

Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation

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Anthropogenic greenhouse-gas emissions continue to increase rapidly despite efforts aimed at curbing the release of such gases. One potentially long-term solution for offsetting these emissions is the capture and storage of carbon dioxide. In principle, fluid or gaseous carbon dioxide can be injected into the Earth's crust and locked up as carbonate minerals through chemical reactions with calcium and magnesium ions supplied by silicate minerals. This process can lead to near-permanent and secure sequestration, but its feasibility depends on the ease and vigour of the reactions. Laboratory studies as well as natural analogues indicate that the rate of carbonate mineral formation is much higher in host rocks that are rich in magnesium- and calcium-bearing minerals. Such rocks include, for example, basalts and magnesium-rich mantle rocks that have been emplaced on the continents. Carbonate mineral precipitation could quickly clog up existing voids, presenting a challenge to this approach. However, field and laboratory observations suggest that the stress induced by rapid precipitation may lead to fracturing and subsequent increase in pore space. Future work should rigorously test the feasibility of this approach by addressing reaction kinetics, the evolution of permeability and field-scale injection methods.

Atmospheric CO₂ concentration has increased from 280 ppm during pre-industrial times to 380 ppm today as a result of human input, and this is thought to be causing enhanced global warming and ocean acidification¹. Between 2000 and 2005, global CO₂ emissions from burning fossil fuels averaged 26.4 Gt CO₂ yr⁻¹, at or above the highest rates predicted by the Intergovernmental Panel on Climate Change (IPCC)². Stabilization of atmospheric CO₂ below 450 ppm requires a 30 to 85% net reduction in CO₂ emissions by 2050 (ref. 1). Owing to the continuing use of fossil fuels, CO₂ capture and storage should be a component of realistic plans to cap or reduce atmospheric CO₂ concentrations^{3,4}.

Geological formations, such as deep saline aquifers, have been proposed as repositories for anthropogenic CO₂ (refs 3,5,6). The long-term safety and permanence of storage will depend on physical and chemical controls within the storage reservoir. Injection of CO₂ modifies ambient formation waters, inducing fluid–rock reactions that may lead to the immobilization of injected CO₂ (ref. 3), or alternatively to increased permeability⁷. Thus, the permanence and safety of geological CO₂ storage will be determined by *in situ* fluid–rock reactions.

Carbon dioxide storage mechanisms

CO₂ is generally proposed to be injected at >800 m depth, where it is in a supercritical state³. Supercritical CO₂ is buoyant with respect to host rocks, and aqueous fluids at relevant temperatures and pressures. As a result, buoyant CO₂ fluid can migrate back to the surface³. Leakage of buoyant high-mobility CO₂ reduces long-term CO₂ storage, and could contaminate shallow-water resources if dissolved in groundwater⁸. However, various trapping mechanisms can immobilize the injected CO₂. Different trapping mechanisms that are active during different residence times in the reservoir are summarized in Box 1 (based on ref. 3).

As mineral trapping facilitates long-term storage of CO₂ in the form of carbonate minerals, and can provide extremely large storage capacity in certain geological settings, it is of special interest and will be discussed further.

Mineral trapping occurs in a series of reactions. Dissolution of CO₂ acidifies formation water through the following reaction:



CO₂ solubility decreases with increasing temperature and ionic strength of the formation water, and increases with increasing pressure⁹. Dissolved CO₂ will dissociate into bicarbonate and carbonate ions (reaction (1)) and, if divalent cations are in solution, will precipitate as carbonate minerals (reactions (2) and (3)).



Reactions (1) and (2) generate H⁺ ions and will not proceed as written unless these ions are also consumed. Further water–rock reactions, such as calcium plagioclase dissolution (reaction (4)), consume H⁺ ions, driving reactions (1) and (2) to the right, and resulting in precipitation of carbonate minerals (reaction (3)):



Thus, in addition to temperature, pressure and salinity, dissolution of CO₂ into formation waters depends on buffering pH through fluid–rock reactions. CO₂ storage in pore space is optimized in host rocks with a high pH buffer capacity, determined by the mineralogy of the rocks. Generally, reactions with silicate minerals buffer pH decrease owing to reaction (1), enhancing both solubility trapping and mineral storage¹⁰.

Aquifers containing 'basic' silicate minerals with a high proportion of Mg and Ca, such as olivine, serpentine, pyroxenes and plagioclase, have the greatest potential to fix CO₂ as carbonate minerals because they have a high molar proportion of divalent cations and they react rapidly to form carbonate minerals^{11,12}. Deep aquifers in sedimentary basins are often considered the most promising CO₂ storage sites owing to their large storage capacity in pore space, relatively high permeability and geographic ubiquity. However, the dominant rocks in sedimentary basins are sandstone, siltstone, shale and limestone, which generally contain minor quantities of basic silicate minerals¹¹. Xu *et al.*¹¹ simulated the mineral trapping potential of (1) glauconitic sandstone (dominantly quartz,