., 2005; Fest et al., 2007). The other factors refer to:

1. organic matter with or without clay
2. U as single-element factor
3. Nb with Cr and Zr or with Y
4. a combination of silt, Ti and Fe.

The last two factors refer to heavy minerals where associations with rutile and zircon are evident (Deer et al., 2013). These factors are limited in their appearance because the related elements were not always selected in the data set studied.

Trace element composition

The results of the factor analysis point to some common associations among the major and trace elements. These associations may be recognized as a baseline, i.e. a linear relationship between the trace element and a major element, especially Al, that refers to the natural, geochemical composition of the sediments (Huisman et al., 1997; Mol et al., 2012). We will highlight some of these to illustrate

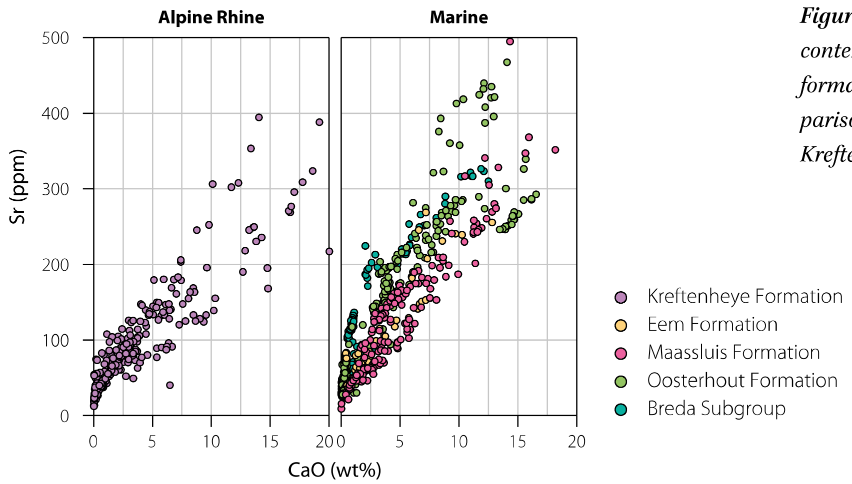


Figure 13.6. Comparison between the total contents of CaO and Sr for pre-Holocene formations with a marine origin. For comparison results are also shown for the fluvial Kreftenheye Formation.

noteworthy similarities and differences in the element composition that can be explained by differences in sedimentary provenance, diagenetic processes or anthropogenic pollution. The data presented concern total element contents as measured with XRF.

Strontium

High total contents of CaO as measured by XRF analyses are indicative for high Ca carbonate contents in clastic sediments. The minor element that is most strongly correlated with CaO is Sr as illustrated in Figure 13.6 for sediments with a marine provenance. The Sr content varies in Ca carbonates but it is overall more abundant in aragonite than in calcite as the larger Sr^{2+} fits better in the aragonite crystal lattice (Carpenter & Lohman, 1992; Deer et al., 2013). The scatter on the cross-plots of Figure 13.6 indicates varying Sr contents in Ca carbonate and varying calcite to aragonite ratios (see section of Carbonates). In Figure 13.6, a steeper slope in the series of data points is noted at low Sr and CaO contents. This slope may be in-

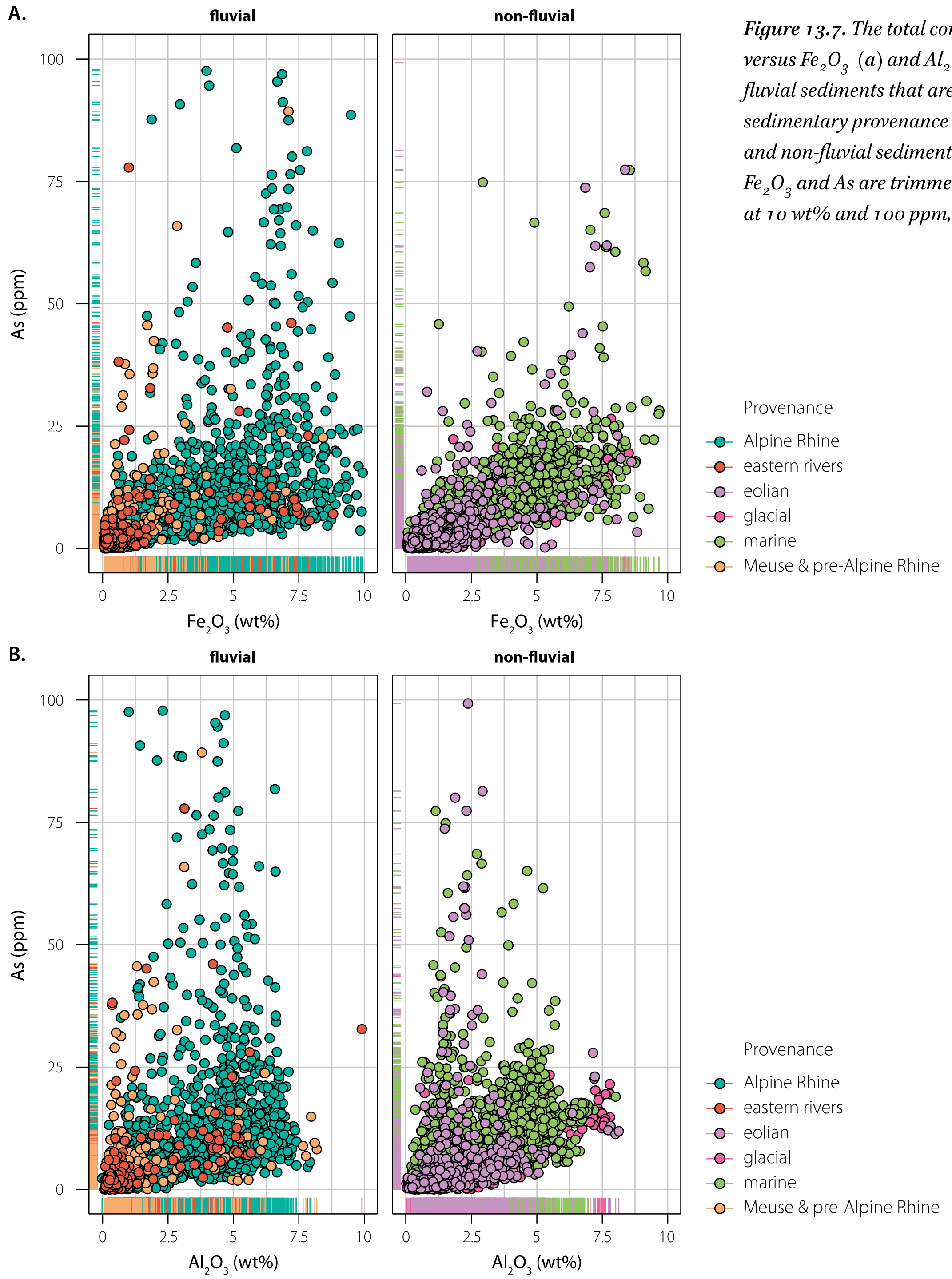


Figure 13.7. *The total contents of As versus Fe_2O_3 (a) and Al_2O_3 (b) for fluvial sediments that are classified by sedimentary provenance (cf. Table 13.1), and non-fluvial sediments. The axes of Fe_2O_3 and As are trimmed for visibility at 10 wt% and 100 ppm, respectively.*

dicative for Sr in feldspars as Sr can be an important substitution for Ca, Na and K in feldspars (Deer et al., 2013). A systematic difference among the marine formations seems present with higher Sr contents for the Breda Subgroup and Oosterhout Formation. The trend for the Breda Subgroup is more curved compared to the other datasets. The data scattering for the fluvial Kreftenheye Formation is comparable, although some high CaO samples possess low Sr.

Arsenic

Arsenic (As) may be present in Dutch sediments at such high contents that the sediment is considered to be naturally polluted with it (Vermooten & Gunnink, 2008). The evaluation of the factor analysis models revealed that As is often in the same factor as S with or without Al and Fe. Figure 13.7 shows that As follows a baseline with considerable variability when plotted against Al_2O_3 or Fe_2O_3, where the correlation with Fe is somewhat better. This is expected since As may be associated with Fe sulphides and oxyhydroxides. Especially marine and Alpine Rhine sediments are enriched with As, with contents up to 100 mg/kg. This is due to secondary enrichments (Vermooten & Gunnink, 2008). Especially bog iron ores are notorious for their high As contents as discussed below.

Trace elements Pb, Ni and Zn

For the visualization of anthropogenic elements, we selected Pb, Ni, and Zn. Overall, the collected samples seldomly refer to sites with anthropogenic pollution from point sources. Total contents from XRF analysis are intercompared in Figures 13.8-13.10 where each heavy metal is plotted against Al_2O_3. For all plots, a linear baseline can be recognized at the underside of the cloud of data points. Anthropogenic influences on the variability of these three heavy metals occur mostly in the soil zone, for which reason we examined the elemental composition of our samples in the following depth intervals: 0-1.2 m, 1.2-10 m and more than 10 m below surface, which reflects decreasing influence from anthropogenic contamination at the surface.

For lead (Pb), the y-axis in Figure 13.8 is trimmed to a maximum value of 100 ppm Pb for clarity. Sandy eolian sediments (Boxtel Formation) show the most enrichments relative to the baseline for the shallow soil zone. Enrichments are also found in marine soils (Naaldwijk Formation) and to a minor extent in the Al_2O_3-rich (i.e. clayey) fluvial soils (Echteld Formation). These Pb enrichments are far less frequently found in deeper layers although they do occur. Depletions relative to the baseline are also found in these deeper layers.

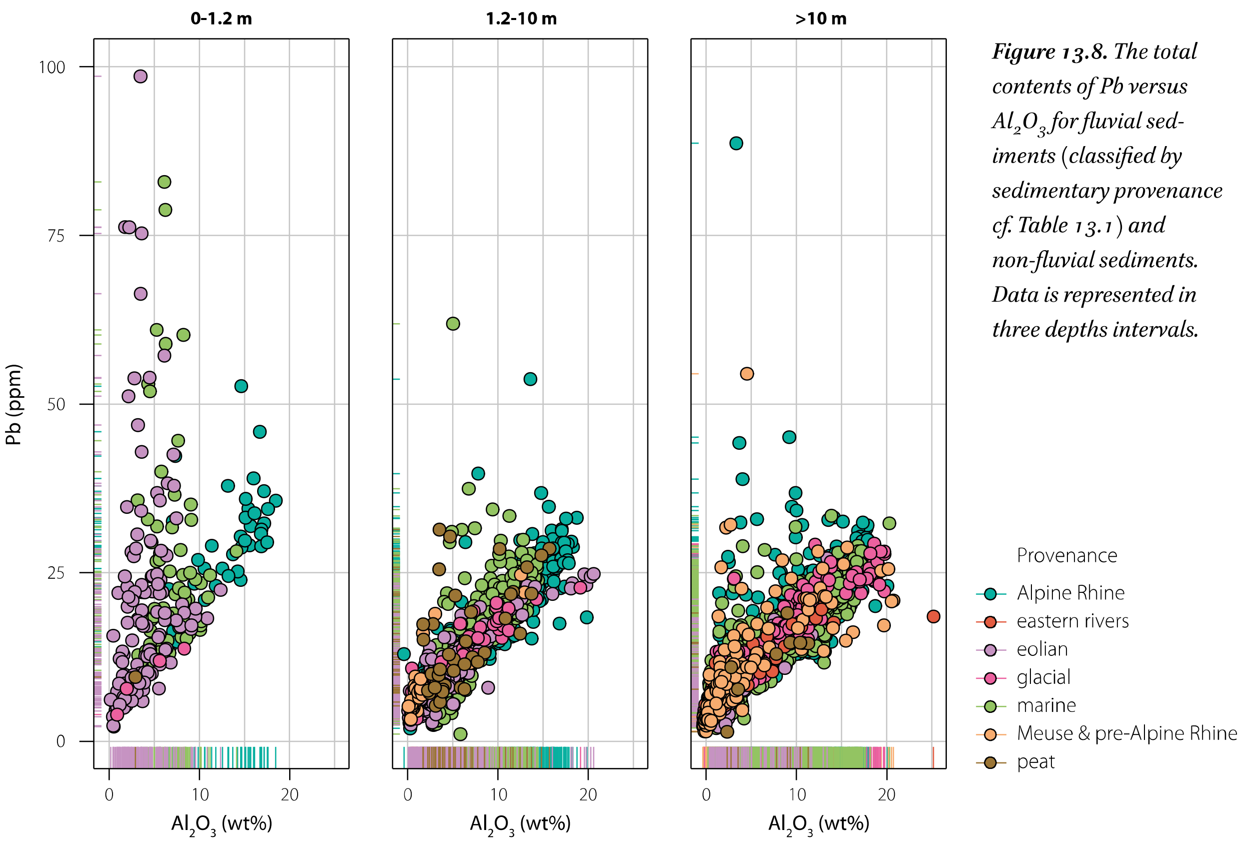


Figure 13.8. The total contents of Pb versus Al_2O_3 for fluvial sediments (classified by sedimentary provenance cf. Table 13.1) and non-fluvial sediments. Data is represented in three depths intervals.

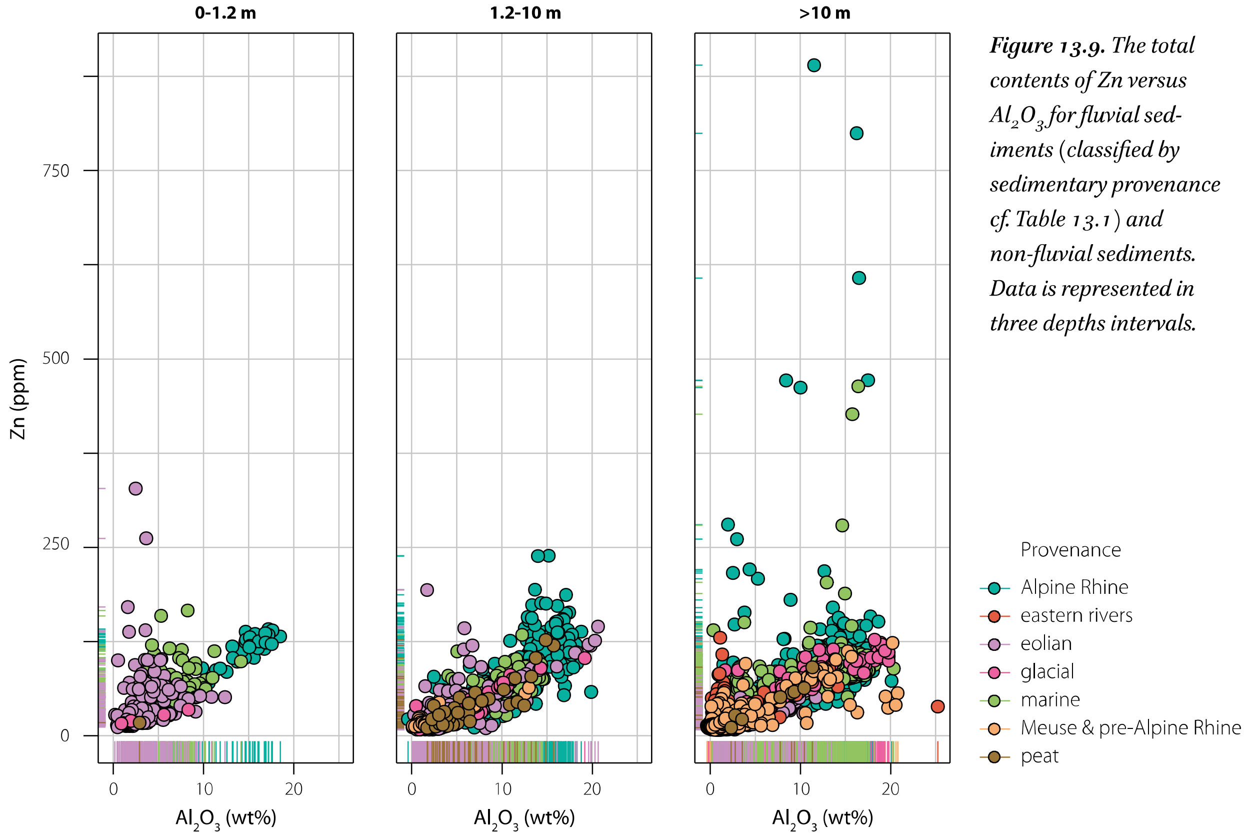


Figure 13.9. *The total contents of Zn versus Al_2O_3 for fluvial sediments (classified by sedimentary provenance cf. Table 13.1) and non-fluvial sediments. Data is represented in three depths intervals.*

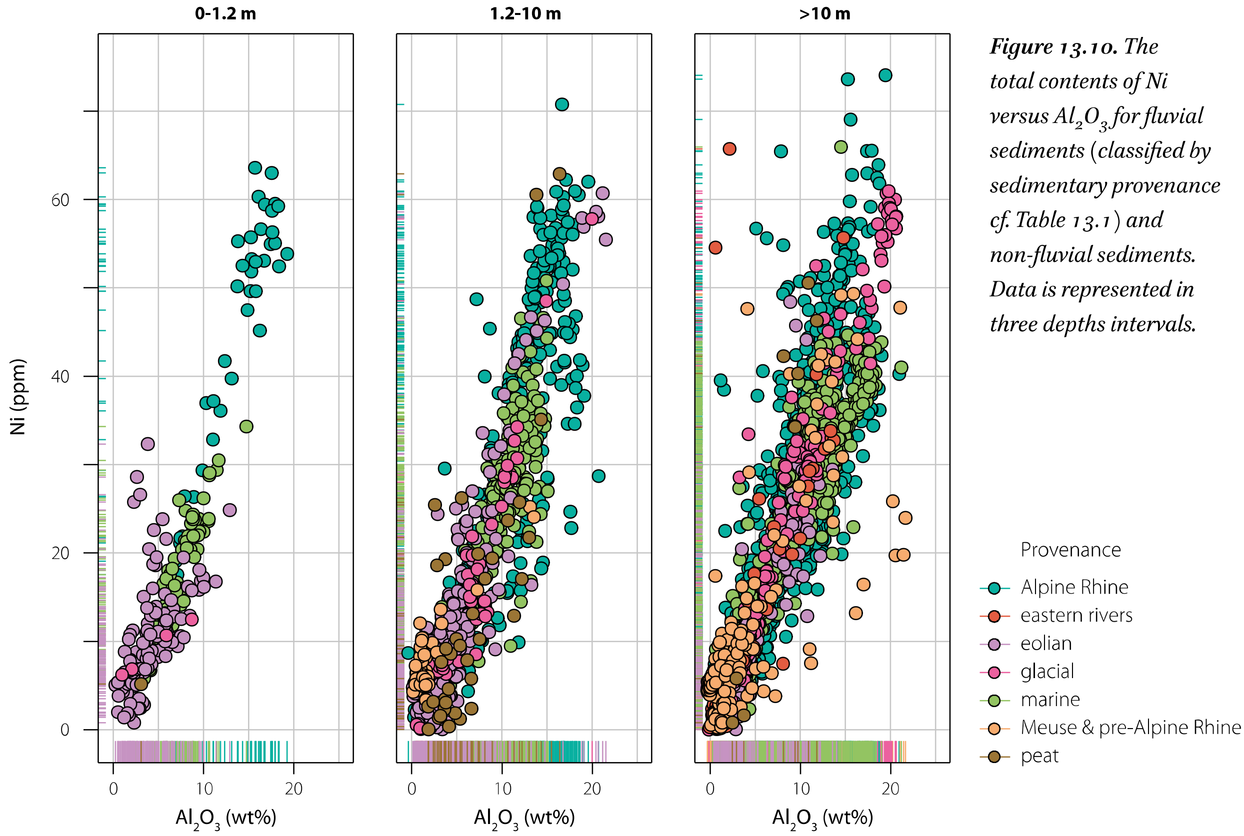


Figure 13.10. *The total contents of Ni versus Al_2O_3 for fluvial sediments (classified by sedimentary provenance cf. Table 13.1) and non-fluvial sediments. Data is represented in three depths intervals.*

The patterns for Zn are broadly similar to those for Pb (Fig. 13.9). The relative enrichments of Zn in the soil layer (0-1.2 m) seem less strong than for Pb, but are occasionally strong in the deepest layer (> 10 m). There is more scatter in the data for the deepest layer, which needs to be explored in more detail.

For Ni, the y-axis in Figure 13.10 is trimmed to a maximum of 75 ppm for clarity. For the upper soil layer, a good correlation with Al_2O_3 is observed, with few exceptions. More data scatter is observed for the deeper layers, showing both depletions and minor enrichments. The depletion in Ni for sediments with a Meuse/pre Alpine Rhine origin is striking and might be indicative for another compositional group.

Gallium

Gallium as chemical element is part of the boron family like Al. The chemical similarity of Ga and Al implies that Ga, being a trace metal, commonly substitutes for Al in Al-bearing silicate minerals. The close geochemical association is also indicated in Figure 13.11 in which a strong linear relationship is shown for Dutch sediments. However, two separate relationships can be recognized. Spijker (2005) showed that this must be attributed to an analytical artefact since the recovery of certain elements (including Ga) changed over time due to changes in instruments in the laboratory of TNO – Geological Survey of the Netherlands. This example illustrates the importance of quality control before data become geo-scientifically interpreted since it is inevitable that data come with errors.

Sediment mineralogy

Recently, research on the mineralogy of Cenozoic sediments in the Netherlands was extensively reviewed by Griffioen et al. (2016). The text below summarizes several of the results of that review and includes some additional findings. The original review was made from the perspective of the depositional environment, whereas here we primarily look at mineral type.

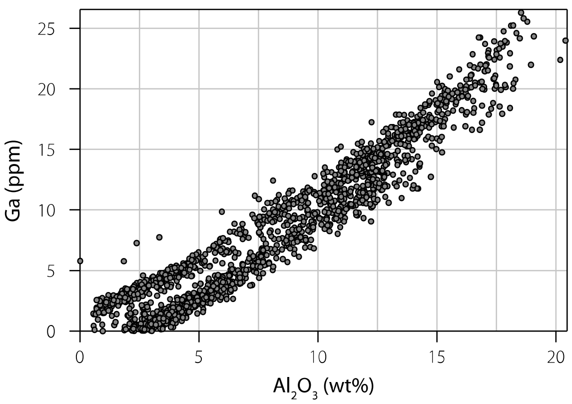


Figure 13.11. The total contents of Ga versus Al_2O_3 for a broad suite of Dutch sediment samples. See text for details.

Quartz and feldspars

Quartz and feldspars are common minerals in Dutch sediments. Quartz is often the most abundant mineral in sandy sediment with usual percentages of 60-90%. It is also abundantly present in clayey sediments with contents of usually 25-55%. Feldspar minerals are also commonly present. The percentages in which they are present vary between different formations where selective weathering may play a role apart from amount deposited. The specific dissolution rate of Ca-plagioclase is highest and that of K-feldspar lowest, with Na-feldspar showing an intermediate behaviour. Consequently, stronger depletion of Ca-plagioclase upon prolonged weathering in sediments or soils is expected.

Usual percentages for both (Na,K)-alkali feldspars and (Ca,Na)-plagioclase feldspars vary several percent around 5%, largely irrespective whether one deals with sand or clay (cf. Fig. 13.5). The reason is that feldspar minerals are strongly associated with the silt fraction due to their hardness. The total Na_2O content may be used as a proxy for the Na-feldspar content. It commonly increases with Al_2O_3 content up to 5.0% Al_2O_3 and is invariant at higher contents of Al_2O_3 (Huisman & Kiden, 1998). Huisman (1999) concluded for the studied fluvial sediments that the Kreftenheye, Urk and Sterksel formations are richest in Na-feldspar, the Neogene Kieseloolite and Peize formations are poorest, and the Waalre and Stramproy formations have intermediate contents, as illustrated by Figure 13.12. This conclusion can be broadened as the fluvial sediments with an Alpine Rhine provenance and the marine sediments show the widest range in Na_2O content while the fluvial sediments with other provenances and the glacial sediments show a much smaller range. It must be realized that Na_2O content as proxy for the Na feldspar content works less well in clayey sediment with Na-rich pore water where the Na occupancy of the cation exchange complex contributes substantially to the Na_2O content, as is evidenced by the wider scattering for marine sediments at high Al_2O_3 content.

For K_2O, the initial linear relationship with Al_2O_3 can be attributed to K-feldspar and the further increase in content to clay minerals, in particular illite that is rich in K and commonly present in tens of percents within the clay mineral assemblage of Dutch sediments (cf. Fig. 13.5). It is noteworthy that similar relationships are observed for many Cenozoic sediments in the Dutch subsurface (Fig. 13.13). An important exception is glauconite-bearing marine sand of the Breda Subgroup as discussed later.

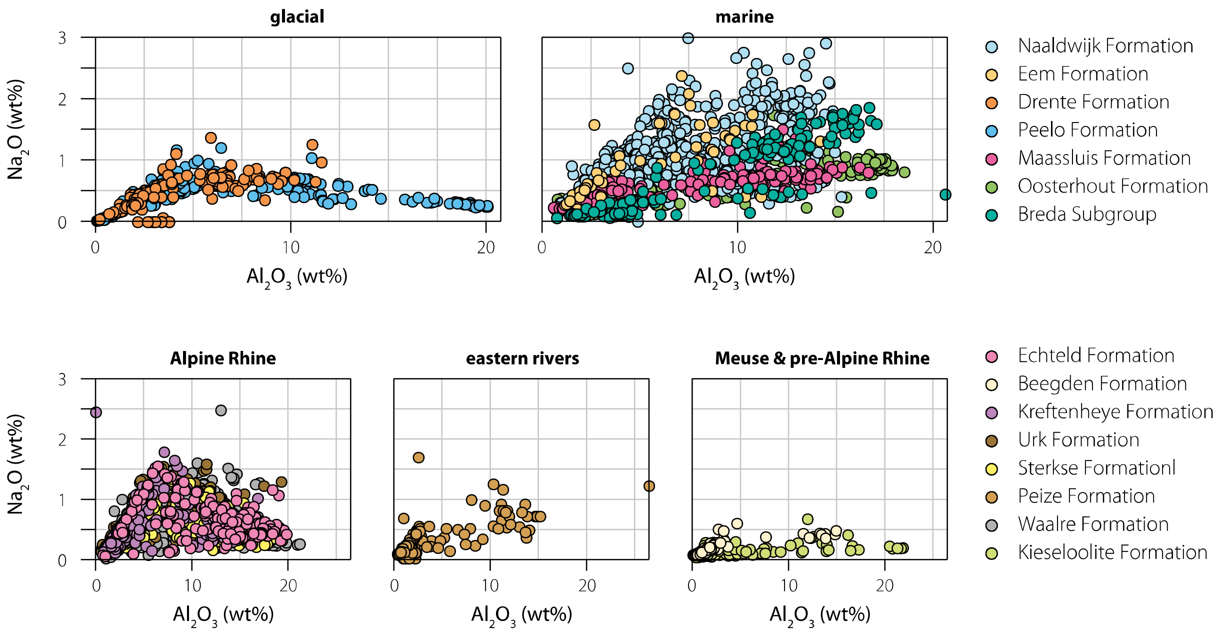


Figure 13.12. The relationships between the total contents of Al_2O_3 and Na_2O for Cenozoic sediments with different sedimentary origins and belonging to different lithostratigraphic formations.

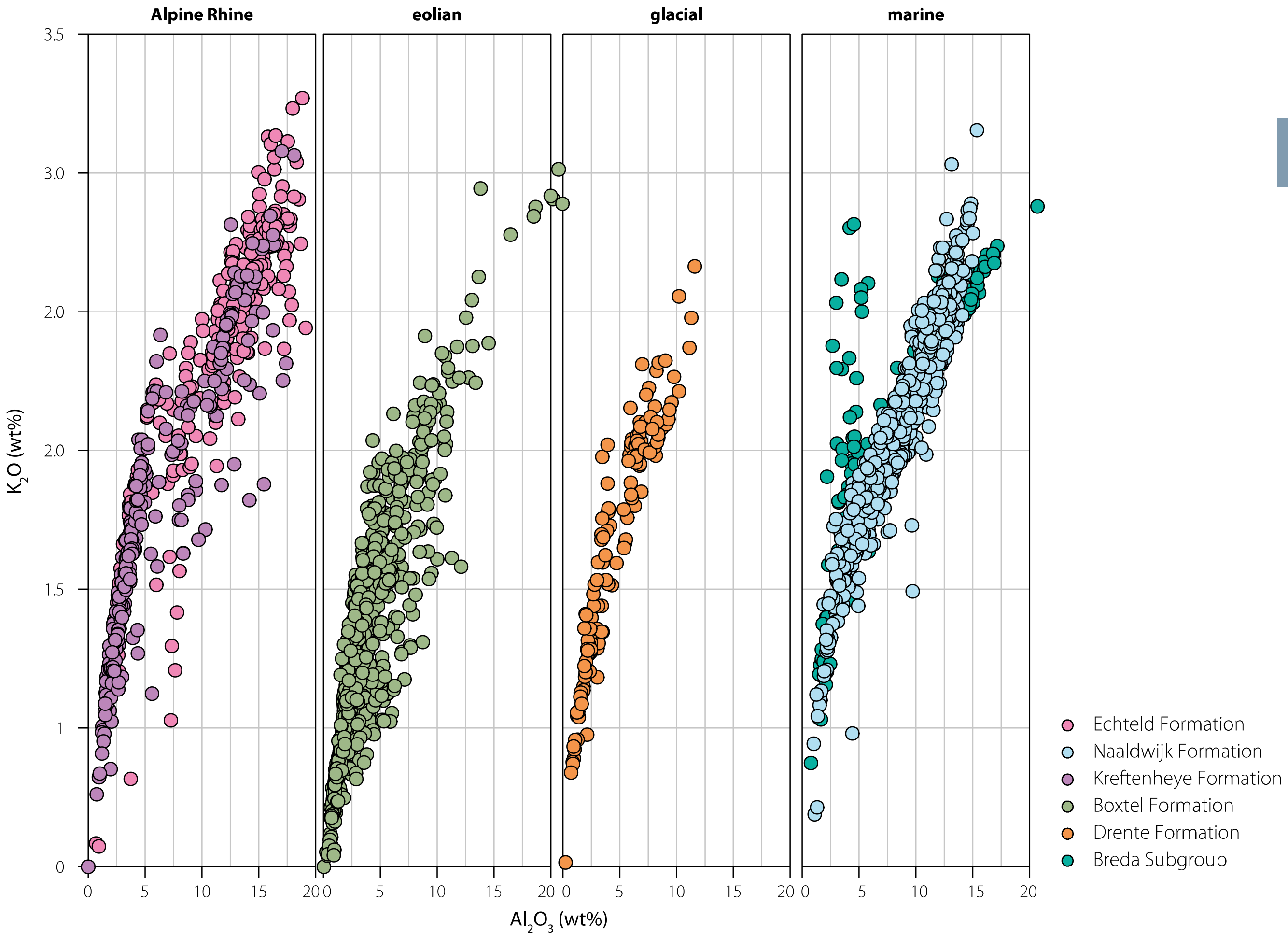


Figure 13.13. The relationship between the total contents of Al_2O_3 and K_2O for Cenozoic sediments with different sedimentary origins and belonging to different lithostratigraphic formations.

Van Baren (1934) pointed out that sediments having an eastern provenance (i.e. the fluvial Peize and Appelscha formations) are dominated by microcline as K-feldspar whereas those with a Rhine provenance by orthoclase as K-feldspar and albite as Na-feldspar.

Heavy minerals

Heavy minerals are defined as those minerals that have a density exceeding 2.85 g/cm³ (Boggs, 2009). In absolute contents, they contribute less than 1 to 2% to the sand fraction (Druif, 1927; Van Andel, 1950; Wartel, 1977). Sand with higher percentages of heavy minerals is found in a beach environment due to dune collapse and washing out of lighter minerals (Crommelin & Slotboom, 1945). Despite their limited occurrence, heavy minerals have been intensively studied since Edelman (1933) as a tool to increase the understanding of the stratigraphy of Dutch sediments based on their provenance and paleogeography.

The concept of mineral associations has been widely used to denote the particular combination of minerals that characterize a sediment. Here, two kinds of associations are distinguished: 1) a stable association with minerals such as zircon, rutile, anatase and tourmaline with or without the metamorphic group index minerals (staurolite, kyanite, chloritoid, sillimanite and andalusite) and 2) an unstable association with epidote, garnet, alterite, saussurite and hornblende. The heavy mineral assemblages are presented in Table 13.3. The deposits of the eastern rivers contain both stable and unstable assemblages. The Beegden Formation, being built from Meuse sediments, is dominated by a stable assemblage and has Vosges hornblende, anatase and chloritoid as particular guide minerals. The Rhine deposits show two shifts in assemblage (Tatzel et al., 2017). A first shift from the so-called pre-Rhine system containing a stable assemblage, to the Rhine system where the Alps became part of the drainage area and a dominance of the unstable assemblage and also a minor admixture of the stable Meuse assemblage. This is combined with the presence of mica flakes, an increase in red-brown particles (i.e. feldspar and sandstone fragments), and decreasing quartz content. After the second shift from the Urk Formation onwards, additional volcanic minerals from the Eifel appear, in particular augite, while the Meuse stable mineral assemblage disappears. The Belgian Stramproy Formation has predominantly stable heavy mineral assemblages.

Table 13.3. *Heavy mineral assemblages as valid for various Cenozoic geological formations (based on Griffioen et al., 2016). X and m denote dominantly and minorly present, respectively. HMA means heavy mineral assemblage.*

Formation/ Member	origin	augite (Eifel volcanics)	garnet	epidote	hornblende	saussurite	saussurite/ alterite	Vosges hornblende	Meuse chloritoid	zircon	rutile	anatase	tourmaline	staurolite	sillimanite	other metam. min.
		unstable								stable				stable/ metamorphic		
Schimmert (BX)	loess		X	X	m					X	X		m	m		m
Kreftenheye	Rhine	X	X	X	X		X									
Eem	marine	m	X	X	X	X							m	m		m
Urk	Rhine	X	X	X	green		X									
Appelscha	eastern		X	X	X								X	X		X
Sterksel	Rhine+Meuse		X	X	X		X			+ stable Meuse HMA						
Beegden	Meuse		X	X				X	X	X	X	X	X			X
Stramproy	Belgian									X			X	X		X
Waalre	Rhine+Meuse		X	X	X		X			+ stable Meuse HMA						
Peize	eastern		X	X	X								X	X	X	X
Maassluis	marine		X	X	X		X									
Kieseloolite	pre-Rhine									X			X	X		X
Oosterhout	marine		m	X	X								m			m
Breda Subgp	marine		m	X	X								m			m

The loess deposits from Limburg, classified as the Schimmert Member (part of the Boxtel Formation) are different from the underlying formations and the recent Meuse deposits. They are dominated by zircon and epidote and are also rich in garnet and rutile. It makes them comparable to the Tertiary group as distinguished by Schuttenhelm & Laban (2005) for seabed sands near the eastern English coast. The heavy mineral composition of the cover sands is a reflection of the underlying pre-Weichselian formations (Crommelin, 1964). In the northern region garnet, tourmaline and metamorphic minerals are dominantly present, similar to what is found in the eastern river deposits. Epidote-saussurite and hornblende-pyroxene groups are more important in the central Dutch region, indicating a Rhine signature. High percentages of tourmaline and metamorphic minerals are found in the southern region as in the Beegden, Stramproy and Kieseloolite formations (cf. Table 13.3).

Clay minerals

Clay minerals are abundant in Cenozoic sediments of the Dutch subsurface. Different types of clay minerals have distinct properties, which are important for the sediment's chemical and physical behaviour. These clay minerals can be indicative of climatic changes. In the Dutch subsurface, the most common clay minerals are of the smectite, illite and kaolinite groups (Fig. 13.14). In addition to these 'pure' clay minerals, mixed-layered illite-smectites are also abundant in Dutch sediments. Chlorite and vermiculite are usually present in minor amounts but can be important as indicator for depositional origin. Clay minerals can form through the following features: neoformation, transformation and inheritance (Galán & Ferrell, 2013). Important factors for the type of clay minerals formed are climate, time, parent material, topography, soil-profile type, transport processes and burial diagenesis (Singer, 1984; Hillier, 1995). In the Netherlands, most clay minerals present in Cenozoic sediments are inherited from pre-existing parent rock or weathered material and have not been transformed or newly formed in the soils and sediments after deposition (Breeuwsma, 1985; Tebbens et al., 1998). Clay minerals in sediments that are buried deeper and experienced diagenesis can be altered by illitization, the transformation of smectite or kaolinite to illite (e.g. Lanson et al., 1996; Molenaar & Felder, 2018). Another transformation mechanism specific for glacial tunnel valleys in Pleistocene sediments in the North Sea is *in-situ* smectitization of illite during a cold climate (Šegvić et al., 2016). Griffioen et al. (2016) give an extensive literature review of the mineralogy of fresh and Cenozoic sediments in the Netherlands, which is summarized below.

Fluvial clays

The dominant clay minerals in fluvial Rhine and Meuse clays are illite, smectite and vermiculite, with minor amounts of kaolinite and chlorite (e.g. Breeuwsma, 1985; Zeelmaekers, 2011; Adriaens, 2014). The clay mineral content varies over time in the Rhine clays (Fig. 13.14). The total illite to total smectite ratio increases from less than one (average 0.7) for the Lower Pleistocene Rhine-Meuse-Scheldt clays, to equal to one for the Mid-Holocene Rhine-Meuse clays, to more than one (around 1.5) for Lower Holocene Rhine and Lower to Mid-Holocene Scheldt clays. Huisman and Kiden (1998) reported that for the lower units of the Waalre Formation (Early Pleistocene Rhine) the clay is dominated by well-crystallized smectite, illite and kaolinite, whereas for the upper units it is dominated by illite and kaolinite. Such large variations in clay mineralogy may be attributed to drastic climate- or provenance changes in time (Tebbens et al., 1998; Alizai et al., 2012; Limmer et al., 2012). Scheldt-derived sediments of the Kreekrak Formation have a smectite-dominated clay-mineralogical composition and low contents of illite (e.g. Huisman & Kiden, 1998). One sample from the Peize Formation, originating from the Eastern rivers, has a higher kaolinite content compared to the other fluvial clays.

Alluvial brook clays from the eastern part of the Netherlands, which are stratigraphically part of the Singraven Member of the Boxtel Formation, have smectite contents that are significantly higher than in sediments from the rivers Rhine and Meuse. The smectites must originate from deposits present in the catchments of these brooks. Possible candidates are Paleogene and/or Neogene marine deposits or Cretaceous carbonates (Breeuwsma, 1985). Clays with such high smectite contents have very specific properties, such as high swelling capacities and cation exchange capacity, and K fixation.

Paleogene and Neogene marine formations

The clay mineralogy of Paleogene and Neogene marine deposits is highly variable along depth profiles. Overall, clays of the Ieper Member (Dongen Formation; NLDO in Fig. 13.14) contain larger fractions of smectite than other marine formations. Kuhlmann et al. (2004) and Zeelmaekers (2011) explain the shifts in clay mineral assemblage over time by changes in provenance. Climate factors seem to affect the contribution of sediments from specific hinterlands, but the climate dependency on weathering of clay minerals is believed to be of minor importance. The high smectite fraction in the Ieper Member clay can be attributed to a contribution of basic pyroclastic material related to the opening of the North Atlantic and connectivity with the North Sea (cf. Zeelmaekers, 2011; Nielsen et al., 2015). The shifts in the clay mineral assemblage of the Late Pliocene to Early Pleistocene record are attributed to

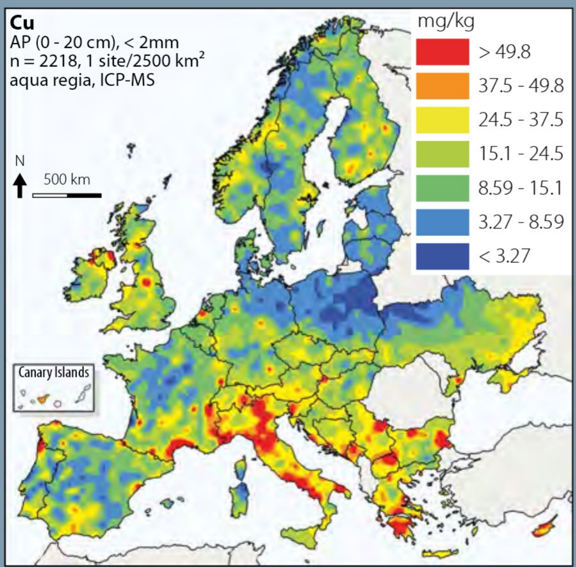
European geochemical monitoring

Geological materials are usually heterogeneous at various scales. Characterization of this heterogeneity is thus also needed at various scales. In the past decades, two large geochemical programmes were performed at the European continental-scale by geochemists employed at European geological surveys and some other organizations under the umbrella of EuroGeoSurveys: the FOREGS programme running in 1997-1999 and the GEMAS programme running in 2008-2009 (De Vos et al., 2005; Salminen et al., 2005; Reimann et al., 2014a,b; Demetriades et al., 2021). The soil samples were not taken at known contaminated sites, in the immediate vicinity of industry or power plants, railway lines, etc. The data thus provide insight in the baselines: the composition is resulting from parent material, its weathering, atmospheric deposition and agricultural use.

The FOREGS programme (weppi.gtk.fi/publ/foregsatlas) includes ca. 3500 samples for solid media: topsoil, subsoil, floodplain sediment, stream sediment and humus. Further, it contains ca. 800 stream water samples. For the soil sampling sites, this averages to approximately one site per 5700 km². Top and subsoil, and floodplain sediment samples were analysed at various laboratories across Europe by X-ray fluorescence, mixed acid extraction with ICP-MS, aqua regia extraction with ICP-AES, Hg analyser and a granulometric method for total organic carbon (TOC).

The GEMAS project assessed the element variation in productive soil at the European scale. Topsoil and subsoil samples were collected from two land-use categories at an average density of 1 site per 2500 km² each. 2024 grazing land soils were sampled and defined as 'land under permanent grass cover' and 2108 agricultural arable soils that are regularly ploughed were sampled. All collected soil samples were prepared in the same laboratory, and subsequently analysed for the same suite of elements and physico-chemical parameters in the same laboratory. The following analyses have been performed until now: 1. aqua regia extraction with ICP-MS analysis, 2. total element content with X-ray fluorescence, 3. mobile metal ion cold leach (MMI), 4. lead isotope ratios, 5. soil pH in 0.01 M $CaCl_2$ solution, 6. total organic carbon, total carbon, total sulphur, 7. cation-exchange capacity at prevailing soil pH, 8. mid-infrared spectra, 9. texture (i.e. sand, silt, clay) and 10. partitioning coefficients for selected elements.

The results show that the distribution patterns are primarily related to geochemical variation of large lithological units. For many elements, a striking difference in composition is observed between northern and southern Europe that coincides with the extension of the Weichselian glaciation. Contamination reflecting urbanized, industrialized areas and regions of intensive agriculture can better be recognized by MMI contents than total element contents. Some cities (e.g, London, Paris) cause anthropogenic trace element anomalies (e.g. Au, Pb, Hg) in their vicinity. Few samples (most of which taken in vineyards) have such high contents that they pose a toxic risk for soil organisms. Oppositely, several minor nutrients (like Cu, Zn) show such low contents across large areas of Europe that trace element deficiency is of concern.



Spatial distribution of copper content in European agricultural soils (based on aqua regia destruction) as established from the GEMAS dataset using kriging (Reimann et al., 2014a; Demetriades et al., 2021). © BGR, 2014.

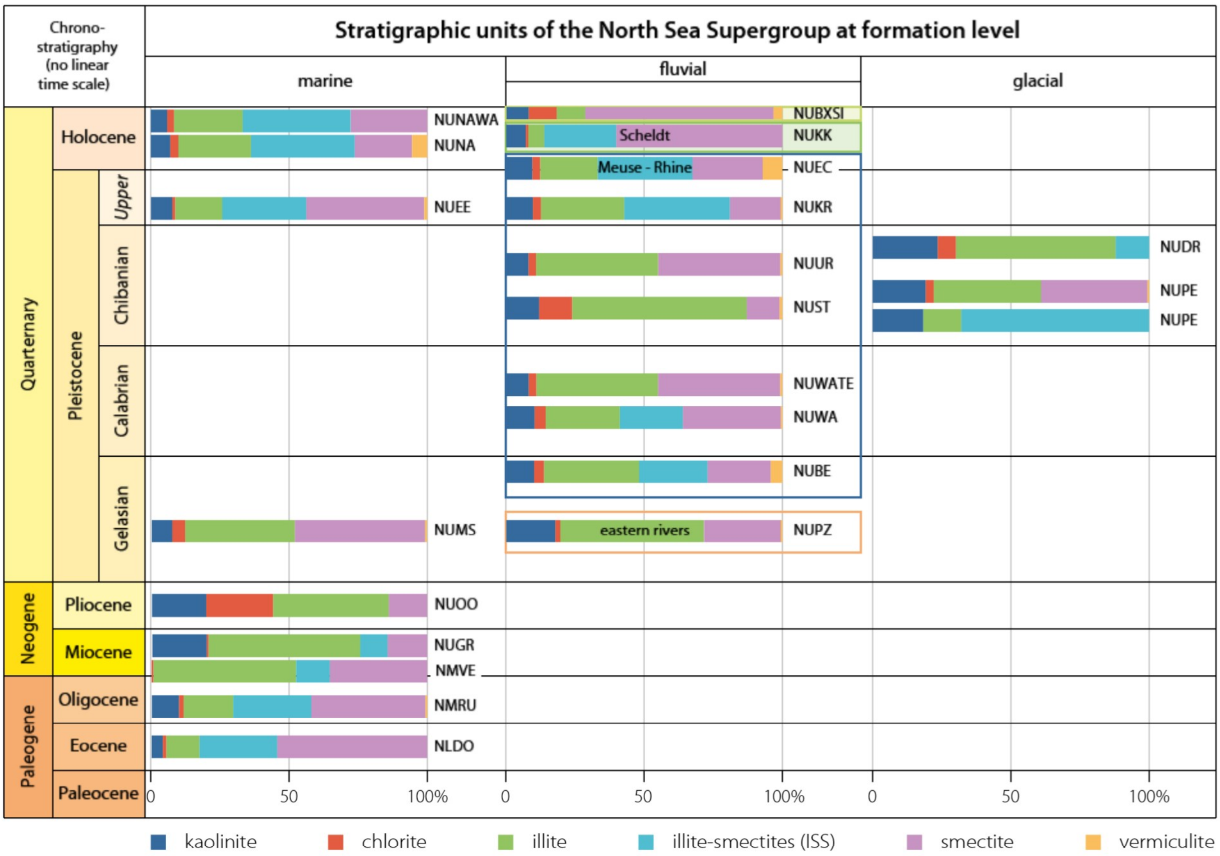


Figure 13.14. Averaged clay mineral assemblages of the <2 µm size fraction in different Cenozoic formations. The clay mineralogy data in this figure originate from several studies: Favejee (1951), CTI-TNO (1970), Breeuwsma & Zwijnen (1984), Breeuwsma (1985), Breeuwsma et al. (1987), Heederik et al. (1989), Irion & Zollmer (1999), Kuhlmann et al. (2004), Adriaens (2014), Koenen & Griffioen (2014), Hemes et al. (2016), Dijkstra et al. (2020) and several unpublished studies performed at TNO. The data was obtained by X-ray diffraction (XRD) using different methodologies. Not all methods are suitable to determine mixed-layer illite-smectites (ISS). When ISS is not specifically analysed it is included in both the smectite and illite contents. Also vermiculite is not measured in each method and can therefore not be compared between studies using different methods. NLDO = Dongen Formation, NMRU = Rupel Formation, NMVE = Veldhoven Formation, NUGR = Groote Heide Formation, NUOO = Oosterhout Formation, NUMS = Maassluis Formation, NUPZ = Peize Formation, NUBE = Beegden Formation, NUWA = Waalre Formation, NUWATE = Tegelen Member of NUWA, NUST = Sterksel Formation, NUPE = Peelo Formation, NUDR = Drente Formation, NUUR = Urk Formation, NUKR = Kreftenheye Formation, NUEE = Eem Formation, NUNA = Naaldwijk Formation, NUNAWA = Walcheren Member of NUNA, NUEC = Echteld Formation, NUKK = Kreekrak Formation, NUBXSI = Singraven Member of the Boxtel Formation.

shifts in the river-borne supply from Scandinavian sources. Illite and chlorite dominate from Scandinavian sources during cold periods, whereas smectite from southern sources dominates during warmer conditions (Griffioen et al., 2016). Apart from differences in mineral assemblages between formations they can also be recognized inside one formation. In the Belgian Boom Clay, Zeelmaekers (2011) observed a higher kaolinite fraction for the more clayey intervals compared to the more silty intervals, following a Milankovitch cyclic pattern. Koenen & Griffioen (2014) observed a similar trend for the clays from the Boom Member (Rupel Formation; NMRU in Fig. 13.14) with more kaolinite/smectite mixed layers and smectite in the clayrich samples.

Recent marine and estuarine sediments

Fluvial and marine clay mineralogies of Dutch Quaternary sediments exhibit some distinct differences. Smectite content in marine clays is similar to that in fluvial clays but has a higher iron content compared to the fluvial smectites. The higher iron-rich smectite content in the marine sediments is interpreted to originate from mixed input of sediment supplied by Dutch rivers and sediment transported northwards via the English Channel along the coast that has a high iron-rich smectite content (Breeuwsma, 1985).

The mineral composition along the entire Dutch coast is highly uniform. There are no significant differences between the muds from the Wadden Sea, the Eastern and

Western Scheldt estuaries, the North Sea floor and suspended material in the tidal inlets. The results of clay-mineralogy (Favejee, 1951) and heavy-mineral studies (Crommelin, 1940, 1943) in the Wadden Sea and the estuaries in Zeeland indicate that the sediments are predominantly marine in origin. Transport studies of marine sediments along the Dutch coast (De Groot, 1963; Terwindt, 1977; Eisma, 1981) all show that the amount of mud originating from the English Channel exceeds the discharge of fine material by the Rhine and Meuse. For the marine part of the Scheldt estuary the clay mineralogy was found to be identical with that of the mudflats along the Belgian coastal zone (Zeelmaekers, 2011; Adriaens et al., 2018).

Glauconite

Glauconite is mineralogically related to clay minerals but unlike other clay minerals in Dutch sediments its origin is primarily autochthonous and not detrital. The mineral glauconite is an iron potassium phyllosilicate of the mica group which has a characteristic green colour. High content of authigenic glauconite is an indicator of low sedimentation rates in a marine environment and is often associated with marine transgression. It is used for sedimentological and sequence stratigraphic interpretations as well as K-Ar dating studies (Adriaens et al., 2018).

The presence of glauconite in marine sand can be chemically recognized by higher K_2O to Al_2O_3 ratios compared to this ratio in glauconite-free sand (Huisman & Kiden, 1998). High K_2O contents in the Breda Subgroup are clearly visible in Figure 13.13 which can be attributed to a high glauconite content. Such high K_2O to Al_2O_3 ratios are also visible in a few samples from the Oosterhout Formation. Very high glauconite contents in the Breda Subgroup are likely due to in situ production whereas lower contents in younger sediments such as the Oosterhout Formation are due to reworking of these layers and mixing with sediments from the hinterland (Vandenberghe et al., 2014).

Carbonates

The carbonate state of sediments is important in two different ways. Firstly, it is used to stratigraphically classify the sediments and to characterize their provenance. Secondly, the presence of carbonate minerals exerts a control on the carbonate chemistry and pH of soil moisture and groundwater. It is an attribute that is routinely considered in borehole descriptions using the HCl effervescence test and visual observations on especially shells and their fragments. The effervescence test is only indicative for the presence of calcite or aragonite but not for dolomite or siderite. Whereas calcium carbonates are well studied in Dutch Cenozoic sediments (Griffioen et al., 2016), considerably less is known about Fe- and Mg-bearing carbonates.

Table 13.4 presents an updated overview of the carbonate state of Cenozoic Dutch geological formations. It essentially refers to the state with respect to calcite and aragonite except for the Waalre Formation for which a remark about siderite is made. Generally, the marine formations are calcareous but the carbonate state varies among

Table 13.4. *General characterization of carbonates of Neogene and Quaternary formations outside the soil zone (based on De Mulder et al., 2003; Klein & Griffioen, 2010; Klein et al., 2015; Griffioen et al., 2016 and a query of the DINO-database in November 2021).*

Formation	Description
Naaldwijk	Very often calcareous; may contain shells and shell fragments
Echteld	Mostly calcareous but also non-calcareous; sporadically fresh water shells
Boxtel	Mostly carbonate-poor or non-calcareous and sometimes rich
Kreftenheye	Mostly calcareous but also non-calcareous
Eem	Mostly calcareous and often shells; locally rich in shells
Drente	Often non-calcareous or carbonate-rich
Drachten	Mostly non-calcareous
Peelo	Carbonate-poor sand and carbonate-rich clay
Urk	Non-calcareous to carbonate-rich
Appelscha	Mostly non-calcareous
Sterksel	Partly calcareous
Beegden	Often non-calcareous
Stramproy	Mostly non-calcareous or carbonate-poor
Peize	Mostly non-calcareous
Waalre	Often non-calcareous or carbonate-rich; contains siderite-bearing clay layers
Kieseloolite	Mostly non-calcareous
Maassluis	Mostly carbonate-rich with shells
Oosterhout	Often carbonate-rich; rich in shells
Breda Subgp	Variable; locally with shells

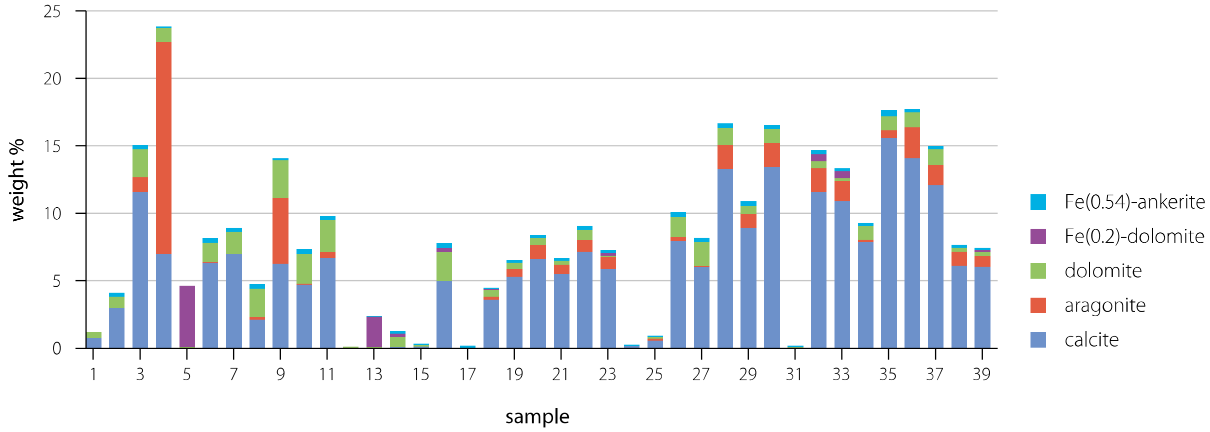


Figure 13.15. *Contents of various carbonate minerals in marine sediments from the surficial Naaldwijk Formation based on XRD-analyses of samples from 9 boreholes in Walcheren, province of Zeeland.*

non-marine formations. Sediments may be non-calcareous upon deposition or they may have been decalcified post-depositionally during pedogenesis or diagenesis. This may have happened under paleohydrological conditions, as is suggested by regional differences in pH and carbonate saturation state of groundwater in the Pleistocene part of the Netherlands (Griffioen et al., 2013) or more recently, following impoldering activities (for example of supratidal flats). A limited number of XRD analyses indicates that both calcite and aragonite are present in marine and other deposits. This is illustrated in Figure 13.15 that indicates a considerable heterogeneity in carbonate mineralogy of the marine Naaldwijk Formation sampled within a limited area in Walcheren (province of Zeeland).

Dolomite is also a common detrital mineral in Dutch sediments. Fractions of around 10% of the total Ca carbonate content have been reported for fluvial, marine and glacial sediments and also in loess (Griffioen et al., 2016). Dolomite tends to become relatively enriched during decalcification (Van der Sleen, 1912; Ritsema & Groenenberg, 1993) as the dissolution rate of dolomite is much lower than that of calcite and aragonite. It thus becomes preserved for a longer period than pure Ca carbonate minerals.

Siderite has been frequently detected in various kinds of geological sediments (Griffioen et al., 2016). It occurs in traces in suspended matter of the Rhine and Scheldt rivers (Crommelin, 1943; Wartel, 1977), which brings forward that it might be detrital when it does not become oxidized post-depositionally. However, a diagenetic origin is more likely as can be illustrated by scanning electron microscopy or just visual observations from borehole samples. The appearance of siderite varies from coatings on Ca carbonate grains via micrometer-size nodules and white substance in gyttja (which are organic-rich lacustrine sediments) to large concretions of ca. 10 cm in clay layers (Huisman, 1998; Griffioen et al., 2016). XRD-analysis as well as EDX elemental analysis indicate that the diagenetic precipitate may also be a carbonate solid-solution containing Fe, Ca, Mn and Mg, which is referred to as ferroan dolomite and ankerite instead of siderite (see Fig. 13.15). The visual observations prove that sufficient time was available for precipitation of Fe-bearing carbonates in Cenozoic sediments, despite the fact that siderite precipitation is kinetically very slow at earth surface conditions and that Dutch groundwater is frequently supersaturated with siderite, which indicates a lack of thermodynamic equilibrium (Griffioen et al., 2013).

Specific features

Bog iron ores

Bog iron ores deserve special attention as they regularly occur at local scale and have a geochemical composition that deviates from regular clastic sediments. They are typically found in sandy deposits at the bottom of peat layers, in alluvial deposits in brook valleys and within peat layers as tubular crusts or powder (Van Bemmelen & Reinders, 1901; Reinders, 1902; Booij, 1986; Landuydt, 1990). Their diagenesis has always been linked to exfiltration of Fe-containing groundwater in low-lying areas. They were mined in Roman times, the Early Middle Ages and the 17th-19th centuries in three major areas: the Vecht (province of Overijssel), Montferland and the Veluwe (Joosten, 2004).

The bog iron ores are notorious for their high contents of trace elements, that get bound during groundwater exfiltration (Van Pruissen & Zuurdeeg, 1988; Joosten, 2004). This is illustrated in Table 13.5, in which two geochemical data sets are summarized. As expected, the Fe content is high and other main metals are relatively low. The P content is also high as PO_4 binds strongly to Fe-oxyhydroxides or forms Fe-hydroxyphosphates during precipitation at high PO_4 to Fe groundwater ratios. The statistics for the trace elements may be compared to the Dutch, aqua regia-based baseline AW2000 value ('Regeling bodemkwaliteit', 2007) and to the Dutch intervention value, above which one speaks of severely contaminated soil or sediment ('Circulaire Bodemsanering', 2013). Both values were derived for sediment with ≤2% clay and ≤2% organic matter. For regular soils and sediments, aqua regia-based contents are often lower than XRF-based contents (e.g. Salminen et al., 2008). However, this difference may be small or absent for bog iron ores as much of the solids will be well soluble in aqua regia. A direct comparison, therefore, seems appropriate. The average contents for trace elements lie above the AW2000 values except for Cu. The averages also lie above the intervention value for As, Ba and Cr, which illustrates the polluted nature of bog iron ore due to secondary enrichments. Within the framework of the Dutch Soil Protection Law, their occurrences may be classified as natural pollution sites. This avoids their classification as anthropogenically contaminated sites and individual parties are not held responsible for the pollution. Bog iron ore fragments are also brought to the surface at the coastal nourishment site of the Sand Motor (Pit et al., 2017). Their surficial occurrence in this recreational area lies within acceptable limits with respect to human toxicological exposure (Van Bruggen et al., 2014).

Trace elements in pyrite

Another topic that deserves attention when it comes to the presence of trace elements is the elemental composition of pyrite. It is widely recognized that trace elements that form sulphide minerals, are present in Fe-sulphides as impurities (e.g. Morse, 1994). These trace elements may become mobilized when pyrite gets oxidized, especially in relation to denitrification. This may induce negative environmental side effects when the concentration becomes high compared to environmental standards. For the Netherland it turns out that this is especially the case for Ni and As (Van Beek et al., 1989; Zhang et al., 2009).

Selective extraction techniques have been used to characterize the elemental composition of pyrite and this has been applied a few times to Dutch sediments. Figure 13.16 summarizes the findings as cumulative frequency distribution plots of the molar ratios between the trace metals of interest and Fe as main constituent of pyrite. The plots illustrate that the ratios are highest for As, Zn, Ni, Cu and Co and vary within two orders of magnitude. For Pb and Mo, the ratios are about an order of magnitude smaller and have a smaller range. The ratio is lowest for Cd but varies three orders of magnitude. Considering the fact that Ni and As show high ratios while they have lower environmental standards compared to Zn and Co, it is not surprising that Ni and As have received the most attention. Copper also has a high ratio but is more strongly sorbed to oxides and humic acids, which makes it less mobile than the other four trace elements. Referring to the earlier discussed results of the factor analysis of geochemical data sets of Dutch sediments, it is worth to point out that an S-factor is frequently observed that contains As but often no other trace elements. This indicates that the trace metals of concern are not majorly bound by sulphides but that specific mobilization is a topic of environmental concern.

***Table 13.5.** Average elemental composition and associated standard deviation of bog iron ore as calculated from 15 XRF-analyses presented by Joosten (2004) and 18 XRF-analyses of bog iron ore as identified in the DINO database. Values below detection limit were set to half the detection limit when calculating the statistics.*

Data set	Main elements (wt%)								
	Fe_2O_3	SiO_2	Al_2O_3	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5
Joosten (2004)	71.5±13.8	22.5±11.6	1.7±0.8	1.8±2.0	1.1±1.2	< 0.1	0.1±0.1	0.4±0.2	3.0±1.7
DINO dbase	32.1±11.6	37.4±15.3	3.97±1.93	1.18±1.18	0.74±0.55	0.07±0.11	0.20±0.10	0.61±0.27	1.1±0.3
	Trace elements (mg/kg)								
	As	Ba	Co	Cr	Cu	Ni	Sr	V	Zn
Joosten (2004)	95.4±90.4	1415±1641	29.3±20.1		< 1	67.9±61.4	123.4±149.8	77.5±68.4	91.6±73.0
DINO dbase	303±322	449±266		47.1±21.9	10.4±2.1	20.7±5.6	55.0±26.1	40.1±21.9	63.6±32.8
AW2000[1]	11.4	49.0	4.3	29.7	19.3	10.9		27.4	59.0
Intervention[1]	43.5	237	54.0	42.1[2]	91.8	31.1		85.7[3]	303

1 note that the AW2000 and intervention values are based on aqua regia destruction and not total element analysis according to XRF;
2 assuming Cr(VI);
3 indicative value

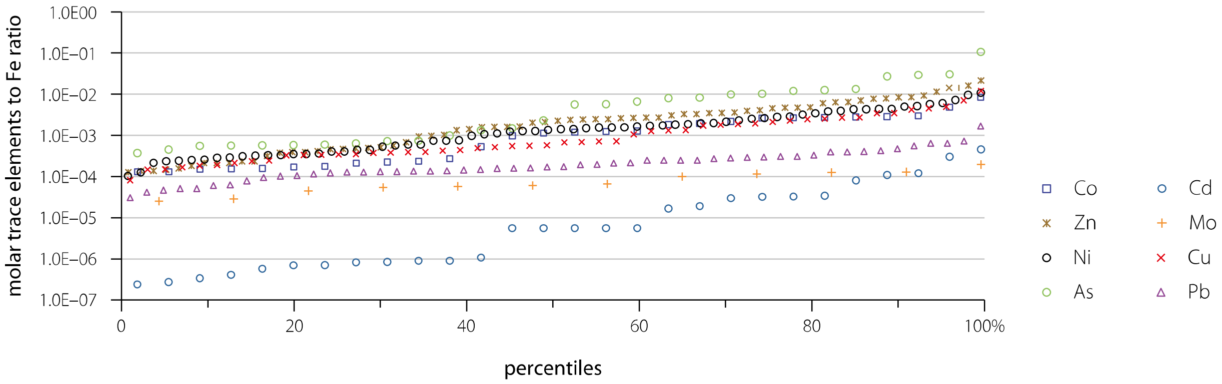


Figure 13.16. Cumulative frequency diagrams for the molar ratio of trace metals to Fe as based on selective extraction of pyrite. Data originates from Griffioen & Broers (1993), Broers & Buijs (1997) and Roskam & Griffioen (2011).

Sulphur in peat

In the Netherlands, peat has been poorly studied mineralogically and geochemically. Many peatlands in the Netherlands cope with subsidence and water quality problems. Drainage of these areas causes the peat to oxidize (e.g. Van Bergen & Koster, 2025, this volume), resulting in subsidence (Fokker et al., 2025, this volume), acidification and eutrophication. The form in which sulfur is originally present in peat, as pyrite (FeS_2), iron monosulfide (FeS), solid elemental sulfur or organic sulfur, influences the dynamics of sulfur cycling and thereby oxidation products and consequences such as acidification or the release of nutrients (Wieder & Lang, 1988; Mandernack et al., 2000). Thus, pyrite does not only play an important role in As and Ni release as pointed out in the previous section.

Studies on sulfur in Dutch peatlands show that sulfur can be present in very high amounts up to 8-9 wt% (Klein et al., 2015). S:Fe molar ratios in peat vary considerably with an average of 22, indicating that in addition to its presence as iron sulfides, sulfur is likely also present as organic sulfur (data from DINO database). The amount of organic sulfur in organic matter can vary considerably with S:C ratios between 1:30 and 1:1000 as measured in different types of peat (Kohnen et al., 1989; Price & Casagrande, 1991; Tipping et al., 2016). It is therefore not possible to estimate sulfur speciation from total organic carbon content or total element analysis of S. In a limited study on the Hollandveen Member of the Nieuwkoop Formation, at four different locations, sulfur was found to be predominantly present in the form of pyrite and organic sulfur species (Kim, 2017). FeS and sulfate were present in very small quantities and the amount of elemental sulfur was negligible.

It is suggested that in peat having had both fluvial and marine input, pyrite is the dominant form of sulfur, while in peatlands having marine influence but lacking freshwater input, organic sulfur is predominant (Kim, 2017). This is thought to be related to the availability of dissolved iron (Fe) at the time of the peat formation. In peat formed in brackish water, dissolved sulfate was abundant from the seawater, while the freshwater input brought Fe-rich suspended matter, and together they eventually formed pyrite (FeS_2) under reducing conditions. Whether such regional differences in sulfur speciation have an influence on potential acidification or eutrophication as a result of drainage or droughts has not been investigated for the Netherlands.

Lead and its isotopes

Lead (Pb) and its isotopes deserve special attention as soil contamination with lead frequently occurs in the Netherlands and there is no threshold value below which bioaccessible Pb can be assumed not toxic when ingested by children, especially (EFSA, 2010). Soil contamination originates from for example white lead ($(PbCO_3)_2{\cdot}Pb(OH)_2$) that was used in paint and from atmospheric deposition resulting from use of leaded gasoline. Historical contamination with Pb is thus widespread in both urban and rural soils. The origin of lead in soils can be traced by analyzing its isotopes. Walraven and coworkers performed a series of studies on the isotope geochemistry of lead in Dutch soils and lake sediments. Firstly, they showed that for unpolluted soils, the four main lithologies distinguished – clay, sand, peat and loess – have distinct natural isotope signatures (Walraven et al., 2013a). This variation can be explained by the soil Al and Zr contents, where Al is indicative for the Al-silicate minerals and Zr for the proportion of U and/or Th containing primary minerals that have a more radiogenic Pb isotope composition. No significant difference was found between marine and fluvial clays, which points to the dominance of a similar sedimentary provenance in the Pb isotope signal.

Anthropogenic Pb contamination of the soil is recognized from the Pb isotope composition, where the sources and their intensity vary for rural soils between atmospheric deposition from coal burning (or galena), incinerator ashes, gasoline, and the application of animal manure and fertiliser salts (Walraven et al., 2013b). For these soils, the highest contamination is found in the Randstad area and near the Dutch borders and the lowest contamination occurs in the coastal dunes and forest areas in the Pleistocene part of the Netherlands. At the national scale, the agricultural contamination of the soil with Pb is not distinctly different from that caused by atmospheric deposition. The history of atmospheric lead deposition can be well recognized in lake sediments from undisturbed sites and the extent of Pb deposition from gasoline can be identified in the vicinity of motorways (Walraven et al., 2014a,b). Lead is a trace metal that is more immobile than, for example, Ni or Zn. However, leaching of Pb to groundwater may have occurred in acid forest soils for which Pb cannot be assumed to be immobile.

Acknowledgments

Pauline van Gaans is thanked for earlier discussions on the factor analysis of geochemical datasets. Eva Hoekstra is thanked for her database activities on the geochemical sediment analyses. The reviewers Mark Hollanders, Bas van der Grift and Rudy Swennen, and the editor Jan de Jager are acknowledged for their constructive comments on an earlier version of this chapter.

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