



## **CO<sub>2</sub> adsorption isotherm on clay minerals and the CO<sub>2</sub> accessibility into the clay interlayer**

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Large-scale CO<sub>2</sub> storage in porous rock formations at 1-3 km depth is seen as a global warming mitigation strategy. In this process, CO<sub>2</sub> is separated from the flue gas of coal or gas power plants, compressed, and pumped into porous subsurface reservoirs with overlying caprocks (seals). Good seals are mechanically and chemically stable caprocks with low porosity and permeability. They prevent leakage of buoyant CO<sub>2</sub> from the reservoir. Caprocks are generally comprised of thick layers of shale, and thus mainly consist of clay minerals. These clays can be affected by CO<sub>2</sub>-induced processes, such as swelling or dissolution. The interactions of CO<sub>2</sub> with clay minerals in shales are at present poorly understood. Sorption measurements in combination scattering techniques could provide fundamental insight into the mechanisms governing CO<sub>2</sub>-clay interaction.

Volumetric sorption techniques have assessed the sorption of supercritical CO<sub>2</sub> onto coal (Gensterblum et al., 2010; Gensterblum et al., 2009), porous silica (Rother et al., 2012a) and clays as a means of exploring the potential of large-scale storage of anthropogenic CO<sub>2</sub> in geological reservoirs (Busch et al., 2008). On different clay minerals and shales, positive values of excess sorption were measured at gas pressures up to 6 MPa, where the interfacial fluid is assumed to be denser than the bulk fluid. However, zero and negative values were obtained at higher densities, which suggests the adsorbed fluid becomes equal to and eventually less dense than the corresponding bulk fluid, or that the clay minerals expand on CO<sub>2</sub> charging.

Using a combination of neutron diffraction and excess sorption measurements, we recently deduced the interlayer density of scCO<sub>2</sub> in Na-montmorillonite clay in its single-layer hydration state (Rother et al., 2012b), and confirmed its low density, as well as the expansion of the basal spacings. We performed neutron diffraction experiments at the FRMII diffractometer on smectite, kaolinite and illite samples. These confirmed that CO<sub>2</sub> enters the interlayer spaces of monohydrated (D<sub>2</sub>O) smectites exchanged with Ca. The changes were proven to be fully reversible and mainly take place between 0 and 60 bar CO<sub>2</sub>. For a smectite exchanged with (CuTrien)<sup>2+</sup> a decrease in intensity of the basal reflections with pressure was recorded, but no expansion of the basal spacing was observed. For kaolinite, similar changes in intensity upon CO<sub>2</sub> addition were observed, but they correspond to a relative decrease of the intensity of the hk reflections. Measurements on illite yielded an unexpected increase in intensity of the basal reflections upon CO<sub>2</sub> charging.