

Peer-reviewed Conference Contribution

# Geochemical Interaction between CO<sub>2</sub> and caprock for safe carbon sequestration

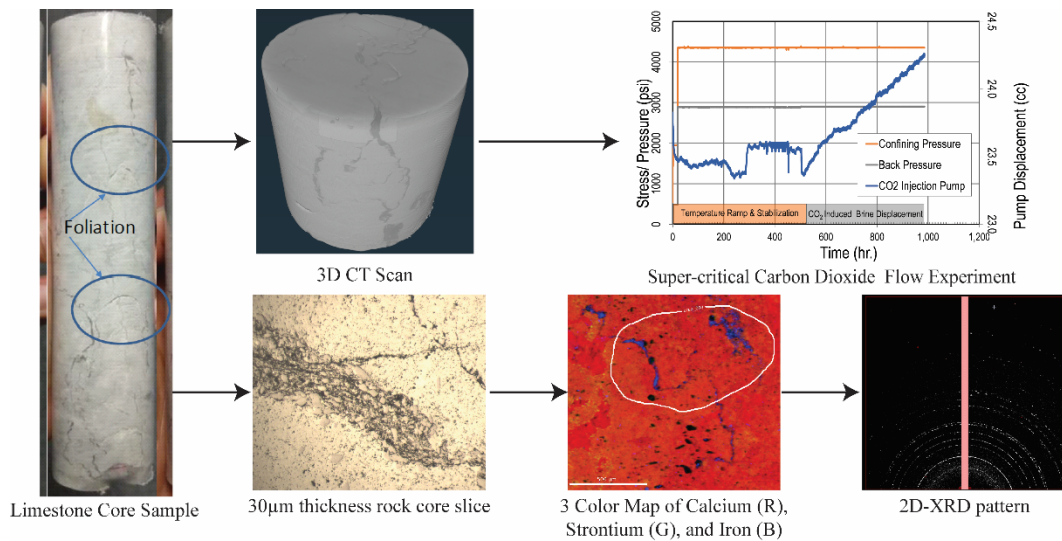
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Carbon dioxide (CO<sub>2</sub>) emission into the atmosphere from human activities and industrial processes continues to pose a major environmental and health threat to public safety worldwide with many governments launching initiatives to reduce the impact of CO<sub>2</sub> emission. Carbon dioxide capture and storage (CCS) is a process of separating CO<sub>2</sub> from industrial facilities and other point sources and injecting it in a deep geological formation such as depleted oil and gas reservoirs for long-term storage [1]. Usually, CO<sub>2</sub> is injected into a deep formation at a depth more than 1000 m where in-situ pressure and temperature is above the critical point for CO<sub>2</sub> (31.1° C and 7.39 MPa [2]), using an injection pressure higher than the in-situ pressure to displace the brine from the pore space. There are many risks associated with CCS which include the potential leak of CO<sub>2</sub> into atmosphere and to groundwater through natural/reactivated faults or man-made operations, mobilization of contaminants, and CO<sub>2</sub> pressure can be a source for seismic damage, fracture of caprock, extended stress, and deformation of overburden materials [3, 4].

Safe CCS requires characterization of the geochemical interaction between CO<sub>2</sub> and caprock at micro and nano scales. Ordovician Kingsport formation limestone rock samples were obtained at a depth of 250 m from Nyrstar Tennessee Mines, USA. The characterization and monitoring of the geochemical and fracture behavior of the rock samples exposed to CO<sub>2</sub>-brine for a long duration were studied using 3D computed tomography (CT), and high-speed coupled micro-beam x-ray fluorescence (μXRF), and micro-beam x-ray diffraction (μXRD) which offers a better understanding of the mineralogical composition of the rock samples, while the CT allows for monitoring changes in rock core pore structure and volume. The limestone rock core was cut into two sets of samples, the first set consists of three cylindrical cores with approximate dimensions of 25.4 mm in diameter x 25.4 mm in height, the cores were initially CT scanned to attain a baseline of the cores' structure and porosity. CT image analyses revealed variation in mineral composition and very low porosity (~ zero) as expected of limestone caprock formation. A set of 30 μm thick slides of the same material (thin sections) were used for the high-speed coupled μXRF and μXRD to characterize the mineralogical composition of the limestone rock. The high-speed coupled μXRF and μXRD experiments were performed at GSECARS beamline 13-ID-E, the Advanced Photon Source (APS), Chicago, Illinois, USA where each of the slices was scanned using a 5 x 5 μm spot-focused beam covering an area of 4 x 6 mm. Analyzing the μXRF spectrum generated from the μXRF data helped in identifying several elements including Ca, Sr, Fe, Si, Mn, Cu, Hg, and Zn. Other elements such as Magnesium (Mg) were not detected even though they are typically present in limestone formations, this is due to the insensitivity of the μ-XRF method at energies relevant to Mg. In addition to Mg, Strontium (Sr) is known to substitute for Calcium (Ca) in the Calcite structure [5]. The μXRD data was used to isolate XRD patterns. Calcite and Quartz were the two major phases identified. Some identified elements (Hg, As) were not successfully matched to XRD-indexed minerals, presumably owing to their small modal proportion, as suggested by low recovered counts for their forming elements.

The super critical CO<sub>2</sub> (scCO<sub>2</sub>) flow experiment was conducted at MetaRock Laboratories on one of the 25.4 mm diameter cylindrical cores, and consisted of applying a 30 MPa confining pressure and 20 MPa back pressure to the core while saturating the core with a 0.1 M NaCl brine. The scCO<sub>2</sub> was then injected at a rate of 0.0017 cc/hr for a period of approximately 500 hours. The results from the flow experiment showed that the scCO<sub>2</sub> injection did not displace the brine and did not penetrate the sample due to the low porosity and permeability of the limestone caprock with the back pressure remaining constant. After the scCO<sub>2</sub> flow experiment, the tested core was CT scanned again to characterize the change in pore structure due to the interaction with scCO<sub>2</sub>.

The results showed no change in the core structure due to interaction with the CO<sub>2</sub>-brine solution, with the core maintaining the same apparent mineral composition and pore structure, and the injection surface maintaining the same features. The lack of geochemical interaction between CO<sub>2</sub> and caprock limits leaks sources which is essential for safe and sustainable carbon geological trapping to ensure that the stored carbon will not escape to the atmosphere and groundwater.



**Figure 1: Experimental work results schematic.**

#### Data Availability Statement

All data, models, or codes that support the findings of this study are available from the corresponding author upon reasonable request.

#### Contributor statement

Elnur contributed to data analysis and results interpretation, writing-original draft. Alshibli developed the research plan and contributed to making thin sections, writing a proposal for beamtime at APS, and contributed to data analysis. Dygert contributed to the research plan and data analysis. Lanzirotti and Neville contributed by performing the high-speed coupled  $\mu$ XRF and  $\mu$ XRD. Zhang and Lu contributed to CT image acquisition. Govindarajan contributed by performing the super-critical CO<sub>2</sub> flow experiment at MetaRock Laboratories.

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#### References

- [1] M. J. Bickle, "Geological carbon storage," *Nature Geoscience*, vol. 2, no. 12, pp. 815-818, 2009.
- [2] N. Spycher, K. Pruess, and J. Ennis-King, "CO<sub>2</sub>-H<sub>2</sub>O mixtures in the geological sequestration of CO<sub>2</sub>. I. Assessment and calculation of mutual solubilities from 12 to 100 C and up to 600 bar," *Geochimica et cosmochimica acta*, vol. 67, no. 16, pp. 3015-3031, 2003.
- [3] F. Cappa and J. Rutqvist, "Seismic rupture and ground accelerations induced by CO<sub>2</sub> injection in the shallow crust," *Geophysical Journal International*, vol. 190, no. 3, pp. 1784-1789, 2012.
- [4] E. J. Wilson, T. L. Johnson, and D. W. Keith, "Regulating the ultimate sink: managing the risks of geologic CO<sub>2</sub> storage," *Environmental Science & Technology*, vol. 37, no. 16, pp. 3476-3483, 2003.
- [5] N. E. Pingitore Jr, F. W. Lytle, B. M. Davies, M. P. Eastman, P. G. Eller, and E. M. Larson, "Mode of incorporation of Sr<sup>2+</sup> in calcite: Determination by X-ray absorption spectroscopy," *Geochimica et Cosmochimica Acta*, vol. 56, no. 4, pp. 1531-1538, 1992.