Grain-rimming kaolinite in Permian Rotliegend reservoir rocks

Svenja Waldmann [a,b,*], Reinhard Gaupp [a]

[a] Institut für Geowissenschaften, Friedrich-Schiller-Universität Jena, Burgweg 11, 07749 Jena, Germany
[b] TNO, Princetonlaan 6, 3584 CB Utrecht, The Netherlands

A R T I C L E   I N F O

A B S T R A C T

Upper Rotliegend sediments of Permian age from the northeast Netherlands show moderate to good reservoir qualities. The predominant control is by the presence of authigenic grain-rimming kaolinite, which has a negative, but in some parts also a positive, effect on reservoir quality. To better understand the formation and distribution of grain-rimming kaolinite, reservoir rocks were studied in terms of composition and diagenetic processes. Petrographic evidence, summarized as a paragenetic sequence, is integrated with geochemical modeling results to identify early mesodiagenetic water–rock interactions under the participation of gases, i.e., CO_2 and H_2S, released from underlying Carboniferous source rocks. The sediments investigated were deposited at varying distance from the southern flank of the Southern Permian Basin. Sediments near the basin margin are mainly attributed to a fluvial environment and comprise medium to coarse-grained sandstones and conglomerates. There, vermicular kaolinite occurs with a lath-like structure. Distal to the basin margin, mainly in sandstones intercalated with fine-grained playa sediments, comparatively high amounts of grain-rimming kaolinite occur. There, the presence of this mineral has a significant influence on the rock properties and the reservoir quality. Geochemical modeling suggests that the formation of such kaolinites cannot be explained exclusively by in situ feldspar dissolution. The modeling results support evidence that kaolinite can be formed from precursor clay minerals under the presence of CO_2-rich formation waters. Such clay minerals could be corrensite, smectite–chlorite mixed-layer minerals, or chlorite that is potentially present in Rotliegend sediments during early diagenesis. Furthermore, the geochemical modeling can reflect several mineral reactions that were identified from petrographic analysis such as the formation of illite and kaolinite at the expense of feldspar dissolution and consequent silica precipitation. Under the presence of sulfate (SO_4^{2-}), partial hematite dissolution and the reduction of Fe^{3+} to Fe^{2+} occur, where the latter is further incorporated in Fe–Mg-rich carbonates. The sulfate is bonded in anhydrite. The results of this study are relevant for reservoir quality predictions in kaolinite-dominated systems, as well as for CO_2 storage projects and the prediction of long-term fluid–rock interactions under the participation of carbon dioxide and/or other gases.

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1. Introduction

Investigations of authigenic kaolinite in siliciclastic settings lead to the theory that their formation is caused by different processes. Kaolinite crystallization is observed under near surface conditions during the entry of meteoric oxygenated freshwaters (e.g., Hancock and Taylor, 1978) after deposition and early burial (eodiagenesis) or after structural inversion (telodiagenesis) (Lanson et al., 2002). It forms especially under semi-arid to humid climate conditions by the interaction of acidic groundwater with alumosilicate minerals, such as detrital plagioclase, K-feldspar, rock fragments, mica, and mud clasts. The precipitation occurs either directly from the formation water or as replacement of detrital grains (Worden and Morad, 2003). The amount of kaolinite depends, among other things, on the volume of unstable alumosilicate minerals, the influx of meteoric waters into the sediment, hydraulic conductivity, and water chemistry. The formation of kaolinite may also be caused by the influx of hydrocarbons or CO_2 and related acidic formation waters. These acidified waters result from maturation of organic matter from adjacent mudstones, shales, or coals carrying high amounts of aluminum–organic complexes (Curtis, 1983; Ehrenberg, 1991; Keer van et al., 1998; Molenaar et al., 2015). For example, Ehrenberg (1991) demonstrated the migration of acidic fluids and the precipitation of kaolinite at the expense of K-feldspar in sandstones from the Garn Formation (Norwegian shelf). Similar observations were made close to the contact of Rotliegend sediments with Carboniferous coals (Gaupp et al., 1993). There, strong feldspar dissolution and the formation of kaolinite occur, whereas farther away from such contacts illite is the dominant clay mineral. The morphology of authigenic kaolinite is constituted as pseudohexagonal platelets arranged as short stacks or vermicular structures in the open pore spaces, or as replacements of detrital alumosilica grains (Lanson et al., 2002; Ziegler, 2006).

* Corresponding author at: TNO, Princetonlaan 6, 3584 CB Utrecht, The Netherlands.
E-mail address: Svenja.Waldmann@mail.com (S. Waldmann).

In this case study, sediments of Permian age (Upper Rotliegend) in the northeast Netherlands show, besides a typical vermicular structure, an additional morphology of kaolinite in the form of single platelets perpendicular to detrital grain surfaces (Waldmann et al., 2014). This grain-rimming kaolinite occurs dominantly in sandstones intercalated with fine-grained playa sediments located distal to the margin of the North German Basin. Near the margin, in fluvially dominated deposits, only vermicular kaolinite is present. The morphology, abundance, and genesis of such grain-rimming kaolinite, and the formation in siliciclastic rocks are only rarely reported in literature (e.g., Watson et al., 2003). In such playa environments, typically grain-rimming smectite–chlorite mixed-layer minerals or corrensite may precipitate directly from alkaline groundwater due to high cation concentrations under the influx of freshwater (Gaupp and Okkerman, 2011). Rotliegend chlorites are considered to be formed from precursor pore-lining minerals, like trioctahedral smectite and corrensite during deeper burial at temperatures of >150 °C. Such pore-lining chlorites are dominantly Mg-rich, but also Fe-rich compositions occur. Specifically, the Fe/(Fe + Mg) molar ratio varies from 0.21 to 0.68. In the direction of the basin center, the chlorites are more Mg-rich and become progressively more Fe-rich towards the basin margin (Hillier et al., 1996). These chlorites show a similar morphology to the grain-rimming kaolinite in this study, and are to be found in adjacent regions to the east of the study area, forming a "chlorite-belt" in distal sandstone-shale intercalations (Gaupp et al., 1993; Hillier et al., 1996). The spatial distribution of grain-rimming clay minerals has a major influence on porosity and permeability evolution of reservoir rocks, and hence on reservoir quality. Several authors have pointed out that early grain-rimming diagenetic chlorite has a positive effect on reservoir quality, whereas little attention has been paid to grain-rimming kaolinite formation, and their impact on reservoir quality development over time (Ehrenberg, 1993; Gaupp et al., 1993; Ziegler, 2006; Ajdukiewicz et al., 2010). In the case when kaolinite precipitates directly from solution, it forms small stacks and vermicular structures, because of the bonding effects between hydroxyl groups at the interlayer base surface of each platelet (Jasmund and Lagaly, 1993). Kaolinite precipitating directly from solution under the supply of freshwater is considered to be not sufficient in Rotliegend sediments to account for the amount of authigenic kaolinite (Ziegler, 2006). On the other hand, kaolinite can be formed by the transformation of precursor clay minerals, like smectite–chlorite mixed-layer, corrensite, or chlorite under the supply of acidic, CO_2-rich formation waters. The transformation to kaolinite occurs according to a direct substitution of cations whilst retaining its external shape (Hutcheon et al., 1980).

In this study, detailed petrographic analysis in combination with geochemical modeling is used to address the possible formation of grain-rimming kaolinite during early mesodiagenesis due to (i) direct precipitation from the formation water, or (ii) as a transformation product of precursor authigenic chlorite. Geochemical modeling tested both hypotheses by reproducing the physicochemical conditions during early mesodiagenesis. The formation of clay minerals is still not a well-understood process because of limited knowledge on kinetic inhibition and initial nucleation. Hence clay formation, and transformation processes from one mineral type to another, is difficult to address by using numerical modeling approaches (Brosse et al., 2003). Nevertheless, the use of geochemical modeling gives insight into mineral precipitation and dissolution behaviour in a broader context and enables the understanding of mineral reaction tendencies during burial diagenesis identified by petrographic analysis.

The knowledge gained in this study can be applied in terms of reservoir quality prediction and provides additional perspectives how the presence of CO_2-rich acidic waters influences water–rock interactions. The latter can be applied to questions concerning the geochemical reactivity of host rocks during injection and storage of waste greenhouse gas (e.g., CO_2) into the deep subsurface. The injection of CO_2 into a storage horizon results in the (partial) dissolution of the gas into the formation water and hence in higher water acidity. This may trigger the dissolution of primary silica minerals and the release of cations and anions into the water phase. Cations like calcium, magnesium, and iron are then trapped as solid carbonate minerals. Previous studies pointed out that CO_2 trapping in the form of solid minerals in the safest way of CO_2 storage (e.g., Lu et al., 2010). Hence it is important to understand the interplay between silica reactions and related carbonate formation in siliciclastic sediments.

2. Geological setting and structural evolution

The study area lies on the southern flank of the east–west striking Southern Permian Basin (Glennie, 1972; Ziegler, 1990). During the Permian, a large saline to hyper saline lacustrine playa lake developed in the basin center, where mudflats and evaporates were deposited under semi-arid to arid climate conditions (Glennie, 1972). Contemporaneously ephemeral fluvial sediments and aeolian sands were deposited near the southern margin (Ziegler, 1990). A gradual change towards a wetter climate at the end of the early Permian resulted in lake expansion and deposition of fine-grained siliciclastics in marginal areas (Amthor and Okkerman, 1998). In the Triassic to Middle Jurassic, regional thermal subsidence occurred mainly in the North Sea area. This extensional phase led to reactivation of late Hercynian fracture systems and thus in faulting and fracturing of Rotliegend deposits of Central and Western Europe. An increasing burial temperature up to ~120 °C at a depth of 1900–2200 m occurred in the northeast Netherlands (Fig. 1). The Jurassic to Lower Cretaceous deformations (including structural inversions) in particular had a major influence on fluid flow, including early hydrocarbon charging (Gaupp and Okkerman, 2011). During the late Jurassic/early Cretaceous, increasing crustal extension changed to local compressional inversions, with regional uplift causing erosion and folding, as well as fault movements. Subsequent ongoing thermal subsidence caused reburial of the sediments (Ziegler, 1990; Amthor and Okkerman, 1998; Gaupp and Okkerman, 2011). Expulsion of hydrocarbons from underlying Carboniferous intervals (van Wijhe and Bless, 1974) took place from the late Triassic to late Jurassic (De Jager et al., 1996). The present gas composition is dominantly methane and ethane with nitrogen (12–26 vol.%), carbon dioxide (0–2 vol.%), and other negligible components. However, it is likely that the gas composition has significantly changed over time while entering the overlying Rotliegend sediments. A major CO_2 expulsion occurred in the late Jurassic from Carboniferous sources (Gaupp and Okkerman, 2011).

Three natural gas fields were investigated in the current study covering different environmental settings of the Upper Slochteren Formation (Upper Rotliegend) (Fig. 2). Field A is located near the basin margin and is characterized by a fining-upward trend of conglomerates and coarse grained sandstones to medium and fine grained sandstones, attributed to alluvial fan and braided river systems. Cross-bedded aeolian sandstones and muddy siltstones, fine-grained sandstones, and mudstones of a lacustrine environment overlie the sequences. Sediments from a desert plain environment in the area of Field B were deposited in dry and damp sandflats, as well as aeolian dune settings, locally intercalated with wet sandflats and interdune pond environments. In some sequences sheetfloods from the southeastern basin margin occur. Distal to the basin margin, where Field C lies, fine grained sand- and siltstones of a deltaic shallow-water environment were deposited. Intercalation of mudflats, dry sandflats, and aeolian dune sediments occur. Representative core sections are shown in Fig. 3. From proximal to distal locations, permeability decreases, whereas the porosity shows no regional trend (Fig. 4). Changes in permeability are mainly caused by higher amounts of authigenic minerals, particularly in the context of clay mineral occurrence.