Carbon dioxide storage through mineral carbonation

Sandra Ó Snaebjörnsdóttir, Bergur Sigfússon, Chiara Marieni, David Goldberg, Sigurður R Gíslason, Eric H Oelkers, Sandra Ó. Snæbjörnsdóttir

MINERAL STORAGE OF CO$_2$

Sandra Ó. Snæbjörnsdóttir[1], Bergur Sigfússon[1], Chiara Marieni[2], David Goldberg[3], Sigurður R. Gíslason[4], Eric H. Oelkers[2, 5]

[1]Orkuveita Reykjavíkur, Reykjavík, Iceland.
[2]CNRS/UMR 5563, Université Paul Sabatier, Toulouse, France
[3]Lamont Doherty Earth Observatory, Columbia University, New York, USA
[4]Institute of Earth Sciences, University of Iceland, Reykjavík, Iceland
[5]University College London, United Kingdom

1. INTRODUCTION:

Carbon dioxide (CO$_2$) levels in the atmosphere are higher and rising faster than at any time in human history, largely because of the use of fossil fuels such as coal, oil, and natural gas. Continued fossil fuel burning will increase CO$_2$ concentrations in the atmosphere at previously unseen rates, raising global temperatures, sea level and ocean acidity with potentially devastating impacts on the availability of food and water, human shelter and coastlines, and energy. Solutions are needed to address this growing threat while continuing to address our energy needs. Limiting this rise in temperature requires a substantial and sustained reduction in the net flow of CO$_2$ into the atmosphere.

The Paris Agreement (UN, 2015) aims to keep the global temperature rise "well below 2°C" from the pre-industrial levels, and to pursue efforts to limit the temperature increase to 1.5°C, "recognizing that this would significantly reduce the risks and impacts of climate change". According to the International Energy Agency (2017) the goals of the Paris agreement can be achieved by pushing already available strategies to their maximum practical limits. This means that we do not need to depend on unforeseen breakthroughs in technology – but it is essential to advance and apply globally already existing technologies.

Carbon capture and storage (CCS) is one of the essential technologies required to achieve the goals of the Paris agreement (IEA 2017, IPCC 2018). CCS is the key technology for 1) reducing emissions from fossil fuel power plants while these are still used for power production; 2) limiting emissions from many industrial processes such as steel, aluminium and cement production; and 3) to deliver "negative emissions" by removing and sequestering CO$_2$ directly from air by the second half of the century. Although the deployment of carbon dioxide removal (CDR) at a large scale has yet to be achieved, all proposed pathways to limit global warming to 1.5°C require some degree of CDR (IPCC, 2018).

CCS includes a range of processes for CO$_2$ capture, separation, transport, storage, and monitoring. Among these, the storage of carbon captured during CCS efforts is challenging due to 1) the large volume of carbon needed to be stored and 2) because pure CO$_2$, whether in a gas or supercritical form, tends to be buoyant and will tend to migrate back to the surface if not adequately stored. Two broad subsurface storage options are currently being explored (Fig. 1). The first is to inject captured carbon into sedimentary basins where the CO$_2$ may be physically trapped below an impermeable cap rock preventing it from migrating to the surface. The key to such storage is to guarantee that the cap-rock in the system is sufficiently robust to assure its long-term storage without leakage. Alternatively, the captured carbon can be stored via injection into reactive rocks such as basalts or ultra-mafic rocks leading to the trapping of carbon within stable carbonate minerals (Fig. 2). By provoking the mineralisation of the injected CO$_2$ into carbonate minerals such as calcite, dolomite or magnesite via its

injection into reactive host-rocks, the injected carbon is permanently fixed and there is a negligible risk of it returning to the atmosphere.

The idea of harnessing this natural mineral carbonation process to mineralise anthropogenic CO_2 was first proposed in the 1990's (Seifritz, 1990; Lackner et al., 1995). Since then, this CO_2 storage method has been studied extensively. Here we review the past and present state of mineral CO_2 storage as means to help address the global CCS challenge. Emphasis will be placed on the recent advances that make subsurface mineral storage cost effective (e.g. Gunnarsson et al., 2018), exploring the limits and future of this technology in terms of potential sites and gas compositions. Finally, we assess the potential impact of CO_2 mineralisation to lower CO_2 emissions and remove already emitted CO_2 directly from the atmosphere.

Text box on the different trapping mechanisms

For carbon storage in sedimentary basins, pure CO_2 is injected into porous sedimentary rocks where ideally the injected CO_2 is trapped below an impermeable cap rock. Eventually some of the CO_2 becomes stuck in small pores, limiting its mobility in a process referred to as structural and residual trapping. Over time, the CO_2 dissolves into the formation water resulting in solubility trapping of the injected gas. Some of this dissolved CO_2 reacts to form stable carbonate minerals, so called mineral trapping. As the injected CO_2 progresses from structural to mineral trapping, it becomes more immobile and thus the storage becomes more secure, though this process can take thousands of years or more (Benson et al., 2005). (B) For subsurface carbonation the CO_2 can be dissolved into water during or prior to its injection into porous reactive rocks. No cap rock is required since the dissolved CO_2 is not buoyant and does not have the tendency to migrate back to the surface. Solubility trapping occurs immediately, and the bulk of the carbon is trapped in carbonate minerals within two years of injection at 20-50°C (Matter et al., 2016).

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2. THE CARBON MINERALISATION PROCESS

All the carbon in the atmosphere, vegetation and oceans is derived from rocks and will end up in rocks, the largest carbon reservoir on Earth. The carbon moves from one terrestrial reservoir to another in the carbon cycle. It has a few years average residence time in the atmosphere, decades in vegetation, centuries to thousands of years in soils and in the oceans, and millions of years in rocks. Such natural evidence suggests that the mineral storage of carbon provides the most stable 'permanent solution' for carbon storage. This solution to carbon storage, however, will only be practical if it is possible to accelerate this natural process at large enough scales to address the current global challenge.

Natural mineral carbonation is most efficient in basaltic and ultramafic rocks due to their high reactivity and their abundance in divalent metal cations contained in silicates (Wolff-Boenisch et al., 2006). Of these, basaltic rocks are the most abundant: Most of the ocean floor, about 70% of the Earth's surface, is basaltic, and somewhat more than 5% of the continents. Although its occurrence is limited, its weathering is responsible for about 30% of the natural drawdown of CO_2 from the atmosphere via silicate weathering on the continents and volcanic islands demonstrating the high potential of these rocks for mineral carbonation (Dessert et al., 2003).

Natural analogues for large scale CO_2 mineralisation can be found in various settings. One of the most significant processes is the carbon uptake of the oceanic crust, where basalts in volcanic submarine geothermal systems receive significant amount of CO_2 from the degassing of magma intrusions in their roots. The oceanic crust thickness is typically 6-7 km, and it has a remarkably consistent stratigraphy on a global basis (e.g., Kappel and Ryan, 1986; Karson, 2002) with the ridge-flank hydrothermal circulation focused in the upper most 1 km. This hydrothermally active crust is a net sink of about 40 $MtCO_2$ per year (e.g. Alt and Teagle, 1999; Coogan et al., 2016).

Based on such systems located onshore in Iceland, the largest landmass found above sea-level at the mid-oceanic ridges, it has been estimated the basaltic bedrock can store over 100 kg CO_2/m^3 (Wiese et al., 2008). From this storage potential estimate, the total storage potential of the oceanic ridges is orders of magnitude larger than the CO_2 derived from burning of all fossil fuel on Earth (Snæbjörnsdóttir et al., 2014). This agrees with other storage capacity estimates that verify the enormous storage capacity possessed in sub-ocean basalts (e.g. Goldberg et al., 2008, 2010; Marieni et al., 2013).

Evidence for natural carbonation is apparent in various other settings onshore, for example in Oman where tectonically exposed mantle peridotites rapidly remove CO_2 directly from the atmosphere resulting in the formation of travertines in natural fluids due to CO_2-water-rock interaction. The reactivity of the peridotites in Oman has been estimated to have consumed over 1 $GtCO_2$ via in-situ carbonation (Keleman and Matter, 2008). The extensive natural carbonation of ultramafic rocks leads to the formation of liswantites, an ultramafic rock that has been successively transformed from serpentine + olivine + brucite to form serpentine + magnesite, then magnesite + talc and finally magnesite + quartz, which serves as a geological analogue for carbon dioxide mineralization (Hansen et al., 2005). The natural carbonation of mafic and ultramafic mine waste tailings is also commonly observed (e.g. Wilson et al., 2009). Similarly, in W-Greenland extensive carbonate mineralisation associated with petroleum migration was documented by Rogers et al. (2006) suggesting that CO_2-bearing fluids may be readily transported, even in extensively altered basalts, provoking carbon mineralisation.

The process of mineral carbonation proceeds through the interaction of water dissolved CO_2 with rocks, and notably mafic or ultramafic rocks. Carbon dioxide-charged water is acidic, typically having a pH of 3-5 depending on the partial pressure of CO_2, water composition, and temperature of the system. This acidic fluid promotes the dissolution of cation-bearing silicate minerals; for example, the dissolution of pyroxene, a common mineral in basalt, can be expressed as:

$$2H^+ + H_2O + (Ca,Mg,Fe)SiO_3 = Ca^{2+}, Mg^{2+}, Fe^{2+} + H_4SiO_4$$
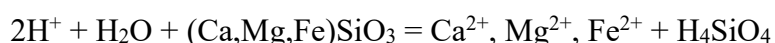
Such reactions promote CO_2 mineralisation in two ways: First it consumes protons, which neutralises the acidic gas charged water – carbonate mineral dissolution is facilitated by the increasing pH of the fluid; and second it provides cations that can react with the dissolved CO_2 to form stable carbonate minerals. The degree to which the released cations form stable carbonate minerals depends on the identity of the element, the pH and the temperature. Dissolved calcium readily precipitates from the reactive aqueous fluid at temperatures below ~280°C once calcite ($CaCO_3$) and/or aragonite is supersaturated. Dissolved magnesium, however, precipitates as the carbonate magnesite ($MgCO_3$) and dolomite ($CaMg(CO_3)_2$) at temperatures above ~80°C or higher (Saldi et al., 2009); at lower temperatures the precipitation of these minerals appear to be kinetically inhibited. At such conditions only less stable hydrous Mg-carbonate minerals, such as hydromagnesite, dypinite and nesquhonite

appear to form (e.g. Turvey et al., 2018). Dissolved magnesium is also readily incorporated into clay minerals such as smectite if substantial aluminium is present in the system, limiting its availability to promote carbonation. The degree to which Fe combines with dissolved carbonate to form substantial carbonates during carbonation efforts remains unclear. In oxic conditions, Fe^{2+} oxidises prior to its potential incorporation as a divalent metal carbonate, and the mineral siderite ($FeCO_3$) is only rarely observed in modern sedimentary and basaltic rocks. The mineral ankerite, ($FeCa(CO_3)_2$ however, may be favoured in at conditions at ambient to moderate temperatures (e.g. Gysi and Stefánsson, 2012).

Other important factors for efficient carbon mineralisation are the permeability and/or porosity of the host-rock formation. These provide pathways for the migrating fluids, access to mineral surfaces that contribute cations to the mineralisation, and space for the carbonate precipitates. The overall mass of carbon bearing precipitates is also affected by the formation of other secondary minerals, which compete with carbonates at higher pH and lower partial pressures of CO_2 for the divalent cations liberated from dissolving primary minerals and for the available pore space. Carbonate and associated precipitates tend to have a higher volume than their primary source minerals, so they could clog flow pathways where they precipitate. It should be noted, however, that during subsurface mineral carbonation efforts, the injected CO_2 or CO_2-rich water will be acidic such that near the injection, minerals will tend to dissolve opening up pore space and flow paths near the injection well; pore filling secondary minerals are only expected to precipitate at a distance from the injection well after sufficient host-rock dissolution has neutralized the acidic CO_2-rich injection fluids.

3. EXPERIMENTAL STUDIES

A large number of experimental studies have verified the capacity of silicate minerals to release cations and thereby promote the formation of carbonate rocks in the presence of CO_2-rich fluids. Notably, many studies have focussed on the dissolution rates of primary silicates that contain the divalent metals necessary for carbonate precipitation. Emphasis on mineral dissolution stems from the commonly accepted view that mineral dissolution is the rate limiting step of any mineral carbonation process. Note that as water charged CO_2 is acidic, and carbonate minerals tend to precipitate only at neutral to basic conditions, substantial dissolution of basic silicate minerals is required for the single step mineral carbonation process such as required for in-situ carbon mineralization. An extensive number of dissolution studies of divalent metal bearing silicates have been reported on minerals such as olivine (e.g. Blum and Lasaga 1988; Oelkers 2000; Pokrovsky and Schott 2000; Rosso and Rimstidt 2000; Golubev et al. 2005; Olsen and Rimstidt 2008; Gadikota et al. 2014), pyroxene (e.g Brantley and Chen, 1995), and plagioclase (e.g. Carroll and Knauss, 2005; Metz et al., 2005; Oelkers et al., 2008; Kampman et al. 2009; Pham et al., 2010; Munz et al.,2012; Hellevang et al., 2013; Gudbrandsson et al., 2014) as well as volcanic glasses (Oelkers and Gislason, 2001; Wolff-Boenisch et al., 2004). These rates tend to be strong functions of fluid pH where the mineral dissolutions rates increase dramatically with decreasing pH in acid conditions – the conditions likely encountered near the CO_2 injection point. Aluminium bearing minerals such as plagioclase, and volcanic glasses have rates that minimize at neutral conditions then increase with increasing pH at higher pH, but the rates of aluminium free minerals, such as olivine and pyroxene tend to decrease continuously with increasing pH, such that the dissolution of these minerals are sluggish at conditions where carbonates tend to precipitate. This has encouraged several to propose a two-step *ex-situ* carbonation process, first dissolving divalent metal bearing silicates in strong acid followed by the formation of carbonate minerals at more basic conditions (see below).

Additional experiments have demonstrated the direct carbonation of divalent metal carbonates. Many of these studies have focused on the carbonation of olivine and serpentines due to their widespread availability and abundance in magnesium. Giammar et al. (2005) were unable to precipitate magnesium carbonates from dissolving olivine at 30 and 95°C but were able to form magnesite in solutions that simulated extensive forsterite dissolution at 95°C and 100 bar of CO_2 pressure. Magnesite has been reported to form at temperatures as low as 65°C (Johnson et al., 2014). The difficulty in precipitating magnesite at lower temperatures was confirmed by magnesite precipitation experiments reported by Saldi et al. (2009). At lower temperatures, hydrous Mg-carbonate minerals such as nesquehonite have been observed to form (Hanchen et al., 2008). Most of the experiments studies on serpentine have focussed on accelerating the carbonation of these minerals though mechanical or thermal treatment (e.g. Maroto-Valer et al., 2005). The carbonation of glassy and crystalline basaltic rocks has also been verified experimentally in a number of studies (e.g .Gislason et al., 1993; Gysi and Stefansson, 2012; Xiong et al., 2017).

The results of experimental studies, which are usually of limited duration have been extended over longer time and spatial scales using geochemical modelling (e.g. Marini, L., 2006, Gysi and Stefansson, 2011; Harrison et al., 2019). Such calculations suggest that the carbonation of basalts and ultramafic rocks through water-CO_2-rock interaction should lead to substantial mineralization of the injected carbon over decade-long timespans.

4. FIELD MINERAL CARBONATION STUDIES

Subsurface Mineral Carbonation

The results of experiments, geochemical modelling, and natural analogues summarized above have motivated two recent larger scale field projects that demonstrate the potential of CO_2 injected into underground basaltic reservoirs to rapidly convert into carbonate minerals, providing a safe, permanent storage solution for captured carbon (Fig. 3):

1) Hellisheidi, Iceland – the CarbFix Project
   In 2012, 230 tonnes of CO_2 and a CO_2-H_2S gas mixture were fully dissolved in locally sourced groundwater during their injection to a depth of ~500 m into basaltic rocks at Hellisheidi SW-Iceland. The temperature of the target basaltic reservoir was ~20-50°C. The method requires significant water – this original injection required ~25 tons of water for each ton of gas injected to fully dissolve the CO_2 at depth, but as the gas-charged water is more dense than fresh water and solubility trapping occurs immediately, this method improves storage security significantly. The injection of this acidic gas-charged water accelerates the metal release from the bedrock and hence the formation of carbonate minerals (e.g. Matter et. al., 2016; Snæbjörnsdóttir et al., 2017). The carbonation process was quantified using reactive and non-reactive tracers, and isotopes, which revealed the rapid mineralisation of the injected CO_2 (Matter et al., 2016; Pogge von Strandmann et al., 2019), but over 95% was mineralised within two years of injection (Fig. 2).

   Following the success of the initial CarbFix project in Hellisheidi, the project was upscaled starting in 2014 with a stepwise increase in amount of gases injected subsequently (e.g. Gunnarsson et al., 2018; Sigfusson et al., 2018). The acid gases (CO_2 and H_2S) are captured directly from the power plant exhaust stream by its dissolution into pure water (condensed steam from the power plant turbines), in a scrubbing tower. The resulting gas charged water is injected to about ~800 m depth into the basaltic reservoir at

temperatures of ~250°C. Currently the method captures and stores $1/3^{rd}$ of the CO_2 emissions from the Hellisheidi Power Plant, or about 12,000 tonnes annually, aiming for injection of over 90% of the CO_2 from the plant in the near future. Injection of CO_2 from the second geothermal plant operated in the area will begin in 2021. At present, ~65% of the injected carbon is fixed as carbonate minerals within two months of its injection. To date there is no sign of decreasing system permeability nor decrease in mineral carbonation rates since the initiation of the carbon injection in 2014.

2) Wallula, USA

This field injection took place in 2013 where nearly 1000 tonnes of pure liquid CO_2 were injected into Columbia River flood basalts at 800-900 m depth near Wallula, Washington-USA. The CO_2 was provided in tanks and the gas stream was heated and pressurized before injection. The liquid CO_2 stream was injected into two brecciated basalt zones at 800-900 m depth, and the reactions between the CO_2, the formation waters, and the basaltic subsurface monitored. Although mass balance calculations to determine the quantity of the injected CO_2 that was carbonated could not be performed, side-well cores retrieved from the storage formation two years post-injection revealed carbonate nodules, primarily ankerite ($CaFe(CO_3)_2$) in pores and fractures in the basalts. Isotopic analysis confirmed that the observed carbonates originated from the injection and, along with chemistry data and isotope analysis, indicated the some of the injected CO_2 was converted to carbonate minerals in the basalt reservoir within two years of injection (McGrail et al., 2017a; McGrail et al., 2017b; McGrail et al., 2014). Geophysical surveys, however, revealed that much of the injected CO_2 was still present in the system as free-phase CO_2 two years after the completion of the injection.

Risks and challenges of subsurface mineral carbonation

CO_2 buoyancy versus water penalty

The two in-situ mineral carbonation projects adopted different methods for carbon injection: the injection of a single CO_2 gas phase, and the injection of water-charged CO_2. Supercritical CO_2 is routinely stored and transported commercially, and its compositional integrity can be assured. It offers efficient production and transportation due to its low viscosity, high density, and low critical temperature (31°C) and pressure (7.4 MPa). Owing to its buoyancy, however, it is essential to ensure secure sealing of the storage reservoir during and after the injection of a pure CO_2 phase. This is especially challenging during onshore injection into volcanic rocks, since these formations are often highly fractured.

The injection of water dissolved CO_2 into the subsurface offers both advantages and challenges. The risks of leaks are mitigated by the dissolution of the CO_2 in water prior to or during injection resulting in almost immediate solubility trapping (Fig. 1). This adds significantly to the security of the method; since the injected gas-charged fluid is denser than the CO_2-free water present in the reservoir it has the tendency to sink rather than rise to the surface. Even though the dissolution of CO_2 requires significant amount of water, the capture method is both simple and cost-effective. The major drawback of this approach is that a large quantity of water may be needed to dissolve the CO_2 gas. This water, however, may be sourced from the target reservoir, therefore both providing access for monitoring the chemistry of the injected gas-rich plume and preventing pressure build-up in the reservoir due to injection. As an example, during the CarbFix pilot injections, the water pumped continuously from the two nearest monitoring wells was equal to the water co-injected with the CO_2 hence no net change of water pressure was observed in the storage formation. A

summary of the mass of water needed to dissolve one ton of CO_2 at 25°C is shown in Fig. 4a. The mass of water required decreases from more than 100 tons of H_2O per ton of CO_2 at a pressure of 3 bars to less than 35 tons of water at a CO_2 pressure of 25 bars. Note, however that the injection of CO_2-charged water promotes and accelerates the mineral carbonation process.

Abundant fresh water may not be readily available for this process in many parts of the world. In such cases seawater may provide an adequate alternative. One additional advantage of CO_2 injection as a water-dissolved gas is that it might considerably lower the cost of CCS. Carbon dioxide and other acid gases can be captured directly from CO_2-rich exhaust stream in fresh or seawater, by mixing the exhaust gas in a scrubbing tower (Gunnarsson et al., 2018). As can be seen in Fig 4b the energy to pressurize both the required water and the CO_2 gas to a pressure of 25 bar and 25°C is less than that required to pressure pure CO_2 to a liquid at this temperature.

The dissolution of CO_2 in water prior to its injection to mitigate leakages might be essential for on-shore operations, but for offshore operations injecting supercritical CO_2 may offer advantages in deep-ocean environments. Potential leaks may pose less of a threat due to the overlying seawater and low-permeability sediment cover that provides primary reservoir sealing (Goldberg et al., 2008, 2010). Offshore leaks would mainly impact the economics and efficiency of the injection, e.g. the cost of injecting the CO_2 making the investment less effective, since these sites are far away from inhabited areas. On the other hand, fully dissolved CO_2 injection in this environment may offer efficiencies using vast seawater resources and minimise energy needs for pumping – both approaches warrant further valuation to determine optimal injection and mineralisation scenarios in diverse geographical locations.

Induced seismicity

One of the main risks of CO_2 injection of any kind is induced seismicity. This may be a greater risk when injecting dissolved CO_2 due to the large volume of fluid that would need to be injected into the subsurface. Prior to any injection activity a site-specific study of the regional seismicity must be performed. To develop an understanding of the seismic risk, the depths, times, locations and magnitudes of seismic events should be studied and characterised.

At Hellisheidi, the seismic risk has been addressed by applying a pre-defined traffic-light protocol where preventive steps are followed to minimise the risks of induced seismicity (Zoback and Gorelick, 2012; Thorsteinsson and Gunnarsson, 2014). The seismic risk can be mitigated considerably by injecting offshore, away from populated areas and infrastructure that could be affected (Goldberg et al, 2013).

Groundwater contamination

Another potential risk of injecting CO_2 is groundwater contamination. During the initial phase of CO_2 injection, a metal-rich plume can be mobilised, which can cause the concentrations of certain elements to exceed the proposed drinking water limits. The formation of carbonate minerals, however, scavenges metals from the water. This can be seen in natural analogues during volcanic eruptions (e.g. Flaathen et al., 2009; Olsson et al., 2014). In locations offshore, however, the lack of underground sources of drinking water will have little or no risk in this regard, and furthermore, the greater the distance from populated areas, the greater the reduction in this risk.

Ex-Situ mineralisation

Ex-situ mineralisation has been extensively considered as an option for carbon capture and storage for industry sources that are located far from potential geologic storage sites, whether they be more traditional sedimentary basins or mafic/ultramafic rocks. The overall global storage capacity of ex-situ carbon mineralization waste products is estimated to be 100 to 200 Gt of material (Sanna et al., 2012). For any ex-situ carbon mineralization effort, the reactive mineral feedstock of the carbonation process, notably reactive mafic rocks, would be removed from its original location and transported to the carbon source. Rocks would be carbonated from the gas streams and then disposed. The US Department of Energy studied ex-situ mineral storage options including studies of the kinetics, process development, and economic evaluation of the processes involved (Gerdemann et al., 2007). They concluded that it would require ~55,000 tons of mineral feedstock to carbonate the daily CO_2 emissions from a 1 GW, coal-fired power plant, such that it was an impractical solution for such large sources. Nevertheless, many have considered this as an option for smaller industrial carbon sources. One key to the success of this approach is the rapid and close to complete carbonation of the silicate source mineral to limit the transport costs and storage volume. In this way ex-situ carbonation differs from sub-surface in-situ geologic carbonation, which due to the vast quantities of subsurface basalts or mafic rocks and potentially large timeframe for the injected CO_2 to interact with the host rocks can be successful if only a few percent of the target rocks are carbonated over time due to the potentially large mass of the rocks involved.

The need for fast and nearly complete carbonation of the mineral feedstock during ex-situ carbonation efforts has led to a large effort to develop industrial methods to rapidly and efficiently carbonate various mafic/ultramafic rocks or minerals. An extensive review of these technologies has been presented by Sanna et al. (2014). Such efforts have included increasing temperature, the addition of aqueous additives, thermal activation of the mineral, and ultrafine grinding of the feedstock minerals. In some instances, and conditions, efficient carbonation can be attained but the costs of such processes may prove to be prohibitive.

An alternative to ex-situ mineralization is the carbonation of mafic or ultrabasic mine waste tailings, such as the kimberlite mines in South Africa (e.g. Mervine et al., 2017) and the brucite mine tailings at the Mount Keith nickel mine (e.g. Harrison et al., 2012; Wilson et al. 2014). Mine tailings are estimated to have the potential to mineralise CO_2 on the order of 400 Mt/yr (Power et al., 2014) and often have the advantage to be situated near a point source of CO_2.

5. MOVING MINERAL CARBONATION FORWARD

As previously discussed, the deployment of CCS has not been at the pace needed for addressing the current global warming challenge on a global scale. In terms of carbon mineralisation, only one industrial injection is currently ongoing in Hellisheidi, Iceland. There are, however, advances in the pipeline that might help accelerating mineral carbonation as global scale contribution to limiting atmospheric carbon concentrations (Fig. 5).

Combining carbon mineralisation with direct air capture.

The favourable conditions for subsurface carbon mineralisation (e.g. the availability of subsurface reactive rocks) are not equally distributed across the globe. Therefore, the pairing of large emission sources and suitable rock formations may be held back by high costs of pipeline infrastructures and long distances. Since CO_2 mixes rapidly in the atmosphere and concentrations are nearly the same everywhere, Direct Air Capture (DAC) installations could

be effective depending on the capture technology used, when installed near suitable formations for carbon storage and appropriate energy sources (Goldberg et al., 2013; Goldberg and Lackner, 2015). DAC refers to a set of technologies that can capture CO_2 from the atmosphere, as opposed to point-source CCS, which captures CO_2 from more concentrated industrial streams. DAC may be an important tool in managing emissions that are hard or costly to eliminate at source, and by combining DAC and CCS it may be possible to create the negative emission pathways contributing to those necessary during the latter part of the century to limit the temperature rise to 1.5°C (IPCC, 2018).

The coupling of DAC and mineral carbonation is being explored in the CarbFix2 project in Hellisheidi, Iceland. A DAC capture unit, based on an alkaline-functionalised adsorbent using heat energy through a temperature-vacuum-swing process and developed by a Swiss company called Climeworks, has been installed at Hellisheidi. The air derived CO_2 stream is then injected and mineralised, achieving a negative emission pathway (Gutknecht et al. 2018). The up scaling of the Climeworks DAC technology in combination with the CarbFix re-injection technology is further being explored across various sites in Iceland. Looking towards the future, the Solid Carbon project in British Columbia is assessing DAC technologies with a similar mineralisation scenario at an offshore site in the Cascadia Basin on the Juan De Fuca plate (Goldberg et al., 2018).

Moving carbon mineralisation offshore

An advantage of subsurface mineral storage of CO_2 lies in the increased storage security and hence diminished need for monitoring. This enables the possibility to couple CCS with DAC for carbon storage in remote locations. Goldberg et al. (2013) set out one example scenario for extraction of CO_2 from the atmosphere using renewable wind energy with sub-ocean basalt storage in a remote offshore environment near Kerguelen Island in the Southern Indian Ocean. Although such technologies need to be advanced to handle remote operations at a reasonable cost, the scaling of these technologies could provide a significant and steady CO_2 supply for mineralisation in high capacity basalt reservoirs with low risks of leakage, few environmental impacts and few human inconveniences.

Two projects are currently centred on offshore injections for carbon mineralisation. In the north-eastern Pacific Ocean, the Solid Carbon project is currently exploring options to inject CO_2 into oceanic basalt below marine sediments, offshore from Washington state and British Columbia. A pre-feasibility study was conducted under the U.S. Dept of Energy CarbonSAFE program to evaluate technical and non-technical aspects of storing ~50 million tons of CO_2 via an offshore storage complex (Goldberg et al., 2018). Conditions at the Cascadia Basin site may tend to facilitate injection as a supercritical fluid, with low risk of degassing below 800 m ocean depths. In the Cascadia Basin region, onshore emitters generate a total of ~40 Mt/yr from stationary sources that could provide steady streams of CO_2 to the offshore reservoir, and DAC technology may be added to these capture scenarios (Goldberg et al., 2018).

The EU-funded CarbFix2 project is preparing for the injection of seawater dissolved CO_2 into submarine basalts. First results indicate that seawater is a suitable medium for the overall carbon mineralisation process that provides vast supply of water in coastal areas and offshore. Its applicability is, however, more limited than using fresh water in terms of its temperature and pH range, due to formation of various secondary minerals (e.g. Wolff-Boenisch, 2011; Luhman et al., 2017).

Exploring the limits of carbon mineralisation

The most feasible formations for carbon mineralisation are ultra-mafic and mafic volcanic rocks due to their reactivity, and in case of basalts, abundant pore-space available for carbon storage. A range of other rock formations have the potential for mineral carbonation, including less reactive rock types, but the boundary has yet to be established on which formations are feasible and which not. Evaluating the chemistry and reactivity of different rock types, the porosity and permeability of the potential reservoir, and its pressure and temperature state during CO_2 injection all strongly influence the rate of the dissolution and carbonation reactions (e.g., Wolff-Boenisch et al., 2004, 2006; Schaef, et al., 2010; Aradóttir, et al; 2012). Some of this potential will be explored as part of the H2020 backed GECO project. The project focuses on developing harmonised methods to assess the reactivity of the different rock types of the potential reservoirs prior to injection (Sigfusson et al., *accepted*).

Water capture of impure CO_2 gas streams

A potential major advantage of mineral carbonation, if coupled with water capture of the gas stream is the cost. The cost of any carbon capture effort, regardless of the approach, increases as the concentration of the carbon source decreases. The energy required to capture CO_2 from a gas stream and estimated marginal cost of this capture as a function CO_2 concentration of the gas stream is summarized in Figure 6. The marginal cost of the capture of CO_2 by its dissolution in water is estimated to be less than \$100/ton CO_2 for all gas streams containing 8% or more CO_2. This cost may prove favourable to alternatives, particularly when considering that this water can be directly injected into the subsurface without any additional separation or depressurizing. Note that adopting a similar approach at Hellisheidi as part of CarbFix2 the overall onsite cost of carbon capture and storage is US \$25/ton including both capital expenditure and marginal costs for capture, transport and storage combined (Gunnarsson et al., 2018).

6. THE FUTURE OF MINERAL CARBONATION

The degree to which mineral carbonation will be developed and adopted at a large scale will be related to how the existing technologies can be generalized and streamlined to limit its costs, its energy demand, and its water demand. Nevertheless, as a tool to combat carbon emissions to the atmosphere it provides several significant advantages.

One advantage of carbon mineralisation is that it provides an alternative solution to the more common injection of CO_2 into sedimentary basins. It can be applied in areas where CCS has not been previously considered, such as fractured mafic and ultra-mafic rocks, including the oceanic ridges and flood basalts for offshore storage (see Fig. 6). This increases the opportunity for pairing of sinks and sources, potentially reduces transport costs. Given the magnitude of global CO_2 emissions, it is unlikely that any single CCS strategy will achieve the desired emission reduction.

Another advantage of carbon mineralisation is the added long-term storage security. Permanence is essential for the success and public acceptance of carbon storage. One economical advantage of the increased security is the diminished need for monitoring of the injection site. Security in also enhanced by the possibility of injection into offshore locations where the largest mass of mafic rocks exists. Such could be facilitated by the pairing direct air capture (DAC) with mineral carbon storage and the appropriate energy sources; this latter combination could enable extensive carbon storage beneath the basaltic ocean floor. The regulatory framework for an offshore storage project, however, will depend strongly on the nature and location of the specific CO_2 sources and reservoirs involved, their corresponding

jurisdictions, and the governing laws at that time (Goldberg et al., 2018; Webb and Gerrard, 2019). Going forward, specifically scoped project developments would help to advance the regulatory requirements in each specific jurisdiction.

One additional advantage is that is some cases, mineral carbonation may be more cost effective that its alternatives. In cases where CO_2 is captured from emission gases by its dissolution into water and this gas-charged water is directly injected into reactive subsurface rocks, the energy costs may be substantially reduced (Fig. 7). This approach could also provide additional value by capturing and storing other acid gases such as H_2S and SO_2 through subsurface mineralization such as demonstrated at Hellisheidi.

The biggest hurdle in applying in-situ carbon mineralization on greater scale is not technological, but the financial incentive for CCS in general. The current cost of capturing, injecting and storing the CO_2 exceeds the cost of emitting. For example, in Europe, within the EU carbon trading scheme, the cost of the rights to emit carbon has since the launch of the trading scheme in 2005, has been far too low to motivate the development and application of CCS (Market Insider, 2019). The rising prices of the CO_2 emission quotas over the last two years (29 EUR/ton CO_2, 01/07/2019) are likely to change the CCS environment in the near future. This current emission quota price as of July 2019 is currently higher than the current onsite costs of the CarbFix injection in Iceland. In the US, recent tax legislation allows for financial incentives for CO_2 storage that are \$50 per ton for saline aquifer injection and \$35 per ton for EOR injection (Folger, 2018).

Even though electricity generation by fossil fuel plants is increasingly being replaced by renewables in many growing markets, numerous industries, including the cement and metal industry, cannot readily avoid carbon emissions. To avoid carbon emissions from such industries will require some form of CCS.

Human emissions have already exceeded global silicate weathering uptake by at least an order of a magnitude (Gaillardet et al., 1999). The technology and advances summarized in this review suggest that carbon mineralisation can help to reverse this trend. Key to maximizing the potential of mineral carbonation will be to define the practical limits where the existing technology can be used (e.g. rock compositions, gas compositions) and to streamline the processes to limit its cost. This requires roadmaps for the most probable reaction paths in natural systems, including studies of reaction rates of different rock types in the subsurface. The effect of the injected fluid composition and the potential use of chemicals or catalysts to alter reaction rates can be defined, to quantify the extent and consequences of host rock formation carbonation at various sites. The most prominent options for CO_2 mineralisation can already be identified, but the increased understanding of the limitations and potential of the method will enable its wider applicability. New field pilot studies should be undertaken to evaluate mineralization options under varying geological conditions, onshore and offshore, with pure CO_2 and mixed source gas compositions to enhance the potential of mineral carbonation as a general tool to combat the challenges of global warming.

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Fig. 1: The trapping mechanisms when a) injecting into sedimentary basins (modified from Benson et al., 2005) and b) when injecting dissolved CO₂ for mineralisation (Sigfusson et al. IJGGC 2015, Matter et al. Science 2016, Snæbjörnsdóttir et al. IJGGC 2017).
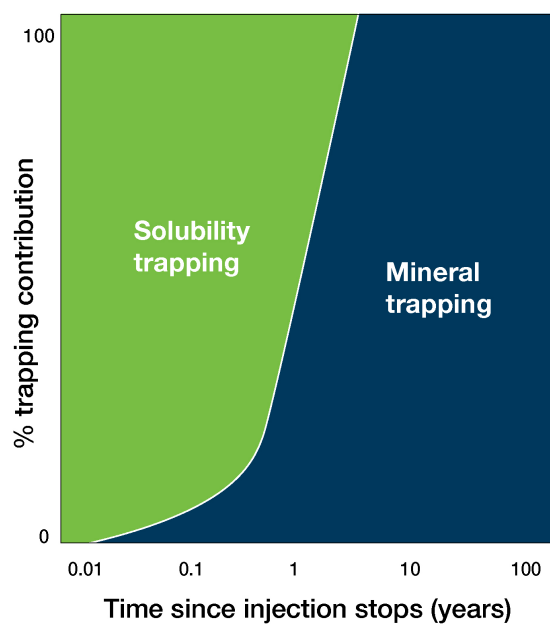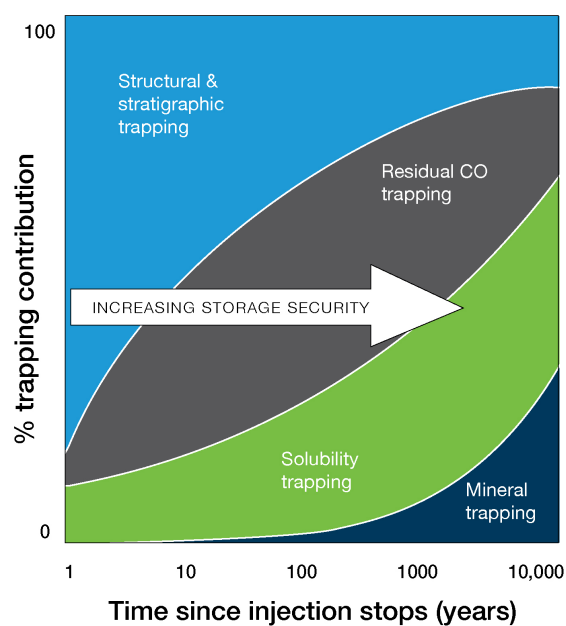
Fig 2: Basaltic core containing carbonates. The core was retrieved from about 450 m depth at the CarbFix pilot injection site in SW-Iceland in 2014 (photo: Sandra Snæbjörnsdóttir).

Fig. 3: Updated figure from Gislason and Oelkers, 2014 comparing diluted CO₂ injections (a-CarbFix) and supercritical CO₂ injections (b-Wallula, CarbonSAFE) in basalts.
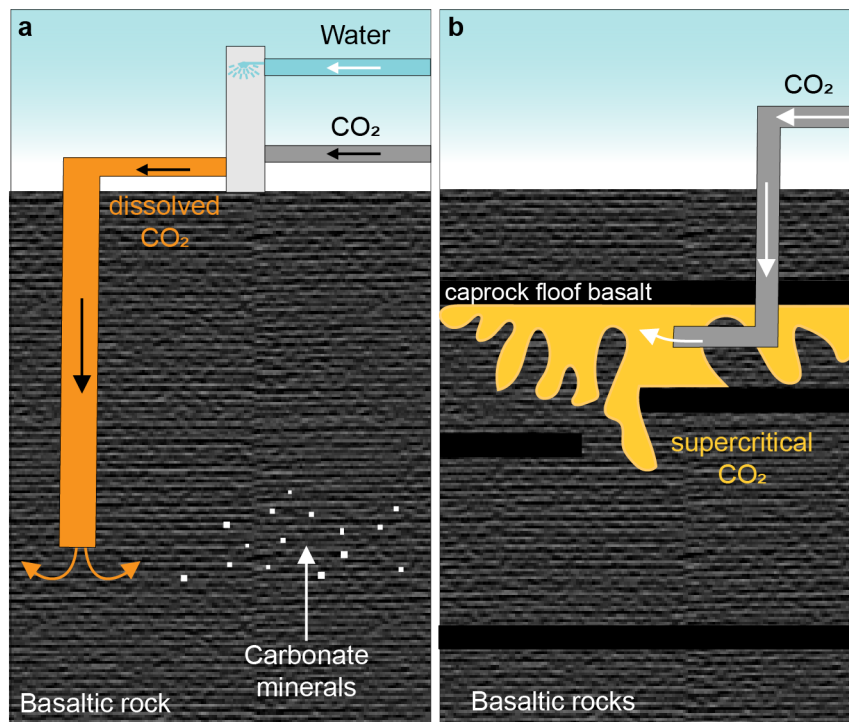
Fig. 4: a) The amount of fresh water (unbroken line) and seawater (broken line) needed at at 25°C and different pressures for dissolving one ton of CO_2 b) The energy demand for pressurizing CO_2 to liquid (red line), CO_2 (grey line), pure water (blue line) and CO_2-charged pure water (light blue line) by the pressuring the two phases individually then mixing these to an equilibrium single phase. In each case the required energy is based on equilibrium isothermal pressuring of the CO_2, and adiabatic pressuring of the water.
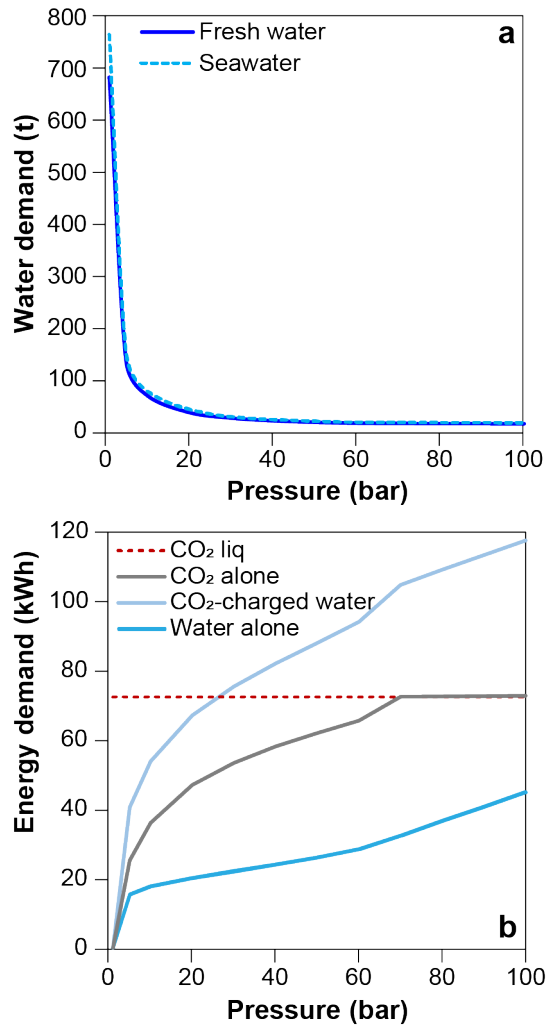
Fig 5: Schematic figure highlighting CarbFix industrial setup, offshore injections and DAC (both on land and offshore). 1. Industrial plant, 2. Water scrubbing tower, 3. Injection well, 4. Production/monitoring well, 5. DAC, 6. Offshore rig, 7. Cargo ship.
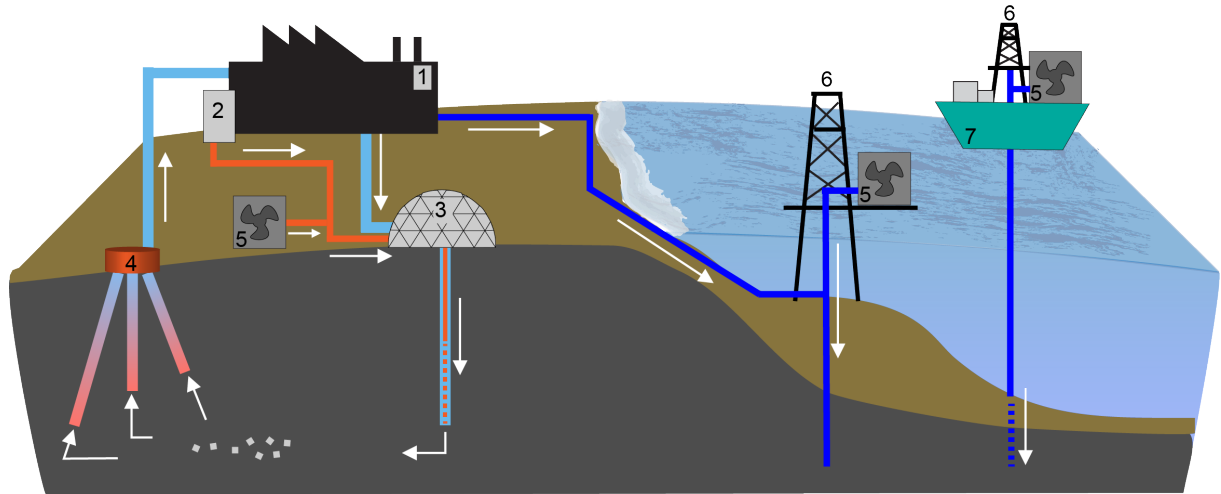
Fig. 6: *Estimated energy and US dollar cost of CO_2 capture by exhaust stream gas dissolution into water as a function of the CO_2 content of a mixed gas for a capture pressure of 30 bars. The calculation is based on first pressuring the mixed gas and sufficient water to dissolve this CO_2 to 30 bars and then mixing these phases to water-CO_2 equilibrium. The calculation was performed assuming ideal gas behaviour and assuming a 50% capture efficiency and an average global energy price of $0.13 per kWh.*
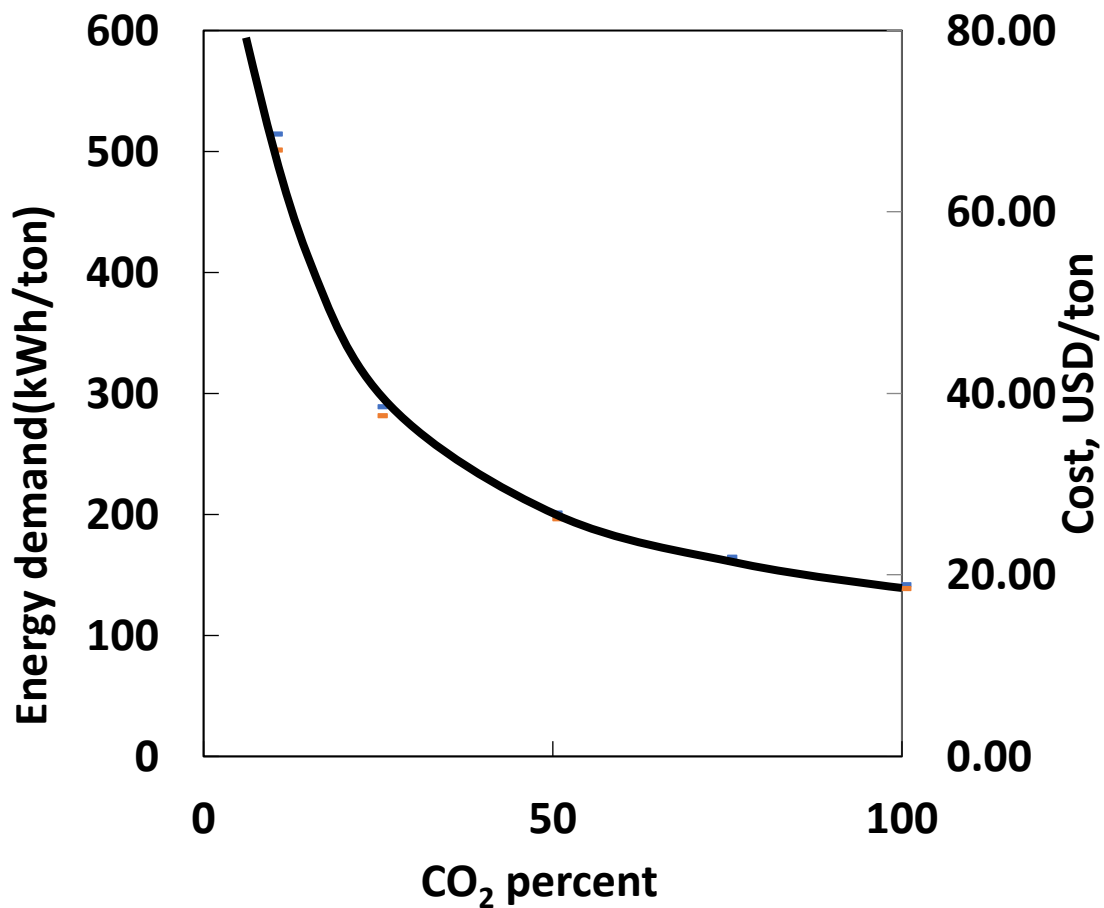
Fig. 7: Potential on-land offshore targets for mineral storage of CO_2. Oceanic ridges younger than 10 Ma are shown in brown, oceanic igneous plateaus and continental flood basalts are shown in pink. Data from Whittaker et al. (2015); Mueller et al. (2016); and Johansson et al., (2018).