

## Assessing freshwater aquifer contamination from Carbon Capture and Storage CO<sub>2</sub> leak

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Carbon Capture and Storage (CCS) refers to a suite of technologies used to separate, compress, transport and store CO<sub>2</sub> produced from large, stationary emissions like coal-fired power plants. If undertaken on a large scale, only very small CO<sub>2</sub> leaks (<0.1%/yr) will be acceptable to achieve the goal of mitigating rising atmospheric CO<sub>2</sub> concentrations. However small, such leaks will be inevitable and may pose a risk to shallow, drinking-water if a significant pH change results. Here, we seek to characterize this risk. We first identify fresh groundwater resources that are geographically coincident over the most likely CCS sites, i.e. deep saline aquifers. The presence of moderate concentrations of naturally occurring aqueous trace metals in some of these aquifers suggests that the host aquifer sediment has a potential for additional release in the presence of CO<sub>2</sub>. We thus narrowed our selection to drinking-water aquifers with reported concentrations of toxic metals to be 10 to 100% of maximum contaminant loads (MCL). We then collected aquifer sediment samples from these locations and subjected subsamples to continuous incubation in water supersaturated with CO<sub>2</sub> for more than 200 days and to a control incubation without CO<sub>2</sub>. Our samples are from the following aquifers: Mahomet (Illinois), Ogallala (Texas), Columbia (Virginia), and Aquia (Maryland). Simulated groundwater samples were regularly analysed. For the pH range reached in our experiments (~4.5 to 5.5), (1) As concentrations generally decreased in comparison to the control; (2) Cd and U both increase significantly in the Mahomet and Ogallala; and (3) most major element cations increase, including Fe and Ca. In conclusion, given the appropriate lithology, CO<sub>2</sub> leaks may pose a risk for release of U and Cd into drinking water; however, additional As releases are probably low. Additionally, a suite of easily detectable elements—Mn in particular—may be suitable for monitoring purposes. The experiment is on-going and ultimately we will extrapolate our analysis of our laboratory incubations to predict locations most susceptible to toxic metal release due to CO<sub>2</sub> leakage from CCS.

## Copper isotope fractionation in seawater: The role of scavenging by ferromanganese crusts

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Dissolved Cu in seawater has a heavy isotopic composition ( $\delta^{65}\text{Cu} = +0.9\text{--}1.5\text{‰}$ ) relative to both rocks ( $\sim 0\text{‰}$ ) and the riverine input (at around  $+0.7\text{‰}$ ). Vance *et al.* [1] suggest that this is a result of partitioning of Cu isotopes between a heavy dissolved phase, where Cu is bound to organic ligands, and a light particulate phase, dominated by Fe-Mn oxides. However, no data exist for the isotopic composition of Fe-Mn precipitates from seawater with which to test this view.

Here we report  $\delta^{65}\text{Cu}$  in Fe-Mn crusts from the three major ocean basins. A Pacific crust (D11) shows no variation in Cu isotopes ( $\delta^{65}\text{Cu} = 0.54 \pm 0.06\text{‰}$ ) over the past 17 Ma. The Atlantic crust (Lesser Antilles, TR079) shows an increase in  $\delta^{65}\text{Cu}$  from 0.11‰ to 0.36‰ from 3 Ma to the present. In the Indian Ocean crust (109D-C),  $\delta^{65}\text{Cu}$  values decrease from  $\sim 0.3\text{‰}$  to  $\sim 0.12\text{‰}$  between 11 and 6 Ma, and then remain constant at  $\sim 0.12\text{‰}$  from 6 Ma to present.

$\mu\text{-XRF}$  element maps and EXAFS of TR079 show that Cu and Zn are predominantly sorbed to the Mn-oxide phase,  $\delta\text{-MnO}_2$ . Sherman *et al.* [2] have shown that  $\delta\text{-MnO}_2$  (birnessite) preferentially sorbs the light Cu isotope from simple aqueous solutions, with a  $\Delta^{65}\text{Cu}_{(\text{diss-sorb})}$  of  $\sim +0.5\text{‰}$ . Thus the direction of fractionation between dissolved Cu in seawater and the Fe-Mn crusts is consistent with an equilibrium fractionation for Cu isotopes between these two phases.

[1] Vance D *et al.* (2008) *EPSL* **274**, 204–213. [2] Sherman *et al.* (2009) *GCA* **73**, A1208.