

Molecular modelling of carbon dioxide adsorption in zeolites

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There is growing concern about the dangers of climate change. The majority opinion is that a major cause is the emission of greenhouse gases such as carbon dioxide (CO₂). Adsorption and separation of CO₂ is therefore a key area of research. Silicate materials are a promising class of material for the adsorption of CO₂ [1][2]. Natural and synthetic zeolites have been chosen as the initial focus of this computational study. They present a good model system as they are microporous and there is experimental data for comparison with simulations.

The computational methods use interatomic potentials to describe the interactions between atoms. Energy minimisation is used to find the most stable configurations of the zeolites. Molecular dynamics is used to study the diffusion of CO₂ in the zeolites while Grand Canonical Monte Carlo (GCMC) simulations are used to generate adsorption isotherms. Zeolites have been modelled in the siliceous form and as aluminosilicates with counter-ions. The main counter-ion that has been considered is Na⁺, but the models are being extended to cope with others including K⁺, Li⁺ and Ca⁺.

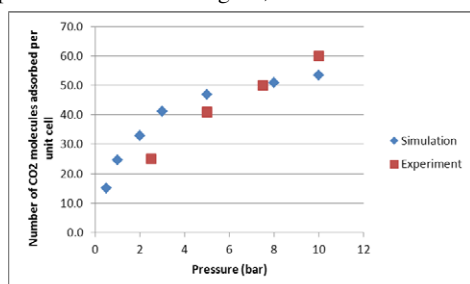


Figure 1: adsorption isotherm of CO₂ in siliceous faujasite, comparing simulations to experimental data [3]

The results gained in this work so far correlate well with experimental data and the work is currently being extended to cover a wide range of other structures and materials to find a good selective adsorbent for CO₂.

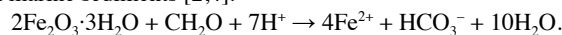
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Fe and C isotopes in BIF carbonates: Evidence for authigenic formation and microbial Fe respiration

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We report here iron ($\delta^{56}\text{Fe}$, vs. IRMM-014 [1]) and carbon isotopic ($\delta^{13}\text{C}$, vs. V-PDB) compositions of Fe-rich and Fe-poor carbonates in two Banded Iron-Formations (BIF): the ~2.5 Ga Hamersley Basin, Australia and ~3.8 Ga Isua Supracrustal Belt (ISB), Greenland [2]. In the Hamersley Basin, Fe-rich carbonates (in the iron-formation) have $\delta^{56}\text{Fe}$ ranging widely from -1.0 to +1.2 ‰ (mean ~ 0 ‰), different from that of Fe-poor carbonates (platform dolomites) that have $\delta^{56}\text{Fe}$ lighter than -0.5 ‰. The $\delta^{13}\text{C}$ of the same Fe-rich carbonates (-8 to -16 ‰) are also distinct to those of Fe-poor carbonates (~ 0 ‰) [3]. The Fe and C isotope compositions are inconsistent with formation of Fe-rich carbonate in the iron-formation in isotope equilibrium with seawater, and instead reflect an authigenic origin via oxidation of organic carbon coupled to near-complete reduction of ferric precursors (e.g., ferrihydrite) in marine sediments [2,4]:



Organic carbon oxidation and ferric Fe reduction likely occurred rapidly following primary deposition at the seafloor, but the Fe and C isotope compositions of Fe-rich carbonates indicate that chemical exchange between pore waters and seawater was far from complete. Most likely, the reaction was mediated by heterotrophic microbes via dissimilatory Fe reduction; thus the Fe and C isotope data record evidence for evolution of microbial Fe respiration by ~2.5 Ga. Further, the authigenic formation of Fe-rich carbonate in the iron-formation implies no constraint on the pCO₂ of the overlying Archean ocean and atmosphere as suggested by [5; also see 6]. Coupled Fe and C isotopic signatures of Fe-rich metacarbonates from the ISB are similar to those of known chemical sedimentary origin from Hamersley Basin [2,7,8]. By analogy, Fe-rich metacarbonates appear to have formed as chemical sediments and preserve isotope evidence that is consistent with the evolution of Fe cataplasms by 3.8 Ga.

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