Mechanical weakening of a mudrock seal by reaction with CO$_2$-charged fluids

Andreas Busch[1,*], Suzanne Hangx[2], Stephanie Vialle[3,4], Roberto Emanuele Rizzo[5,6], and Niko Kampman[7]

[1]Lyell Centre, Heriot-Watt University, Edinburgh EH14 4BA, UK
[2]High Pressure and Temperature Laboratory, Utrecht University, 3584 CS Utrecht, Netherlands
[3]School of Earth and Planetary Sciences, Curtin University, Bentley, WA 6845, Australia
[4]Commonwealth Scientific and Industrial Research (CSIRO Energy), Perth, WA 6151, Australia
[5]Department of Earth Sciences, University of Florence, 50121 Florence, Italy
[6]School of Earth Sciences, University of Edinburgh, Edinburgh EH8 9XP, UK
[7]Harwell Science & Innovation Campus, Nuclear Waste Services, Didcot OX11 0GD, UK

ABSTRACT

The long-term interaction of CO$_2$-charged fluids with low permeability cap rocks is important for seal integrity assessment. To address this potential risk, we studied long-term geomechanical changes in a reservoir seal due to fluid-rock interactions with CO$_2$-charged fluids, focusing on a natural CO$_2$ analogue near Green River, Utah, USA. The observed chemo-mechanical changes are on the millimeter scale, which required small-scale petrophysical, mineralogical, and micromechanical analyses. Results showed that over the 7 cm thick reaction front, the low permeability cap rock underwent mechanical weakening, as indicated by indentation tests. This weakening is inferred to be due to dissolution of dolomite and hematite, with the former leading to porosity decrease, as shown by small-angle neutron scattering, while the latter likely led to loss of electrostatic forces between the clay particles. This resulted in loss of cohesion, compaction, and formation of bedding-parallel fractures. Microfracturing occurred in situ, as evidenced by fractures infilled with pyrite and gypsum. This study demonstrates that mechanical weakening of cap rocks might occur, but only over time scales of ~100,000 yr and over small distances. Considering the thickness of cap rocks above CO$_2$ storage reservoirs, we do not anticipate a considerable threat of losing containment integrity over time scales of hundreds to thousands of years as a result of these small-scale fluid-rock interactions.

INTRODUCTION

Large investments are required to significantly reduce carbon emissions into the atmosphere and to meet the Paris Agreement's goal of a maximum global temperature increase of 1.5–2 °C (Horowitz, 2016). A key technology to meet these targets is carbon capture and storage (CCS) (Metz et al., 2005). Key requirements for safe, long-term (i.e., >10^4 yr) CO$_2$ storage operations are reservoir seals with low matrix/fracture permeability and high capillary entry pressure (Busch and Kampman, 2018) and wells that are engineered to a standard that prevents CO$_2$ from leakage (Carroll et al., 2016). Geochemical cap rock alterations leading to porosity changes may change mechanical properties, such as strength, elastic properties, or fracture toughness (Aman et al., 2017; Hangx et al., 2015; Sun et al., 2016). It should be noted here that mechanical property changes depend on the rate of reaction between cap rock minerals and CO$_2$-charged fluids. Due to the low permeability of suitable cap rocks, the reaction rate and extent will be dominated by the rate of diffusion of the fluid into the formation, as was observed in the Green River natural CO$_2$ field (Kampman et al., 2016).

In this study, we focused on quantifying the mechanical implications of diffusion-driven mineral reactions in a clay-rich cap rock matrix, thereby highlighting changes resulting from these reactions on the micrometer to millimeter scale. The cap rock section used in this study was drilled in 2012 through naturally CO$_2$-charged siliciclastic formations near Green River, Utah, USA. We obtained core material from two Jurassic sandstones (Entrada, Navajo) and one interbedded claystone (Carmel) formation (Kampman et al., 2014, 2016). The Carmel Formation under investigation here represents the sealing unit on top of the CO$_2$-charged Navajo Sandstone, and it is composed of a succession of shallow-marine clay, silt, and sandstones. Previous research on the impact of CO$_2$-water-rock reactions on geomechanical rock properties has shown that dissolution of carbonates and/or sulfates could lead to localized weakening of the rock (Hangx et al., 2015; Rohmer et al., 2016). Unreacted argillaceous Carmel claystone contains finely dispersed primary dolomite cements (~8%) and primary hematite (~3.5%) as the main reactive minerals, so we expected that mechanical changes would not be localized but rather occur on bulk-rock scale. As such, we assumed, and therefore studied, the diffusion-controlled reactions of these mineral phases and implications for bulk-rock mineralogy. Previous studies have also shown that the mineralogical profiles observed are not caused by depositional but by diffusion-reaction processes associated with CO$_2$-rich fluids (Kampman et al., 2016). Time scales for reactions that have taken place in Green River are on the order of 10^5 yr (Kampman et al., 2016), longer than the 10^4 yr required to ensure safe CO$_2$ storage. The Green River case is hence closer to long-term CO$_2$ storage time scales than the 10^0 yr typically obtained from laboratory reaction experiments.

METHODS

We used a combination of mineralogical, micromechanical, neutron scattering, and image

Andreas Busch [ID] https://orcid.org/0000-0002-3279-5202
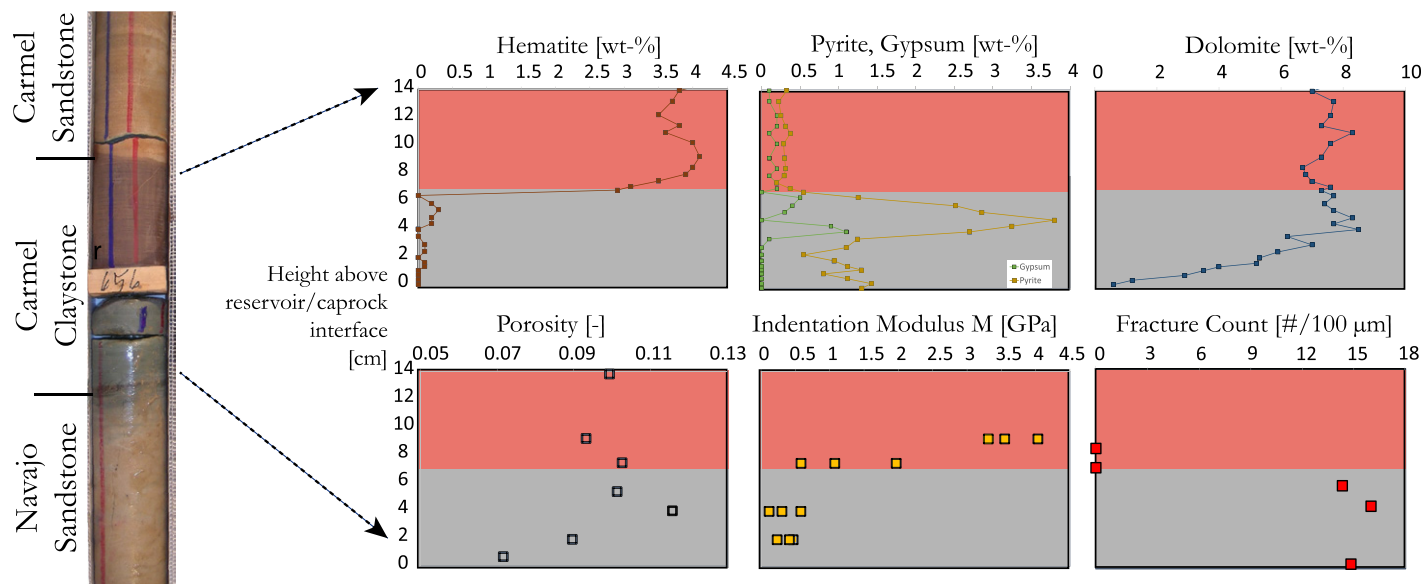*A.Busch@hw.ac.uk

Figure 1. Detailed analysis of 14-cm-thick Carmel claystone section above Navajo Sandstone containing CO_2-charged fluids.

analyses to obtain information on the mineral content, pore volume and distribution, and indentation modulus, as well as fracture density and orientation of Carmel Formation samples (see method description in the Supplemental Material[1]). In order to assess geomechanical rock properties, conventional methods require testing of rock sample plugs with dimensions of at least 2.5 cm (1 in.) diameter and 5.0 cm (2 in.) length. However, the reaction front in the Carmel claystone occurs at a much smaller scale, and mineral reactions have led to disintegration of the material, meaning that testing on such conventional samples was not feasible. Instead, we used thin sections cut parallel and perpendicular to bedding to analyze the microstructure, pore volume, and micromechanical properties of the CO_2-reacted and unreacted material, combined with image analysis and statistical evaluation of (micro-) fractures. Note that the mineralogical composition and methods used for the Carmel samples shown in Figure 1 have been extensively reported on previously (Kampman et al., 2016).

RESULTS AND DISCUSSION

The lowermost part of the Carmel Formation has been analyzed in detail in terms of coupled reaction-diffusion processes, and it was shown that CO_2 migrated only ~7 cm from the reservoir–cap rock interface into the base of the

claystone over ~10^5 yr (Kampman et al., 2016). This limited penetration depth is mainly due to reactive fluids triggering chemical reactions that significantly slow down the diffusional front. Predictions suggest that fluids would have migrated upward by over 8 m if only aqueous CO_2 diffusion was at play (Kampman et al., 2016). Mineralogical observations within the reacted claystone section provide clear evidence for hematite and dolomite dissolution as well as precipitation of pyrite and gypsum (Kampman et al., 2016). These reactions have led to a reduction in the matrix porosity toward the base of the reacted section (Fig. 1). A petrographic scanning electron microscope (SEM) analysis across the cap rock section is provided in the Supplemental Material (Figs. S5–S8), showing the differences in mineral assemblages in the bleached and unbleached sections, as well as evidence for fracturing (bleached) and the absence of fracturing (unbleached), respectively. It was hence concluded that rock-buffering reactions are effective in establishing fluid-mineral equilibria over centimeter length scales and that CO_2-charged fluid-mineral reactions can locally enhance cap rock integrity over time scales comparable to effective geological carbon storage.

Diffusion-driven mineral reactions are not only deterring migration of leaking fluids, but they can also result in changes in geomechanical properties. We here report such changes by using nano-indentation and microstructural analyses to verify coupled chemical-mechanical changes of the Carmel cap rock section on the millimeter scale. Mineralogical changes of the cap rock section have been reported previously (see Fig. 1; Kampman et al., 2017). The dissolution of hematite throughout the reacted section and the gradual dissolution of dolomite from the base to the top of the profile are

evident. This has caused secondary precipitation of pyrite and gypsum, volumetrically to a much lesser extent, however (Kampman et al., 2016). It is therefore rather counterintuitive that porosity has decreased in the summation of dolomite and hematite dissolution and gypsum and pyrite precipitation, especially within the lowermost 2 cm of the profile. Changes in pore volume across the pore-size distribution, obtained from small-angle neutron scattering, show that the pore volume associated with the smallest pores is similar for all samples tested (Fig. 2). This pore space is mainly attributed to nanoporosity in and around clay minerals, which make up ~80% of the total mineralogy. For the samples closest to the reservoir–cap rock interface (i.e., NPS069 and NPS073), a generally lower pore volume is seen associated with pore sizes larger than ~5 nm, indicating a uniform decrease across the scales, rather than within a specific range.

Nano-indentation test results on reacted and unreacted Carmel cap rock material indicate that the indentation modulus, M, is consistently less than 1 MPa for CO_2-reacted material, while values for unreacted Carmel claystone are significantly higher, varying between ~0.5 and 6 GPa (Fig. 3). Figure 1 shows the peaks of the indentation moduli (full distribution provided in Fig. 3) in relation to mineralogical changes and changes in microfracture densities observed in SEM images. These values are generally low in comparison to many other studies done using either centimeter-scale plug or micron-scale nano-indentation methods. They are, however, not outside the range of values reported previously (Gudmundsson, 2011; Wensaas et al., 1998) for various mudrocks, but they are lower than values for nano-indentation tests on several gas shales reported previously (Goodarzi et al.,
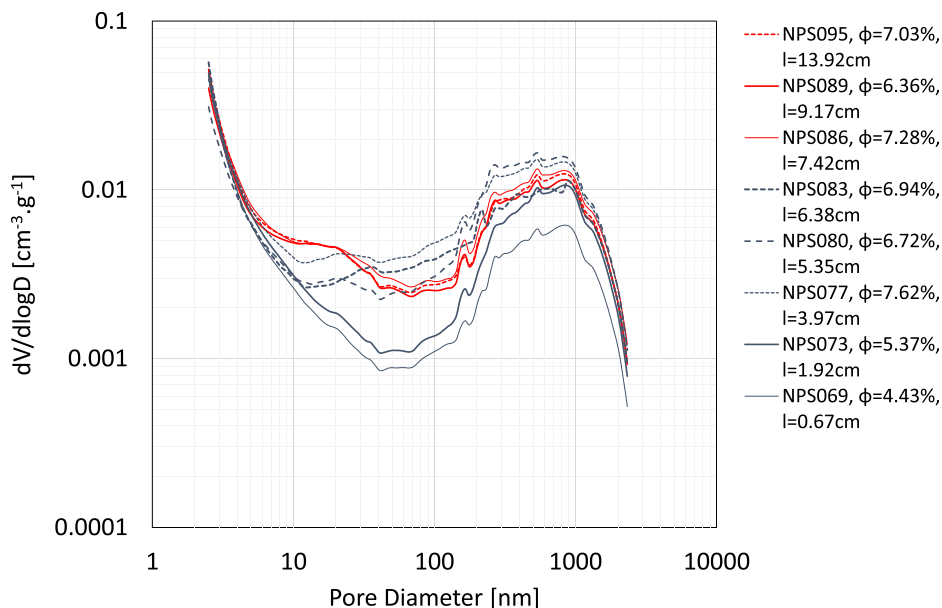
Figure 2. Differential pore-size distributions (*dV/d*log*D*) for eight samples across reaction profile showing reacted (gray) and unreacted (red) samples.

2017; Graham et al., 2021). The reasons for the low values are difficult to explain in full and are likely a combination of (very) high clay contents of ~80% for the entire claystone profile and the dissolution of cementing phases in the reacted section. In any case, a qualitative assessment of the differences in mechanical properties is the key observation here, while it would be interesting to run conventional mechanical tests on plugs of these specific samples in the future.

Microfractures (summarized in Fig. 1) occur parallel to bedding and were determined along a scan line normal to bedding. It was found that the unreacted section of the Carmel claystone profile showed no evidence of microfractures, whereas the reacted part developed ~15 fractures over a distance of 100 μm. We observed microfractures partly filled with gypsum in the reacted section forming in situ (Kampman et al., 2014), indicating that these fractures formed at depth and have provided permeable conduits for fluids to flow. Figure 4 shows a full assessment of the fracture network using an automatic fracture segmentation algorithm (for more details, see Supplemental Material), where we can see the bedding-parallel orientation of the fractures as well as evidence for fractures filled with gypsum.

Overall, the nano-indentation data indicate that, although porosity is reduced due to reaction with CO_2, the indentation modulus decreases considerably, indicating a reduction in stiffness.

This is counterintuitive, as rocks will typically become stiffer when porosity decreases (Farrokhrouz et al., 2013; Horsrud, 2001). Little work has been reported in the literature providing evidence for reaction-induced rock weakening, especially at the pore scale. The Carmel claystone reaction profile provides an excellent case study where reaction occurred through natural processes, taking place over thousands of years. It is therefore evident that CO_2 (and traces of H_2S), diffusively migrating into the claystone, dissolved hematite and dolomite at grain-grain contacts while locally precipitating clusters of pyrite and Fe-rich carbonate. This was further supplemented by an increase in the density of small, tensile fractures, as we observed significant bedding-parallel (micro-) fracturing of the altered section (Fig. 4), where fractures are partly filled with gypsum and therefore provide evidence for in situ fracturing. It is likely that when core was recovered to the surface, resulting in stress unloading and possibly some dehydration, an increase in apertures and possibly additional bedding-parallel fracturing occurred, resulting in the non-cemented fractures shown in the textures in Figure 4. The fracture density should therefore be regarded with some care. It should be noted that the fractures occur at a spacing much larger (millimeters) than the nano-indentation spot size (micrometers) and were therefore not systematically sampled in the indentation tests. As such, lower indentation moduli are not related to any fracturing of the CO_2-reacted Carmel claystone material.

Therefore, we infer that the observed mechanical weakening, in terms of reduced indentation moduli, or, indirectly, the elastic moduli, was mainly caused by hematite dissolution at grain contacts as a consequence of reaction with CO_2-charged fluids. Despite its relatively small proportion in the total mineral-
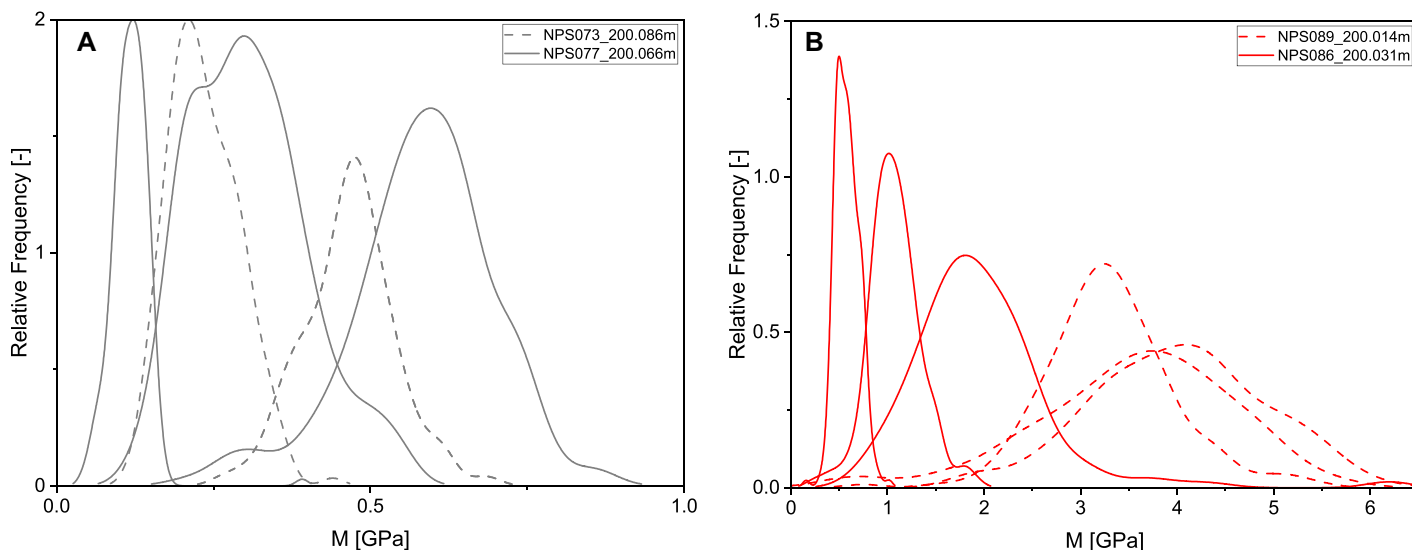

Figure 3. Nano-indentation results on reacted (A) and unreacted (B) Carmel Formation cap rock material.
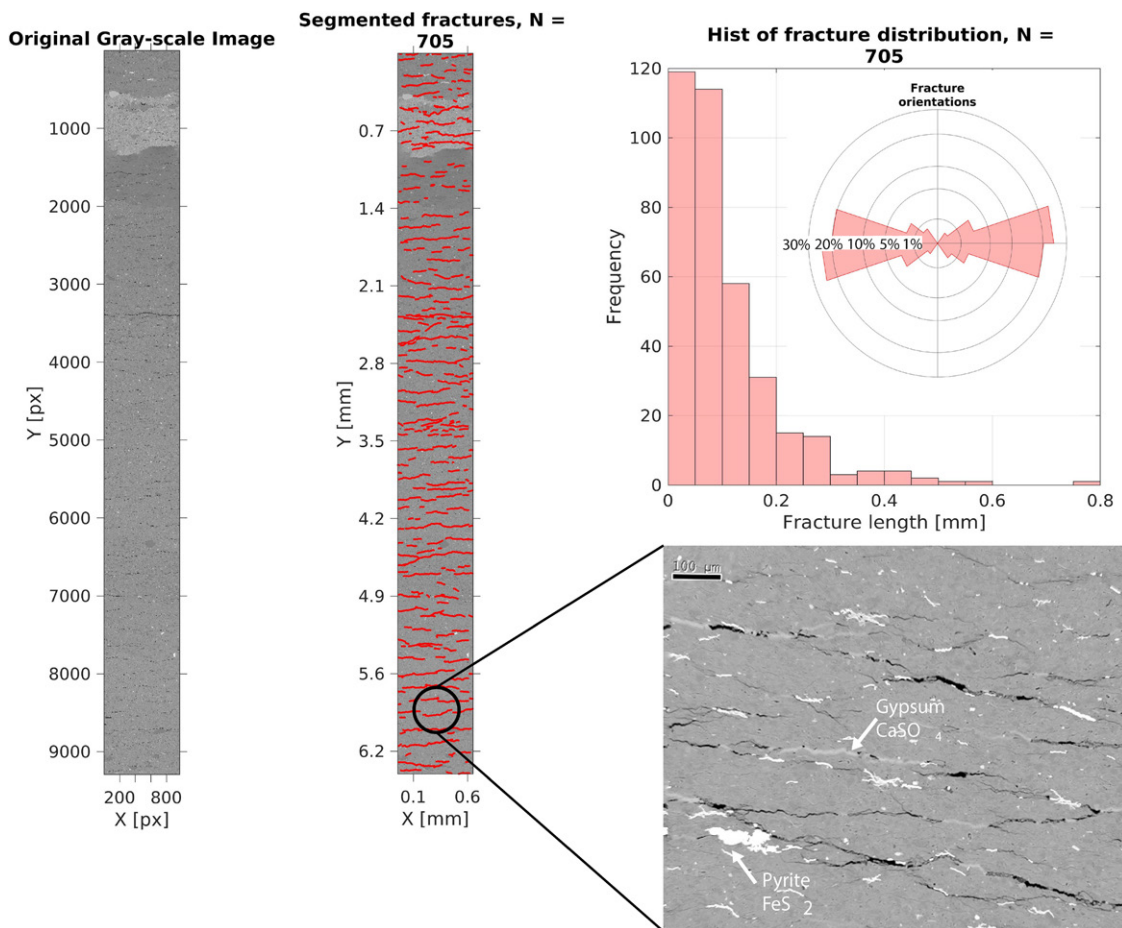
Figure 4. (Left) Vertically integrated scanning electron microscope image for reacted section of cap rock profile showing microfractures with horizontal orientation. Red lines are segmented fracture traces obtained using automatic fracture segmentation algorithm. (Right) Derived fracture orientation and length obtained from semi-automated fracture detection algorithm. Mineralization of microfractures with pyrite and gypsum indicates in situ fracturing and circulation of fluids.

ogy, the removal of finely interspersed, grain-coating hematite likely homogeneously affected the mechanical properties of the entire profile. This reduction in cohesion resulted in tensile fractures parallel to bedding that subsequently stimulated the circulation of fluids and precipitation of gypsum. By contrast, dissolution of dolomite, typically forming larger grains, will rather result in local porosity changes when dissolved and is expected to only have a limited impact on the mechanical strength of the material (Hangx et al., 2015). Previous studies have shown that the presence of hematite coatings on illite particles leads to face-to-face association, or aggregation, of the illite. The formation of such larger particles has been shown to increase the (Bingham) yield stress of the material due to the greater interparticle attraction energy (Ohtsubo et al., 1991). Therefore, the overall weakening observed in the Carmel claystone is inferred to be largely attributable to the loss of grain-coating hematite, thereby reducing the interparticle forces. A smaller contribution to the observed reduction in indentation modulus with prolonged CO_2 reaction can be ascribed to the increase in fracture density, which led to an increase in the mechanical anisotropy of the material. Similar observations were made on Jurassic Summerville Siltstone, obtained near Green River, in the area of our study (Espinoza

et al., 2018), though for the Summerville Siltstone, hematite dissolution was accompanied by an increase in matrix porosity from 4.8% to 10.2%, which further contributed to mechanical weakening.

In conclusion, the observed changes in mineralogy and formation of veins are clearly linked to the emplacement of CO_2-charged fluids into Navajo Sandstone and diffusive migration of CO_2 into the Carmel claystone. Subsequent reaction-induced mechanical weakening of the Carmel cap rock evolved over time scales on the order of 10^5 yr. No immediate effects following CO_2 injection over engineered time scales of 10^1 to 10^2 yr are to be expected for this type of cap rock material. Furthermore, the observed mechanical weakening of the intact material only prevailed for several centimeters into the cap rock, meaning that no large-scale impact of fluid-rock interactions is to be expected. Related conclusions have been drawn by Lu et al. (2009), who documented 12 m penetration of CO_2 over $7–8 \times 10^7$ yr into a cap rock in the Miller Field in the UK North Sea, which is comparable to the 7 cm penetration depth over ~10^5 yr.

CONCLUSION

This study provided new insights into mechanical weakening of a claystone overlying a naturally CO_2-charged reservoir. Our research

combined mineralogy, pore structure, nano-indentation, and image analysis of fractures. The main mineralogical changes comprised dissolution of dolomite and hematite, with local precipitation of sulfur-bearing minerals. This resulted in a net decrease in total grain volume. However, we observed a general decrease in matrix porosity, which can be explained by matrix compaction. In addition, we identified bedding-parallel fractures that are partly filled with gypsum and pyrite, indicative of in situ formation. Nano-indentation tests on bedding-parallel layers across the profile showed a decrease in stiffness, interpreted as the result of dissolution of hematite and loss of electrostatic forces between the clay particles. This resulted in a general decrease in cohesion, resulting in bedding-parallel fractures. Although mineralogical, pore structural, and micromechanical changes were observed within this reaction profile, they occurred on the millimeter to centimeter scale over a time scale of 10^5 yr. This demonstrates that mineral reaction–driven mechanical alterations are slow and take longer than the time scales relevant for carbon storage projects.

data using the MATSAS code (https://github.com/matsas-software/MATSAS).

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