Non-adiabatic calculations of ultraviolet absorption cross section of Sulfur Monoxide; Isotopic effects on the photodissociation reaction

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Understanding the mechanism of the sulfur isotopic fractionation of SO_2 in a reduced atmosphere and under high fluxes of UV light has become a key feature in explaining the mechanisms that produced the large sulfur mass independent fractionation (S-MIF) signal deposited in the geological record [1,2]. However, all modeling studies conducted for the Archean atmosphere assume that the life time of the intermediate product after the photodissociation of SO_2 (SO) is short lived and no further photochemistry can produce additional isotopic enrichment or depletion. We set out to test this hypothesis by theoretically calculating the ultraviolet absorption cross sections of the main and substituted sulfur monoxide isotopologues. The theoretical framework for this work includes a newly developed R-Matrix expansion. The calculated absorption cross section of $^{32}S\ ^{16}O$ were compared with reported experimental spectra, calculations and experiments are in good agreement although the there is some come concern with certainty of the experimental data. Our calculations show that according to the energy of the photon flux the involved exited states can produce a fast photodissociation or a long lived SO* photoexited fragment. In order to test these new results the obtained spectra were introduced in an improved sulfur isotope photochemical Archean model [3]. The improvement to our model includes the addition of hydrocarbon chemistry, chemical formation and deposition of organic sulfur haze.

[1] Danielache et al.. (2008) J Geophys Res **113**, D17314. [2] Farquhar et al.. (2001) J Geophys Res **106**, D32829. [3] Ueno et al.. (2009) PNAS **106**, 14784-14789.

Modelling the propagation and dissolution of CO_2 into reservoir brines: implications for CO_2 sequestration.

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The Earth's climate is changing and the release of carbon dioxide (CO_2) and other greenhouse gases into the atmosphere is recognised as the principal cause. Long-term and secure geological storage of CO_2 through Carbon Capture and Storage (CCS) within reservoirs is seen as a solution; however, knowledge of the trapping mechanisms, in conjunction with understanding the effect of injected CO_2 on the reservoir formations themselves, is fundamental to assessing the viability of long-term storage. Developing a greater understanding of the flow of CO_2 through a porous medium and the associated reactions between the host rock formation and the fluid is therefore of great importance to understanding whether a CO_2 storage site is likely to fail.

Dissolution of CO2 into ambient brine is a prospective stable trapping mechanism. This study examines the enhanced rates of dissolution found during injection into a layered, heterogeneous formation using analogue experiments and numerical models. The analogue experiments, designed to approximate an Enhanced Oil Recovery (EOR) setting, show that during fluid propagation, pore-scale viscous fingers grow and retreat providing an increased surface area between the flow and the ambient reservoir fluid, which is likely to enhance the dissolution of CO_2 in reservoir brines. The numerical simulations provide a useful comparison with the analogue experiments and give constraints on the timescale and magnitude of CO_2 dissolution and the consequent fluid-mineral reactions in a heterogeneous reservoir. The study addresses whether carbonate or silicate mineral dissolution can provide the CO_2 with a leakage pathway through corroded caprocks and fault seals, or assist pathway sealing.