GHGT-12

Observed CO_2-induced reactivity in Werkendam gas field, the Dutch storage analogue

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Abstract

Natural CO_2 fields provide important insights in the long-term geochemical behaviour of CO_2 in a reservoir and the potential of permanent trapping in carbonate minerals. The Werkendam gas field in The Netherlands, discovered during gas exploration activities in 1991, contains >70% CO_2. Core samples were selected from the Werkendam natural analogue (WED) as well as from the nearby Barendrecht-Ziedewij (BRTZ) and Waalwijk-Noord (WWN) CH_4-bearing reservoirs. The three gas reservoirs are all Triassic Bunter sandstones, with BRTZ and WWN containing respectively ~0.8% and 1.4% CO_2. Mineralogical and petrographic analyses were performed to unravel the diagenetic evolution of each field for comparison.

Early diagenetic mineral reactions were similar for the three field. Minor differences are attributed to variation in primary mineralogy and the K^+/H^+ ratio of the formation water. The late stage mineral reactions that are observed in WED which are absent in BRTZ and WWN were interpreted to be induced by the influx of CO_2. These include the (additional) dissolution of K-feldspar and anhydrite, and the precipitation of Mg-rich siderite, quartz and barite. Even though carbon isotope analysis could not confirm (but also not exclude) this, petrographic analysis gave strong indications for the precipitation of siderite in WED as a result of the high CO_2 partial pressure. The estimated amount of carbon trapping in siderite is 20% to 58% of the total CO_2. Barite precipitation was probably the result of K-feldspar and anhydrite dissolution, since barium is a common impurity in K-feldspar. In the overall reaction between the sandstone and carbonized brine, several unknowns remain. A sink for calcium, potassium and aluminium from anhydrite and K-feldspar dissolution was not observed in the samples from WED. In addition, potential sources of magnesium and iron for Mg-rich siderite could not be deduced from the comparison of the fields. Possibly, these sinks and sources can be found in the clay-rich intervals within the sandstone reservoir. Future research should investigate the effect of heterogeneity within storage complexes on mineral trapping.

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1. Introduction

Geological storage of CO_2 in depleted gas fields is one of the potential solutions to limit greenhouse gas emissions. The dissolution and dissociation of CO_2 in the irreducible formation water will lower the pH, thereby affecting the geochemical equilibrium. On the long-term, CO_2 storage benefits from carbon trapping in carbonate minerals because of the permanent nature of this trapping mechanism. The rate and extent of trapping is known to be site specific and depends on e.g. the mineralogy and pressure and temperature conditions in the reservoir [1].

Experimental studies investigating geochemical reactions only cover a limited time scale (months to years) and are highly dependent on experimental conditions [2]. Generally, geochemical modelling is applied to assess the site specific rock-water-gas interactions on the long-term and to evaluate the potential for trapping. In addition, it can be used to assess the effects of varying reservoir conditions relatively easily [3]. However, these models are simplifications of complex geological systems and they are prone to uncertainties [1]. Natural CO_2 fields can provide us with important insights into the long-term geochemical interactions between CO_2, formation water and reservoir rock [4]. We investigated a Dutch natural CO_2 field, the Werkendam-Deep gas field, which is to a certain extent representative for many potential Dutch storage sites. This Triassic sandstone reservoir, which is located onshore near Rotterdam, contains a gas cap with > 72% CO_2 which is thought to be related to Jurassic volcanism [5]. An oil rim is present below the gas cap. Mineralogical and petrographic analyses were performed on rock samples of the Werkendam-Deep reservoir (WED) as well as samples from two nearby, CH_4-bearing stratigraphic equivalents, the Barendrecht-Ziedewij (BRTZ) and Waalwijk-Noord (WWN) fields. The CO_2 concentration in BRTZ and WWN is only ~0.8% and ~1.4%, respectively. For each field the diagenetic evolution was unravelled, and they were subsequently compared to evaluate the mineral reactions in WED which can be attributed to the presence of CO_2. The comparison of WED and BRTZ was previously described in Koenen et al. [6]. New insights from an extended study and the comparison with WWN is presented.

2. Methods

Basin modelling was performed to assess the burial history and corresponding temperature evolution for the WED, BRTZ and WWN. For this purpose, the software PetroMod v11 of Schlumberger was used. Basic data requirements for the 1D modelling of the burial and temperature history are the present-day geometry, lithological description of the layers based on true vertical depths, the formation properties, absolute ages for stratigraphic layers, times of non-deposition and erosion, boundary conditions such as paleo-surface temperature, heat flow and water depth. The data used in the modelling is publicly available a www.nlog.nl.

From WED, BRTZ and WWN, respectively 13, 7 and 8 sandstone samples of the Triassic Röt Fringe Sandstone Member were selected from core material for analysis. The mineralogical and petrographic study included:
- X-ray diffraction (XRD) for identification and quantification of the crystalline phases;
- Optical microscopy and scanning electron microscopy (SEM) for microstructural analysis;
- Energy dispersive X-ray (EDX) detector for semi-quantitative chemical analysis;
- Bulk stable carbon isotope analysis for carbon source determination.

3. Geological setting and burial history

Our area of interest is the West-Netherlands Basin (WNB), a small inverted basin [7] bounded to the north by the Central Netherlands Basin and the Broad Fourteens Basin, and to the south by the London-Brabant Massif (Fig 1A). During the late Carboniferous thick layers of organic material were deposited that became the main source rock for CH_4-gas in the Triassic sandstones [8]. At the end of the Carboniferous the sedimentation stopped. Between Late Permian and Middle Jurassic, sedimentation continued and mainly clastic sediments were deposited [8]. These deposits formed the reservoir rocks for the three selected gas fields. The WNB experienced a late Kimmerian rifting event (Late Jurassic to Early Cretaceous) which formed the main tectonic elements in the subsurface.
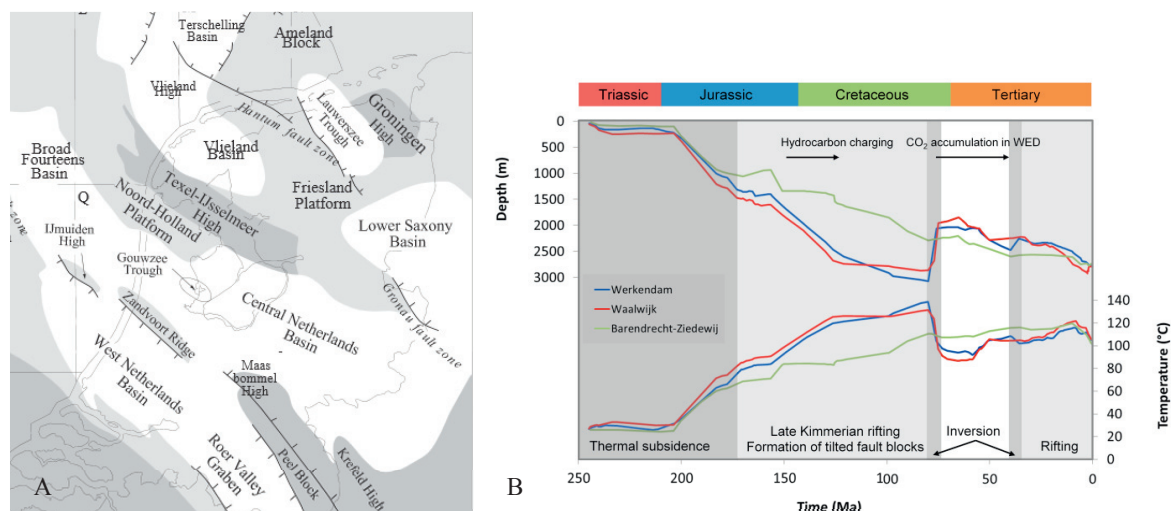
Fig. 1. A) Structural elements map of the Netherlands with the location of the West Netherlands Basin [9]; B) Burial history and corresponding temperature evolution for the three reservoirs. WED and WWN show very similar burial histories, while BRTZ experienced a different evolution.

The Triassic Bunter sandstones, including the Röt Fringe Sandstone Member, formed tilted half blocks during late Jurassic rifting; structures that were able to trap gas [10]. Gas generation of Carboniferous coal and carbonaceous shales accelerated during Late Jurassic due to increased heat flow during rifting [8]. Subsequent hydrocarbon charging of the reservoirs occurred around that time. In addition, the rifting event initiated volcanism in the basin [11]. During Early Cretaceous the major faulting came to an end [10], after which the WNB was influenced by the Alpine inversion. The amount of uplift within the WNB varies per subarea [12].

Basin modelling results (Fig. 1B) showed that the three reservoirs experienced continuous subsidence from the time of deposition until Late Cretaceous. Subsidence was slower for the BRTZ field. Both WED and WWN experienced major uplift during Late Cretaceous inversion, with a corresponding temperature decrease from approximately 140°C to below 100°C, followed by subsidence. The BRTZ field shows continuous subsidence without major uplift episodes.

4. Diagenetic evolution

4.1. Mineralogy

The rock samples analysed by XRD are all quartz-rich silt- to sandstones with variable amounts of K-feldspar, albite, 2:1 Al sheet silicates (mainly illite, some micas), anhydrite and different types of carbonates. Significant differences in mineralogy between the three fields are observed:
- BRTZ contains primary biotite and muscovite, WED and WWN contain only muscovite;
- Illite is the only clay mineral present in WED, whereas BRTZ and WWN also contain kaolinite up to 9 and 2.5 wt% respectively;
- Barite is identified in WED up to 1.8%, but not in BRTZ and WWN;
- Carbonate types and contents vary (Fig. 2A): WED and BRTZ both contain mainly dolomite and siderite, whereas WWN contains high amounts of ankerite. WED has the highest siderite and total carbonate content.

4.2. Petrographic analysis

Detailed optical microscopy and SEM analysis on thin sections of the different fields was performed to develop the diagenetic evolutions. The results are summarized in Fig 3. Oil remnants were observed in several WED samples, implying the occurrence of oil prior to CH_4 and CO_2 charging. Comparison of the observed mineral reactions and their relative timing showed similarities in eodiagenetic (early diagenesis) and early mesodiagenetic (burial diagenesis) phases. These reactions include the formation of dolomite, pyrite and alumino-sulfate-phosfate minerals, followed by Fe- rich dolomite and ankerite, partial albitization of K-feldspar, K-feldspar overgrowth and partial K-feldspar dissolution and alteration to clay. The amount and composition of the dolomite with Fe-rich dolomite and ankerite zones vary for the fields (Fig. 2), but they all represent relatively early phase diagenesis. Pore
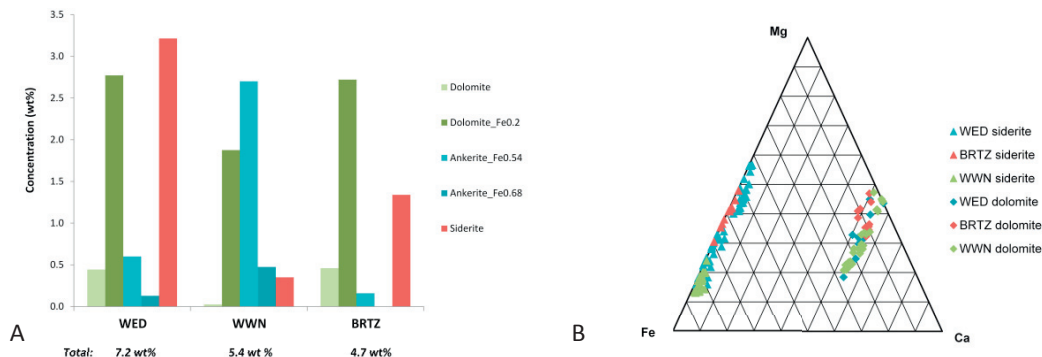

Fig. 2. A) Average carbonate content from XRD for Werkendam (n = 7), Waalwijk (n = 4) and Barendrecht-Ziedewij (n = 5) subdivided over the different carbonate types. Dolomite_Fe0.2 = $Mg_{0.8}Fe_{0.2}Ca(CO_3)_2$, Ankerite Fe0.54 = $Mg_{0.46}Fe_{0.54}Ca(CO_3)_2$ and Ankerite_Fe0.68 = $Mg_{0.32}Fe_{0.68}Ca(CO_3)_2$. B) Ternary diagram with siderite and dolomite composition for the three fields from EDX analysis.
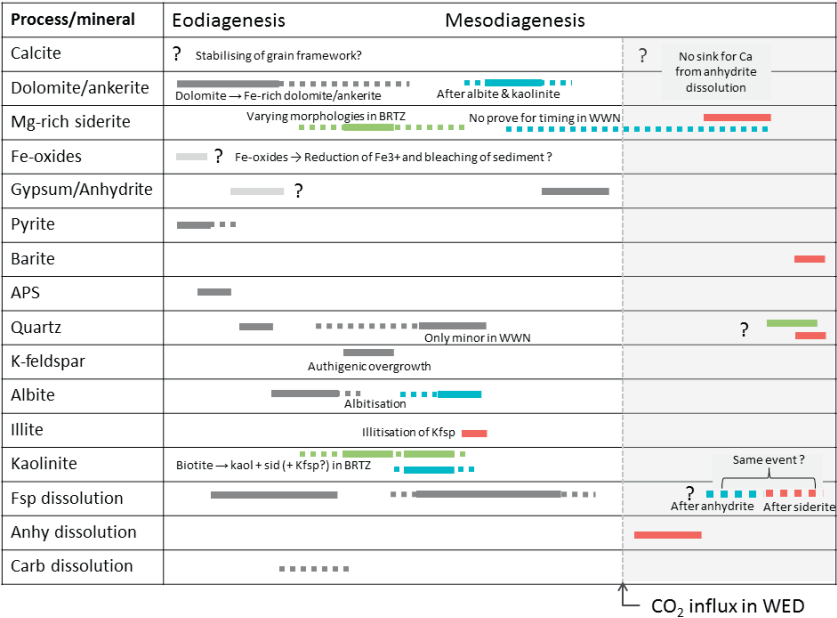

Fig. 3. Summary of the diagenetic evolution of WED (red), WWN (blue) and BRTZ (green). Processes observed in all three fields are in grey. Kfsp = K-feldspar, kaol = kaolinite, sid = siderite, anhy = anhydrite, carb = carbonate.

filling anhydrite cement is present in each field and encloses (and hence post-dates) the authigenic (Fe-rich) dolomite, ankerite, clay and quartz, as well as secondary pore space after K-feldspar dissolution. Anhydrite therefore represents a late stage cementation phase. Important differences between the fields were observed (Fig. 3):
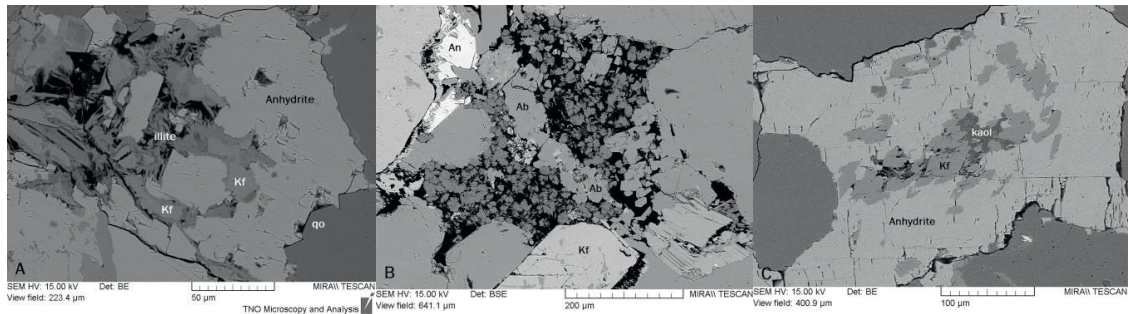

Fig. 4. SEM Back Scattered Electron images. A) WED image of K-feldspar (Kf) partially altered to illite, prior to anhydrite cementation; B) WWN image of partially albitized (Ab) K-feldspar altered to kaolinite (booklets in open pore space); C) BRTZ image of K-feldspar alteration to kaolinite (kaol) prior to anhydrite cementation.
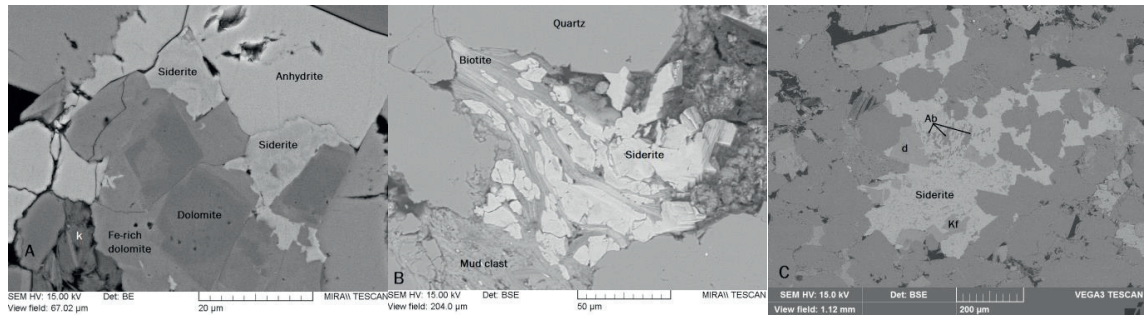

Fig. 5. SEM Back Scattered Electron images. A) BRTZ image of dolomite enclosed by Fe-rich dolomite, then by siderite and finally by anhydrite; B) BRTZ image of siderite associated with biotite alteration; C) WWN image of pore-filling siderite enclosing dolomite (d) and replacing albite (Ab) and K-feldspar (Kf) minerals.
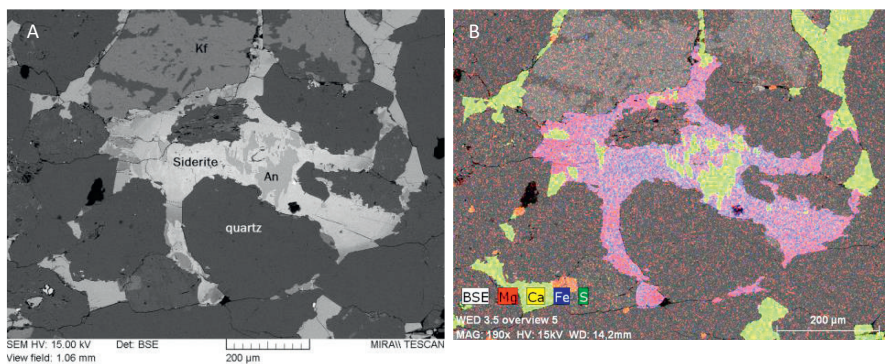

Fig. 6. A) WED SEM Back Scattered Electron image and B) corresponding EDX element map showing partially albitized K-feldspar (Kf) and patchy siderite with varying magnesium content replacing earlier anhydrite (An) cement.

- K-feldspar dissolution in WED resulted in (occasional) precipitation of illite (Fig. 4A), while kaolinite was formed at the expense of K-feldspar and biotite in BRTZ and WWN (Fig. 4B and C).
- Siderite is present in each of the fields, but the morphology, relative timing and composition is different. In BRTZ varying morphologies were observed. Dolomite crystals are generally enclosed by siderite blobs (Fig. 5A). Most of the siderite is associated with biotite alteration and/or mud clasts (Fig. 5B). The magnesium content of the siderite is variable (Fig. 2B). Relative timing of the different morphological types is complex, but the siderite surrounding dolomite is subsequently enclosed by, and hence prior to, anhydrite cement (Fig. 5A). Siderite in WWN and WED is pore-filling, thereby aggressively replacing framework silicates like quartz and feldspars. In WWN, siderite is only locally present. It post-dates the ankerite, but contact with anhydrite to define their relative timing, was not observed. The composition of the siderite in WWN is consistent, with low magnesium contents (Fig. 2B). Pore-filling siderite is abundant in WED and appears patchy in SEM BSE images as a result of highly varying magnesium contents (Fig. 2B). Anhydrite has partially dissolved and is replaced by the patchy siderite (Fig. 6).
- In addition to the anhydrite replacement by siderite, a late stage dissolution of K-feldspar and precipitation of quartz and barite cement was observed in WED. These reactions were not observed for BRTZ and WWN.

4.3. Carbon isotope analysis

Whole rock carbon isotope analyses were performed on selected samples with varying dolomite and siderite contents. The results are shown as a function of the amount of dolomite (Fe-rich dolomite and ankerite combined) in percent of the total amount of carbonate (Fig. 7). The results for WED and BRTZ show parallel linear relations, with values of -4.1 ‰ and -4.7 ‰ for dolomite (at 100 % dolomite) and -1.4 ‰ and -1.8 ‰ for siderite (at 0 % dolomite), respectively. The values are not significantly different. The values for WWN do not show a linear relation, which is partially because of the low siderite content. The carbonates in WWN are mainly Fe-rich dolomite and ankerite. The samples with very high ankerite content show higher $\delta^{13}C$ values (green circle in Fig. 6) than the samples with high dolomite content. Also for WED and BRTZ, a lower contribution of pure dolomite results in higher $\delta^{13}C$ values, implying an increase in $\delta^{13}C$ values of the available carbon with time.

The $\delta^{13}C$ value of the CO_2 from WED is -4.4‰ (PDB), but was not measured for BRTZ and WWN. CO_2 from a magmatic origin generally has values in the range of -4 to -7‰, whereas biogenic decay of organic matter can result in values of 15 to -30‰ [13]. Therefore, the value as measured in WED does not discriminate between the two sources, and the lack of a significantly different $\delta^{13}C$ value of siderite for WED and BRTZ does not allow any conclusions for the source of carbon.
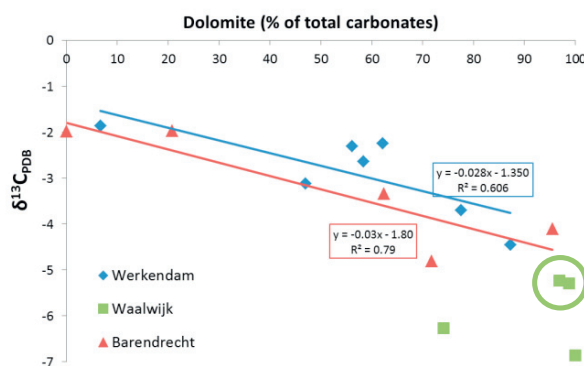

Fig 7. Whole rock stable carbon isotope values as a function of the amount of dolomite in % of the total carbonates. The values for WWN in the green circle represent mainly ankerite.

4.4. Discussion

The first part of the diagenetic evolutions of WED, WWN, and BRTZ are similar and show mineral reactions which are commonly related to burial diagenesis. The presence of authigenic illite in WED, and kaolinite in WWN and BRTZ suggests different brine compositions during early diagenesis. The formation of kaolinite from K-feldspar dissolution is a well-known reaction which occurs generally at shallow depths due to intense leaching by meteoric water, or by increased acidity [14]. Illite can be directly formed from K-feldspar dissolution instead of kaolinite at a higher K^+/H^+ activity ratio. The reaction of kaolinite and K-feldspar to illite and quartz is generally used to describe kaolinite illitization at temperatures >70°C [15]. However, illitization of kaolinite was not observed for WWN and BRTZ where K-feldspar and kaolinite are both present. According to [14, 16] the illitization reaction requires a high energy barrier to be overcome, which can be achieved by an increase in K^+/H^+ activity ratio. This increased ratio could, however, never be met by K-feldspar solubility unless very high temperatures are reached, corresponding to burial depths >4000 meters [16]. These considerations are important for the geochemical modelling which readily predict this reaction, even at lower temperatures [17].

Hydrocarbon charging in the three reservoirs probably occurred during Early Cretaceous. In WED, both CH_4 and oil were present, prior to influx of CO_2. Since extensive quartz cementation occurred prior to anhydrite cementation, and assuming that major quartz cementation in sandstones in the North Sea Basin started at ~90°C [18], we conclude that anhydrite precipitation occurred during Late Cretaceous (Fig. 1). In WED several mineral reactions were observed which were interpreted to have occurred *after* anhydrite cementation, and which are absent in both WWN and BRTZ. Based on this, we believe that CO_2 influx occurred during or right after the major uplift (Fig. 1), thereby replacing most of the methane in the reservoir and pushing down the oil. Subsequently, CO_2 dissolution and dissociation lowered the pH of the formation water, resulting in a disequilibrium with the mineralogy, and initiating mineral reactions, including the precipitation of Mg-rich siderite. Dolomite and ankerite are known to be prone to dissolution at decreasing pH conditions but we did not observe any signs of ankerite and/or dolomite dissolution. Possibly, an oil film around the crystals could have inhibited contact between the crystals and carbonized brine, since these carbonate minerals are preferentially oil-wet [15].

Much siderite is also present in BRTZ, but here it is mainly early diagenetic and/or related to biotite alteration. Biotite is absent as a primary mineral in WED and WWN, which explains the lack of an early diagenetic siderite phase in these reservoirs. The small amount of siderite in WWN has a similar pore-filling and feldspar replacement morphology as in WED, but the magnesium content is consistently low and anhydrite replacement was not observed. Based on these differences in siderite occurrence, we conclude that siderite in WED has trapped part of the supercritical CO_2 present in the reservoir, even though this could not be confirmed (but also not excluded) by carbon isotope analysis. The amount of CO_2 which is trapped is estimated based on an average siderite content of 0.6-3.2 wt% for the analysed samples, a CO_2 density of 420 kg/m^3 based on a pressure of 210 bar and 120°C, an average porosity of 7.2% and the assumption that no CO_2 has leaked from the reservoir. This gives a range of 20 - 58 % of the CO_2 which is trapped in siderite.

The following overall reaction is attributed to the presence of CO_2 in WED:

$$\text{K-feldspar} + \text{anhydrite} + CO_2 \rightarrow \text{Mg-rich siderite} + \text{quartz} + \text{barite}$$
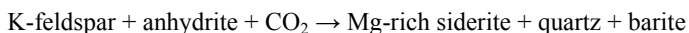
Barium is a common impurity in K-feldspar. Hence, K-feldspar and anhydrite dissolution can liberate barium and sulfur for barite precipitation. In addition, K-feldspar dissolution can result in silica release for quartz precipitation. Yet, the overall reaction leaves several unknowns. A sink for calcium from anhydrite, and potassium and aluminium from K-feldspar dissolution was not observed. The anhydrite is partially replaced by Mg-rich siderite, without incorporating calcium. In addition, the source of magnesium and iron for the siderite is currently unknown. Possibly, ion diffusion to and from the clay-rich intervals within the Röt Fringe Sandstone occurred and hence the interaction between clay and sandstone rocks might have played an important role in the gas-water-rock interactions.

Extensive anhydrite cement removal, dissolution of K-feldspar and barite precipitation was also observed in the Triassic sandstones in the Montmiral natural CO_2 site in France [19]. In contrast to the observations in WED, Gaus et al. [19] observed the precipitation of dolomite/ankerite and kaolinite, and hence they have a sink for calcium and

aluminium, but not for potassium. Unfortunately, the source of iron and magnesium for carbonate formation is not discussed in the paper.

5. Conclusions

The development and subsequent comparison of the diagenetic evolutions of WED, BRTZ, and WWN show similar early diagenetic evolutions. Yet, even though the gas reservoirs are closely located and situated in the same geological interval, differences in primary mineralogy and formation water composition seem to have had a significant impact on the mineral reactions. The presence of authigenic illite in WED and kaolinite in BRTZ and WWN suggest different K^+/H^+ activity ratios during early diagenetic alteration of K-feldspar and/or biotite. In addition, the presence and alteration of primary biotite in BRTZ resulted in the formation of significant amounts of siderite. In WWN significant amounts of ankerite were observed, which are absent in the other fields.

Late stage mineral reactions observed in WED that are absent in BRTZ and WWN, might be induced by the influx of CO_2, which probably occurred during the Late Cretaceous inversion event. These reactions include the (additional) dissolution of K-feldspar and anhydrite cement, and the precipitation of Mg-rich siderite, quartz and barite. It is unclear why the calcium released by anhydrite was not used in the formation. Ankerite did not dissolve as it was possibly protected from the carbonized brine by an oil film due to the presence of oil prior to CO_2 charging. Even though carbon isotope analysis could not confirm this, petrographic analysis gave strong indications for the precipitation of siderite in WED as a result of the high CO_2 partial pressure. The estimated amount of carbon trapping in siderite is 20% to 58% of the total CO_2.

In the overall reaction between the sandstones and the carbonized brine, several unknowns remain. A sink for calcium, potassium and aluminium from anhydrite and K-feldspar dissolution was not observed in the samples from WED. In addition, potential sources of magnesium and iron for Mg-rich siderite could not be deduced from the comparison of WED with BRTZ and WWN. The interaction between the sand-/siltstone and clay-rich intervals need further investigation since the sinks and sourced might be found there. In general, the effect of heterogeneity and the migration of elements between varying intervals might have significant impact on the CO_2-induced reactions and should be assessed in future research.

Acknowledgements

References

[1] Gaus I. Role and impact of CO_2-rock interactions during CO_2 storage in sedimentary rocks. International Journal of Greenhouse Gas Control 2010; 4, 73-89.

[2] Gaus I, Audigane P, André L, Lions J, Jacquemet N, Durst P, Czernichowski-Laurios I and Azaroual M. Geochemical and solute transport modelling for CO_2 storage, what to expect from it? International Journal of Greenhouse Gas Control 2008; 4, 73-89.

[3] Czernichowski-Lauriol I, Rochelle C, Gaus I, Azaroual M, Pearce J and Durst P. Geochemical interactions between CO_2, pore-waters and reservoir rocks. In: Advances in the Geological Storage of Carbon Dioxide: International Approaches to Reduce Anthropogenic Greenhouse Gas Emissions 2006; 65, 157-174.

[4] Pearce JM. What can we learn from natural analogues? In: Advances in the Geological Storage of Carbon Dioxide: International Approaches to Reduce Anthropogenic Greenhouse Gas Emissions 2006; 65, 129-140.

[5] De Jager J and Geluk MC. Petroleum geology. In: Geology of the Netherlands. Royal Netherlands Academy of Arts and Sciences 2007, 241-264.

[6] Koenen M, Wasch LJ, van Zalinge ME and Nelskamp S. Werkendam, the Dutch natural analogue for CO_2 storage – long-term mineral reactions. Energy Procedia 2013; 37, 3452-3460.

[7] De Jager J. Inverted basins in the Netherlands, similarities and differences. Netherlands Journal of Geosciences 2003; 83, 355-366.

[8] Van Balen RT, van Bergen F, de Leeuw C, Pagnier H, Simmilink H, van Wees JD and Verweij JM. Modelling the hydrocarbon generation and migration in the West Netherlands Basin, the Netherlands. Netherlands Journal of Geosciences 2000; 79, 29-44.

[9] Van Adrichem Boogaert HA and Kouwe WFP (1993-1997). Stratigraphic nomenclature o the Netherlands, revision and update by RGD and NOGEPA. Mededelingen Rijks Geologische Dienst (Haarlem) 50.

[10] De Jager J, Doyle MA, Grantham PJ and Mabillard JE. Hydrocarbon habitat of the West netherlands Basin. Rondeel et al. Geology of gas and oil under the Netherlands 1996, 191-206.

[11] Sissing W. Paleozoic and Mesozoic ignesous activity in the Netherlands, a tectonomagmatic review. Netherlands Journal of Geosciences 2004; 83, 113-134.

[12] Nelskamp S and Verweij JM. Using basin modeling for geothermal energy exploration in the Netherlands – an example from the West Netherlands Basin and Roer Valley Graben. TNO internal report 2012, 113p.

[13] Wycherley H, Fleet A and Shaw H. Some observations on the origins of large volumes of carbon dioxide accumulations in sedimentary basins. Marine and Petroleum Geology 1999; 16, 489-494.

[14] Lanson B, Beaufort D, Berger G, Baradat J and Lacharpagne J-C. Illitization of diagenetic kaolinite-to-dickite conversion series : late-stage diagenesis of the lower Permian Rotliegend Sandstone reservoir, offshore of the Netherlands. Journal of Sedimentary Research 1996; 66(3), 501-518.

[15] Worden RH and Burley SD. Sandstone diagenesis: the evolution of sand to stone. In: Sandstone diagenesis – Recent and Ancient 2003; 4, 3-44.

[16] Lanson B, Beaufort D, Berger G et al. Authigenic kaolin and illitic minerals during burial diagenesis of sandstones : a review. Clay minerals 2002; 37, 1-22.

[17] Haszeldine RS, Quinn O, England G, Wilkinson M, Shipton ZK, Evans JP, Heath J, Crossey L, Ballentine CJ and Graham CM. Natural geochemical analogues for carbon dioxide storage in deep geological porous reservoirs, a United Kingdom perspective. Oil & Gas Science and Technology 2005; 60 (1), 33-49.

[18] Bjorlykke K and Egeberg PK. Quartz cementation in sedimentary basins. AAPG Bulletin 77; 1993, 1538-1548.

[19] Gaus I, Le Guern C, Pearce J et al. Comparison of Long-term geochemical interactions at two natural CO_2-analogues: Montmiral (Southeast Basin, France) and Messokampos (Florin basin, Greece) case studies. Proceedings of the 7th International Conference on Greenhouse Gas Control Technologies, Volume 1; 2004, 561-569.