nature geoscience

FOCUS | PROGRESS ARTICLE

PUBLISHED ONLINE: 8 NOVEMBER 2009 | DOI: 10.1038/NGEO683

Permanent storage of carbon dioxide in geological reservoirs by mineral carbonation

Jürg M. Matter* and Peter B. Kelemen

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 CO_2 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 acidification[1]. Between 2000 and 2005, global CO_2 emissions from burning fossil fuels averaged 26.4 Gt CO_2 yr^{-1}, at or above the highest rates predicted by the Intergovernmental Panel on Climate Change (IPCC)[2]. Stabilization of atmospheric CO_2 below 450 ppm requires a 30 to 85% net reduction in CO_2 emissions by 2050 (ref. 1). Owing to the continuing use of fossil fuels, CO_2 capture and storage should be a component of realistic plans to cap or reduce atmospheric CO_2 concentrations[3,4].

Geological formations, such as deep saline aquifers, have been proposed as repositories for anthropogenic CO_2 (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 CO_2 modifies ambient formation waters, inducing fluid–rock reactions that may lead to the immobilization of injected CO_2 (ref. 3), or alternatively to increased permeability[7]. Thus, the permanence and safety of geological CO_2 storage will be determined by *in situ* fluid–rock reactions.

Carbon dioxide storage mechanisms

CO_2 is generally proposed to be injected at >800 m depth, where it is in a supercritical state[3]. Supercritical CO_2 is buoyant with respect to host rocks, and aqueous fluids at relevant temperatures and pressures. As a result, buoyant CO_2 fluid can migrate back to the surface[3]. Leakage of buoyant high-mobility CO_2 reduces long-term CO_2 storage, and could contaminate shallow-water resources if dissolved in groundwater[8]. However, various trapping mechanisms can immobilize the injected CO_2. 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 CO_2 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 CO_2 acidifies formation water through the following reaction:

$$CO_2(aq) + H_2O = H_2CO_3 = HCO_3^- + H^+ = CO_3^{2-} + 2H^+ \quad (1)$$

CO_2 solubility decreases with increasing temperature and ionic strength of the formation water, and increases with increasing pressure[9]. Dissolved CO_2 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)).

$$(Ca,Mg,Fe)^{2+} + HCO_3^- = (Ca,Mg,Fe)CO_3 + H^+ \quad (2)$$

$$(Ca,Mg,Fe)^{2+} + CO_3^{2-} = (Ca,Mg,Fe)CO_3 \quad (3)$$

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)):

$$CaAl_2Si_2O_8 + 2H^+ + H_2O = Ca^{2+} + Al_2Si_2O_5(OH)_4 \quad (4)$$

Thus, in addition to temperature, pressure and salinity, dissolution of CO_2 into formation waters depends on buffering pH through fluid–rock reactions. CO_2 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 storage[10].

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 CO_2 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 CO_2 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 minerals[11]. Xu *et al.*[11] simulated the mineral trapping potential of (1) glauconitic sandstone (dominantly quartz,

Lamont-Doherty Earth Observatory of Columbia University, 61 Route 9W, New York 10964, USA, *e-mail: jmatter@ldeo.columbia.edu