CO_2 dissolution in formation water as dominant sink in natural gas fields

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A primary concern facing Carbon Capture and Storage (CCS) technology is the proven ability to safely store and monitor injected CO_2 in geological formations on a long-term basis. However, it is extremely challenging to assess the long-term consequences of CO_2 injection into the subsurface from decadal observations of existing CO_2 disposal sites.

Noble gases are conservative tracers within the subsurface, and combined with carbon stable isotopes, have proved to be extremely useful in determining both the origin of CO_2 and how the CO_2 is stored within natural CO_2 reservoirs from around the world [1, 2]. This presentation will identify and quantify the principal mechanism of CO_2 phase removal in nine natural gas fields in North America, China and Europe. These natural gas fields are dominated by a CO_2 phase and provide a natural analogue for assessing the geological storage of CO_2 over millennial timescales. Our study highlights that in seven gas fields with siliciclastic or carbonate-dominated reservoir lithologies, dissolution in formation water at a pH of 5–5.8 is the major sink for CO_2 [2]. This pH range is obtained by modelling the carbon isotope fractionation that results from dissolution of CO_2(g) to varying proportions of H_2CO_3(aq) and HCO_3^-(aq). This is a major breakthrough as accurate subsurface pH measurements are notoriously difficult to obtain. In two fields with siliciclastic reservoir lithologies, some CO_2 loss through precipitation as carbonate minerals cannot be ruled out, but this is minor compared to the amount of CO_2 lost to dissolution in the formation water within the same fields.

Our findings imply mineral fixation is a minor CO_2 trapping mechanism within natural reservoirs and hence suggests long-term models of geological CO_2 storage should consider the potential mobility of CO_2 dissolved in water.

[1] Gilfillan *et al*. (2008) *GCA* **72**, 1174-1198. [2] Gilfillan *et al*. (2009) *Nature*, doi:10.1038/nature07852.

Diverse pathways of sulfur cycling in the modern Black Sea captured in rare sulfur isotope signatures

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The modern Black Sea offers a unique natural setting to explore mass-dependent sulfur isotope fractionations. Moving from the oxic inner shelf to the euxinic (anoxic and sulfidic) deep basin, geochemical proxies (TOC, DOP, Mn and Fe) record increasing organic matter content and iron enrichments. We complement these proxies with a systematic study of the multiple sulfur isotope composition ($^{33}S/^{32}S$, $^{34}S/^{32}S$ and $^{36}/^{32}S$) of porewater sulfate and iron sulfides (AVS and pyrite) from the underlying sediments. Trends in these data closely track the environmental context defined previously from independent measures of spatially and temporally varying depositional redox. For example, sulfide isotopes ($\Delta^{33}S$ and $\Delta^{36}S$) reveal signatures correlated to given depositional conditions ranging from oxic bioturbated sediments on the shelf to high sulfate reduction rates along the euxinic margin and syngenetic pyrite formation in the deep euxinic basin. $\Delta^{33}S$ values of sulfides deposited on the shelf record an earlier chemocline shoaling event and span the environmental endmembers expected with vascillating redox conditions. Overall, fractionation factors calculated from these data are consistent with the signatures expected for systems with active sulfate reduction and sulfur disproportionation.

Transitions between environmental extremes in the Black Sea are expressed in parallel isotopic trends that trace the relative contribution of microbial processes, which in all cases described here are dominated by sulfate reduction (over sulfide oxidation). However, it is the mixing of these processes that yields the observed range of minor isotope values recorded in iron sulfides. Thus, calibration of biogenic sulfur signals within the Black Sea offers an interpretive tool for studying basin-wide sulfur cycling in the ancient ocean and specifically transitions from oxygen deficient to fully aerobic conditions.