

Assessing geochemical carbon management

Jennie C. Stephens · David W. Keith

Received: 5 May 2005 / Accepted: 11 April 2008 / Published online: 24 June 2008
© Springer Science + Business Media B.V. 2008

Abstract The challenge of reversing rising atmospheric CO₂ concentrations is growing with the continued expansion of CO₂-emitting energy infrastructure throughout the world and with the lack of coordinated, effective measures to manage and reduce emissions. Given this situation, it is prudent for society to explore all potential carbon management options, including those with seemingly low probability for success. Recent initiatives for advancing and enhancing carbon storage options have focused primarily on the physical trapping of CO₂ in underground geologic formations and on the biological uptake of CO₂; less attention has been given to approaches that rely primarily on geochemical reactions that enhance transformation of CO₂ gas into dissolved or solid phase carbon by liberating cations to neutralize carbonic acid. This paper provides a structured review of the technical status of these geochemical approaches, and also presents a simple framework for assessing the potential and limitations of various proposed geochemical approaches to assist prioritizing future research in this area. Despite major limitations, geochemical approaches have unique potential to contribute to CO₂ reductions in ways that neither physical nor biological carbon storage can by allowing for the direct removal of CO₂ from the atmosphere with minimal requirements for integrating with existing infrastructure. Recognizing the severity and urgency of the need for carbon management options, we argue for an increase in research activity related to geochemical approaches to carbon management.

J. C. Stephens (✉)

Environmental Science and Policy Program, Department of International Development,
Community, and Environment, Clark University, 950 Main Street, Worcester, MA, 01610, USA
e-mail: jstephens@clarku.edu

D. W. Keith

Department of Chemical and Petroleum Engineering, Department of Economics,
University of Calgary, 2500 University Drive NW, Calgary, Alberta, T2N 1N4, Canada
e-mail: keith@ucalgary.ca

1 Introduction

Although stabilizing atmospheric CO₂ is recognized as essential to mitigating the risks associated with climate change (IPCC 2001, 2007), the magnitude of emission reductions required has so paralyzed public policy that coordinated and effective measures to reduce CO₂ emissions remain elusive. The challenge of reversing the rising atmospheric CO₂ concentrations for climate change mitigation is increasing with the rapid growth of fossil-fuel-based, CO₂-emitting energy technology infrastructure throughout the world. Despite the many options for transitioning to low or no-carbon emitting technologies (Holdren 2006; Pacala and Socolow 2004), the rate of emissions growth continues to accelerate and there is little objective evidence that such a transition is underway (Canadell et al. 2007; Raupach et al. 2007). Prudent action requires a systematic exploration of all plausible avenues toward reducing the concentrations of CO₂ in the atmosphere. In addition to increasing energy production from renewable sources, switching to low-carbon-intensity fuels, improving energy efficiency, and promoting energy conservation, capturing CO₂ and storing the associated carbon in a reservoir other than the atmosphere has potential for cost-competitive large-scale reductions of atmospheric CO₂ (Anderson and Newell 2004; Herzog 2001; IPCC 2005; Parson and Keith 1998).

Many approaches to storing the carbon released from the burning of fossil fuels in a reservoir other than the atmosphere have been proposed. These different approaches can be categorized either by location, i.e. land surface, ocean, or geosphere, or by the mechanism of storage, i.e. whether biological, chemical or physical processes are the primary mechanism for storage (Table 1). Within this categorization scheme, biological approaches rely on the photosynthetic process to capture and convert atmospheric CO₂ into organic carbon, chemical approaches rely on a chemical reaction to transform the carbon in gas-phase CO₂ into dissolved or solid-phase carbon, and physical approaches rely on barriers that confine gas-phase CO₂ in a location isolated from the atmosphere. Among these three approaches, physical storage of CO₂ in geologic reservoirs is increasingly becoming the focus

Table 1 Characterization of carbon storage by both location and mechanism of storage

Mechanism	Location		
	Land surface	Ocean	Geosphere
Biological	Enhancing carbon content of soils	Fertilization to accelerate biological pump	Use of anaerobic biological reactions to reduce CO ₂ to CH ₄ in strongly reducing environments
	Afforestation		
Chemical	Industrial production of stable carbonates	Acceleration of CaCO ₃ dissolution	Subsurface dissolution of carbonates or silicates by brines acidified by injected CO ₂
		Addition of alkalinity	
Physical		Formation of 'lakes' of liquid CO ₂	Physical confinement of gas phase CO ₂ in underground formations

of carbon storage research, and some regulatory and management regimes have incorporated incentives for enhancing biological carbon storage. Although there has been some research focused on chemical (or geochemical) approaches to carbon storage, these approaches have received less attention than either physical or biological approaches, and the limited funding previously available for research on geochemical approaches has decreased in recent years. While both physical and biological approaches to carbon storage provide more feasible near-term (within the next decade) options for carbon storage than geochemical approaches, sustained research on geochemical approaches to carbon storage has potential for high societal-value over a longer time-frame.

Major current limitations of geochemical approaches to carbon management (reviewed in more detail below) include negative environmental impacts resulting from large scale material requirements and high costs resulting from the difficulty of accelerating the slow kinetics of geochemical reactions (Gerdemann et al. 2007). Despite these critical limitations, geochemical approaches have unique potential to contribute to CO₂ reductions in ways that neither physical nor biological carbon storage can by allowing for the direct removal of CO₂ from the atmosphere with minimal requirements for integrating with existing infrastructure. In addition geochemical approaches to carbon management also have potential to bypass several crucial limitations associated with both physical and biological approaches to carbon storage; these include, for physical storage, leakage from underground reservoirs and uneven distribution of storage reservoirs, and, for biological storage, short decade-scale timeframe and ecologically precarious monoculture plantations.

This paper has two objectives: (1) to review the potential, current limitations, and risks of geochemical approaches to carbon management in a way that compliments previous reviews of this topic (Lackner 2002; NRC 2003) by highlighting comparative potential benefits and barriers of different approaches, and (2) to provide a novel framework within which to compare various options to assist in prioritizing future research related to carbon storage.

Given the lack of discernable progress in slowing the growth of CO₂ emissions (Canadell et al. 2007; Raupach et al. 2007), there have been calls for increased research on novel approaches to carbon management including geoengineering (Cicerone 2006) and on advancing strategies that could directly remove CO₂ from the atmosphere (Broecker 2007). A lively dialogue and debate about the role and responsibility of scientists in considering and researching geoengineering approaches to confronting climate change resulted from the recent publication of Crutzen's speculative paper on the possibility of injecting sulfur aerosols into the stratosphere to offset the earth's warming with cooling derived from engineered enhanced albedo from the sulfur particles (Crutzen 2006). One of the main objections to this and other geoengineering ideas that seek to alter the earth's radiative balance is that they attempt to treat the symptoms rather than the cause (Kiehl 2006), and thus ignore and may even exacerbate other environmental problems caused by high atmospheric CO₂ concentrations (Bengtsson 2006; MacCracken 2006). Given these important concerns and objections, as well as recent calls for combined mitigation and geoengineering approaches (Wigley 2006), increased attention to and consideration of other novel engineered approaches that can directly reduce atmospheric CO₂ concentrations is appropriate; the geochemical approaches to carbon storage reviewed below fall into this category.

A need for more serious consideration of geochemical approaches has been recognized by Lackner (Lackner 2002) and also in a National Research Council meeting organized by the Committee on Novel Approaches to the Management of Greenhouse Gases from Energy Systems held in February 2003 (NRC 2003). This paper incorporates these contributions and further develops the current state of understanding of the feasibility of these proposed chemical approaches, providing a systematic examination of how these approaches compare to other mitigation strategies including the more advanced carbon capture and storage methods and radical geoengineering strategies.

In addition to providing a structured review of the technical status of these geochemical approaches, we provide a simple framework for prioritizing future research in this area. Systematic research prioritization is important given (1) the minimal amount of research funding made available for geochemical carbon storage, particularly in light of the growing focus on advancing geologic carbon storage in underground reservoirs, (2) the heterogeneity of different chemical approaches with potential to justify further research, and (3) the fact that many of these approaches have a low probability of near-term practical implementation but potential as longer-term methods of carbon management. Although these approaches appear unlikely to contribute substantially to the imminent need for carbon management strategies that can reduce atmospheric concentrations within the next few decades, sustaining research in these alternative approaches is prudent as we continue upon a dangerous and uncertain path of increasing atmospheric CO₂ concentrations. Despite the currently unresolved technical difficulties and the major economic and implementation challenges associated with most of these geochemical approaches to carbon management, continued attention to and research on the geochemistry associated with carbon management may prove useful within a few decades when human society could be desperate for alternative options to reduce atmospheric CO₂ concentrations.

This discussion is limited to chemical approaches that could plausibly exceed a gigaton (Gt) per year reduction of atmospheric CO₂ concentrations, so chemical approaches with potential for smaller scale reductions, including the utilization of CO₂ in the production of chemical products (Aresta 2003) or other industrial processes including cement manufacture and steel production that may provide potential niche opportunities for cost-effective chemical storage of CO₂ (Stolaroff et al. 2005), are not included.

2 Background

2.1 History of chemical approaches to carbon storage

Initial proposals for disposing of anthropogenic CO₂ somewhere other than the atmosphere focused on physical approaches, such as injecting CO₂ either underground or into the deep oceans (Marchetti 1977). More than a decade later Seifritz (Seifritz 1990) proposed the first storage scheme that relied on chemical conversion of the CO₂ gas into a carbonate solid, followed by the first detailed exploration of this approach (Lackner et al. 1995). Subsequent work has elaborated on this idea of enhancing the formation of carbonate solids, often referred to as mineral

carbonation (IEA 1999; Lackner et al. 1997; Nilson and Hundley 1999), as well as other chemical approaches that rely on the chemical conversion of the carbon in CO₂ gas to dissolved carbon in seawater, primarily in the form of the bicarbonate ion, HCO₃⁻ (Caldeira and Rau 2000; Rau and Caldeira 1999). Each of these ideas involves the reaction of carbonic acid (the weak acid formed by CO₂) with basic minerals from the earth's crust, so these ideas are all related to natural mineral weathering cycles.

Before presenting the details of several different geochemical approaches to carbon management, we first briefly review the natural mechanisms of the carbon cycle that geochemical carbon management options have been proposed to accelerate.

2.2 Geochemical carbon cycling

The carbon cycle is complex and involves biological, geochemical and physical processes with a broad range of timescales. In considering the potential of geochemical carbon management, four different time scales can be identified corresponding to different mechanisms for carbon cycling: (1) on a time scale of years, atmospheric carbon is transferred to the surface ocean and/or is exchanged with carbon in biological material through photosynthesis, respiration, and microbial decay. On this same time-scale both the biological pump and the solubility pump transport carbon from the euphotic zone to the ocean's interior, (2) on a century-long time scale, dissolved carbon in the surface ocean is mixed with deeper ocean water, (3) on a time scale of tens of thousands of years the dissolved CO₂ in the deep ocean is partially neutralized by the dissolution of carbonates at depth increasing the ocean's capacity to absorb more CO₂ from the atmosphere, and finally, (4) on a million-year time scale carbon is exchanged between the atmosphere and the lithosphere as silicate mineral weathering provides the cations that neutralize CO₂ as buried carbonate sediments.

Of these four carbon cycle mechanisms with different time scales, it is the two longest time-scale mechanisms that are most relevant to geochemical carbon management. The carbon management approaches to be reviewed in this paper (Section 3) aim to counter the anthropogenic flux of carbon to the atmosphere resulting from fossil fuel burning by engineering opposing fluxes that return carbon to less geochemically active forms. These schemes may be regarded as attempts to artificially accelerate to decadal timescales the mechanisms associated with the two longest time scales described above. Before detailing the specific approaches, we briefly explain in more detail the natural mechanisms associated with two longest time scales to provide background and context for understanding the proposed approaches.

2.2.1 The tens-of-thousand-year time scale

On the ten-thousand-year time scale, shifts in the carbon chemistry of the oceans determine the oceanic uptake of atmospheric CO₂ by influencing the dissolution and precipitation of carbonates. The total dissolved inorganic carbon stored in the oceans is distributed among three species, dissolved CO₂ (CO₂ and H₂CO₃), bicarbonate (HCO₃⁻), and carbonate (CO₃²⁻) linked by the following set of reactions:





The distribution of these dissolved species, particularly the concentration of the carbonate ion (CO_3^{2-}), influences both precipitation and dissolution of carbonate minerals.

Of these three species, most inorganic carbon in ocean waters is present in the form of carbonate or bicarbonate, the ocean's dominant anions, and their total charge is effectively equal to the supply of base cations, called the alkalinity, as shown the following equation:

$$2 \times [\text{CO}_3^{2-}] + [\text{HCO}_3^-] \cong [\text{A}] \quad (4)$$

Due to this balance between alkalinity and dissolved inorganic carbon, processes that increase the alkalinity of the surface oceans accelerate the uptake of atmospheric CO_2 (Feely et al. 2004). Although the total average alkalinity of the oceans has remained constant over recent geologic time, regional differences in alkalinity, for example in coastal regions where water with higher alkalinity enters the oceans, are associated with higher oceanic uptake of atmospheric CO_2 (Sabine et al. 2004).

Due to the relatively constant total alkalinity of the world's oceans, rising atmospheric CO_2 is altering both the distribution of marine inorganic carbon and the pH of the oceans (Kleypas et al. 2006; Pelejero et al. 2005). As dissolved CO_2 in the ocean increases surface seawater becomes more acidic and CO_2 combines with carbonate ions represented in this net chemical reaction:



Increasing atmospheric CO_2 concentrations is altering the carbon chemistry of the oceans by increasing bicarbonate ion concentrations, reducing carbonate ion concentrations, reducing the saturation state of CaCO_3 , and, therefore, increasing CaCO_3 dissolution.

2.2.2 The million-year time scale

Interactions between atmospheric CO_2 and silicate mineral weathering and subsequent carbonate formation dominate the longest time scale, the million-year time scale (Fig. 1). The following set of reactions traces the carbon from an atmospheric CO_2 molecule during the weathering of the Ca-silicate mineral, enstatite (CaSiO_3 ; reaction 6) to the subsequent formation of the Ca-carbonate mineral, calcite (CaCO_3 ; reaction 7). The net reaction (reaction 8) demonstrates that for every mole of Ca-silicate mineral weathered one mole of carbon is removed from the atmosphere:



The bicarbonate (HCO_3^-) released to solution during the weathering reaction 6 is transferred to rivers and eventually to the ocean where half of the carbon is removed

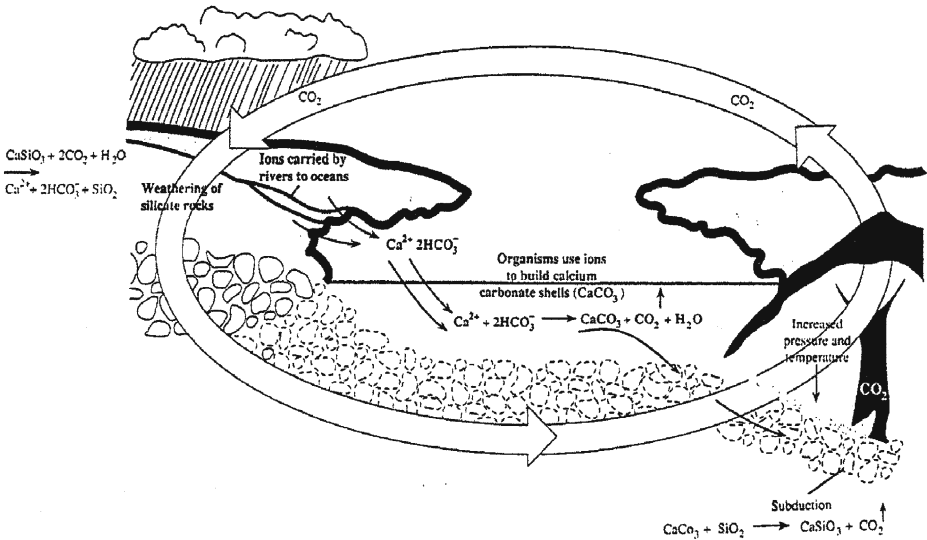


Fig. 1 The longest time scale processes in the carbon cycle involving interactions between the atmosphere and the lithosphere (reprinted from Biogeochemistry by W.H. Schlesinger 1997 with permission from Elsevier)

from the oceans as Ca (or Mg to a lesser degree) carbonate minerals (reaction 7; Berner et al. 1983), while the other half is released as CO₂ to the surface oceans. Marine carbonates are formed primarily by biological processes, and when these carbonaceous organisms die, some fraction of the biogenic carbonate is sedimented, and ultimately undergoes metamorphism under high pressures and temperatures to form silicates and CO₂ again. This CO₂ is eventually released back into the atmosphere in seismically active areas like Mammoth Mountain, California where CO₂ gas is escaping from a natural underground reservoir (Stephens and Hering 2002). It is through the coupling of the two processes represented in reactions 6 and 7 that mineral weathering is considered the primary sink for atmospheric CO₂ over geological time scales (Fig. 1).

3 Review of geochemical approaches to carbon management

This section reviews details of proposals to engineer geochemical carbon storage. First, various methods of forming carbonate minerals are discussed, followed by a review of proposals to manipulate the ocean alkalinity to increase the oceanic store of dissolved carbon. Finally we review approaches that take advantage of these geochemical reactions in situ, in locations with favorable natural mineralogy. All of these geochemical approaches involve liberating cations to neutralize carbonic acid; specifically many involve accelerating the weathering of Mg or Ca silicate minerals so that the cations are available either to form carbonates and/or to increase the alkalinity of the oceans.

In discussions of enhancing silicate mineral weathering to facilitate carbon storage, Mg-silicate minerals are often targeted for two critical reasons: (1) Mg-silicate minerals are found in more concentrated and larger deposits than are Ca-silicate

minerals (Goff et al. 2000; Yegulalp et al. 2001) so they are more accessible for large scale mining, and (2) Mg-silicates are more reactive than Ca-silicates (Herzog 2002; Yegulalp et al. 2001). Despite the apparent interchangeability of Mg and Ca silicates for some of these proposed engineered processes, it is important to recognize the distinctions between the ultimate fate of weathered Ca and Mg. Most significantly, in the current carbon cycle Mg is not incorporated into carbonate solids to the same degree as Ca. While biogenic carbonates do contain Mg, the primary sink for marine Mg is ionic exchange rather than carbonate formation (Schlesinger 1991). At hydrothermal vents deep on the ocean floor, Mg is removed from seawater into the crustal rock, while both major (Ca, Ba) and transition metals (including Fe, Mn, Zn, and Cu) are leached from the rock into the sea water (Chester 1990). Moreover, in marine environments Mg^{2+} kinetically inhibits the formation of non-biogenic calcite (Deleuze and Brantley 1997), so Mg plays a role in minimizing carbonate precipitation in the surface oceans that are supersaturated with respect to calcium carbonate; Mg^{2+} binds with carbonate ions reducing the carbonate free ion concentration and the likelihood of carbonate precipitation (Mucci and Morse 1983). Under current conditions, the increase in alkalinity associated with an increase in oceanic Mg^{2+} drives carbonate precipitation in spite of the Mg^{2+} inhibition effect. Given these differences between Ca and Mg, there are critical unanswered questions about potential impacts of altering the Mg fluxes.

3.1 Making solid carbonate minerals

Carbonation, the formation of solid carbonate minerals, is appealing because in the presence of suitable bases, carbonates are the lowest energy (or more precisely, lowest free energy of formation) state for carbon, lower than carbon which is fully oxidized as CO_2 . The formation of carbonates from CO_2 , therefore, is exothermic. The stability of carbonates means that carbon within them can be immobilized for millennia.

Industrial carbonation, engineered facilities designed to convert carbon in CO_2 into solid carbonates to dispose at or near the earth's surface, would mimic a natural process; some of the carbon released from the lithosphere by burning fossil fuels will, over millennia, naturally be converted to carbonates and returned to the lithosphere by weathering (Section 2.2.2). Engineering carbonation may therefore be described as the anthropogenic return of carbon to the lithosphere (Dunsmore 1992), or the acceleration of a natural carbon flux in the opposite direction of the carbon flux being accelerated by the burning of fossil-fuels.

Ca and Mg are the most common elements to form stable carbonates, so attention has focused on the potential formation of Ca and Mg carbonates (Goldberg et al. 2001; Herzog 2002; Lackner 2002). Fe is another common element that forms stable carbonates, and although the potential of forming Fe carbonates has been recognized (O'Connor et al. 2004b), the engineered acceleration of iron carbonate formation has not yet been extensively explored (NRC 2003).

In principle there are three potential sources of cations required for carbonation: the oceans, ultramafic igneous rocks, and cation-rich subsurface brines. In practice extracting cations from the oceans to make carbonates on land does not make sense because the net effect would be to increase atmospheric CO_2 because the removal of

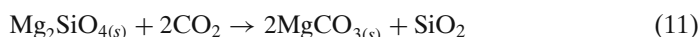
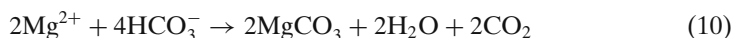
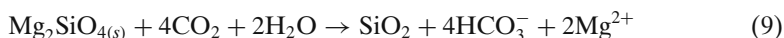
ocean alkalinity would decrease the oceans store of dissolved carbon. Both deposits of ultramafic igneous rocks (Ca and Mg containing silicate minerals) and subsurface brines rich in Ca and Mg are, however, potentially viable sources of cations for carbonation.

3.1.1 Carbonation: silicate minerals as cation sources

Ca and Mg silicate minerals are abundant; calcium and magnesium each make up about 2% (in molar percent abundance) of the earth's continental crust. Deposits of Ca and Mg silicates greatly exceed quantities of fossil fuels so enhanced weathering of these minerals could, theoretically, compensate for all the CO₂ entering the atmosphere from the burning of fossil fuels. The kinetics of the chemical reactions critical to carbonation, particularly the weathering of silica minerals to provide the source of cations, is extremely slow. Research in this area, therefore, has focused on the acceleration of these reactions at elevated temperatures and pressures with various pretreatments.

The reaction between gas-phase CO₂ and Mg- or Ca-silicate minerals is slow even at elevated temperatures and pressures (Jia and Anthony 2003; Lackner et al. 1997), so studies on accelerating the kinetics have focused on aqueous phase reactions. One approach to accelerating the direct solid-gas reaction is to react CO₂ with Mg oxides or hydroxides rather than directly with the silicate minerals (Goff and Lackner 1998; Lackner et al. 1997), relying on a preceding step to extract the oxides or hydroxides from the silicate minerals-using hydrochloric acid, an adapted aqueous process developed for magnesium extraction during World War II (Houston and Kerr 1945).

Research on accelerating the kinetics of aqueous silicate mineral weathering and subsequent carbonation has focused more intently on Mg-silicates rather than Ca-silicates because they are more easily accessible and found in more concentrated deposits. Olivine (Mg₂SiO₄) and serpentine [Mg₃Si₂O₅(OH)₄] are the most abundant Mg-silicates; although serpentine is more abundant and accessible than olivine, olivine has a higher molar concentration of Mg than serpentine and reacts more rapidly, so olivine is the mineral studied most extensively. The chemical reactions for aqueous phase conversion of olivine to magnesite (MgCO₃) are:



In this and similar reactions the kinetics are typically limited by dissolution of the silicate to produce aqueous metal ions (reaction 9) rather than by the subsequent reaction of the metal ions with bicarbonate to produce carbonates (reaction 10). During simultaneous dissolution and carbonation, interactions among the species involved in both reactions can alter the overall rate of carbonation, i.e. the formation of the carbonate phase can coat the silicate phase hindering dissolution.

To accelerate these naturally slow reactions to time scales that might be manipulated to reduce atmospheric CO₂ concentrations, various different mechanical and thermal pretreatments, in addition to high temperature and pressure reaction

conditions have been examined (Albany Research Center 2003; Gerdemann et al. 2003, 2007; O'Connor et al. 2004b, c). Activation of the minerals has been achieved by both thermal and mechanical pretreatments. An increase in reactive surface area, by various different methods of grinding and by heating to remove chemically-bound water, is thought to be the primary mechanism by which both of these pretreatments methods increase reaction rates (O'Connor et al. 2002, 2004b). These experiments, which have had more success accelerating the carbonation of olivine than the more abundant serpentine, demonstrate a set of complex tradeoffs among the degree of pretreatment required, the amount of ore required, and the cost of the accelerated process. For example, the quantity of ore required can be decreased by 75% with pretreatment to activate the mineral surface; the pretreatment could double the processing cost per ton of ore while cutting the total cost of carbonation in half (O'Connor et al. 2004b). These studies demonstrate that increasing the temperature from 25°C to 100°C can increase the carbonation reaction rates of olivine by ten times (less for serpentine), while an increase in pressure from 25 to 150 atmospheres can increase the olivine carbonation reactions rates by four to five times (O'Connor et al. 2004b). These studies quantified the simultaneous dissolution of the silicate minerals and the subsequent precipitation of the carbonate mineral, so due to interactions between these reactions the results for dissolution alone could be different. The applicability of these results is limited in considerations of pretreatment options to enhance Mg silicate dissolution rates in the oceans, where simultaneous carbonation is not occurring.

3.1.2 Carbonation: brines as cation sources

The idea of using brines, groundwater rich in accumulated cations, as cheap, easily accessible sources of Ca and Mg, for input into an industrial process to make carbonates has been given some consideration (Dunsmore 1992). Within the context of long-term biogeochemical cycling, dissolved Ca and Mg cations in brines are simply products of already weathered material so isolating these cations for carbonation requires considerably less effort than extracting the cations from silicate minerals. Because this approach bypasses the silicate weathering step, it avoids the slow kinetics of silicate dissolution and the associated problem of simultaneous carbonate formation which coats the silicate surface thus hindering further silicate dissolution.

This idea was developed with the suggestion that calcium-rich, saline brines could be pumped from the subsurface to a chemical plant located near power plants or oil refineries, and calcium carbonate could be precipitated with the CO₂ from the power plant and the calcium chloride solution of the salty brine (Dunsmore 1992). This process could be viewed as the conversion of one acid, carbonic acid, into another acid, hydrochloric acid. With each mole of carbonate precipitated two moles of hydrochloric acid would be formed; within this context, the challenge becomes how to effectively dispose of large amounts of hydrochloric acid (the quantities would be so large that usage in secondary industries would be negligible). Waste brine and spent acid could be injected back to the subsurface while surplus carbonates could be disposed of in coal pits (Dunsmore 1992). Assuming it was injected into igneous rocks the hydrochloric acid would eventually dissolve sub-surface bases making salts, so the whole process may be viewed as a two-step method of solution mining base minerals. Saline brines are often located in the same sedimentary basins as oil and gas

reserves and power plants so transportation might be manageable. Large-scale use of brines as cation sources is likely limited by the availability of aquifers with sufficient permeability to enable large scale production with acceptably-low requirements for brine pumping energy.

3.1.3 Barriers to industrial carbonation

The most important barrier to using industrial mineral carbonation is the slow kinetics associated with extracting the required base cations, reactions that occur very slowly in nature (IEA 2002). Elevated temperatures and pressures are the most obvious means to accelerate the reactions, but high-pressure reaction vessels are expensive and a successful process will only be possible if very high reaction rates can be achieved so that the high capital cost of the pressure vessels can be offset by high material throughputs. Likewise, while heat can accelerate the reactions the thermal energy inputs will need to be small (per mole of carbon) in comparison to the energy released by combustion of the fossil fuels that generated the carbon. Although there is no fundamental physical barrier, results to date do not allow design of industrial processes that would be cost competitive with other means of managing carbon. Estimates of the cost of an engineered olivine carbonation process have exceeded \$250 per ton of carbon¹ (O'Connor et al. 2004b), and more recent estimates have brought that down to just under \$200 per ton of carbon (Gerdemann et al. 2007). These estimates are roughly an order of magnitude larger than the costs of geologic disposal by direct injection of CO₂ into the subsurface

Beyond the challenges of kinetics and cost, the other critical challenge is the massive volume of mineral material required to supply a sufficient quantity of bases and the associated environmental and economic costs of mining those minerals and disposing of the carbonates. Carbonating all the CO₂ from a 1 GW coal-fired power plant would require ~55 kt of mineral per day (Gerdemann et al. 2007; O'Connor et al. 2004a), five to ten times more than the mass of coal consumed by the plant. For a given quantity of electricity, it would be necessary to extract, process and dispose of a mass of silicates and carbonates that are several times larger than the mass of coal. Offsetting this unfavorable mass ratio is the fact that coal is often found in relatively narrow seams which require displacement of a considerably larger mass of overburden than the mass of coal, whereas magnesium silicates are, in some locations, found in very large deposits which would require displacement of a relatively small amount of overburden per unit silicate. It is therefore plausible that, in favorable circumstances, the total mass of materials (including overburden) that would need to be moved for the carbonation process would be smaller than that required for the coal. The same might be true of the amount of surface area disturbed by mining. On the other hand the environmental impacts of such 'hard rock' mining will likely be larger than the impacts of coal mining per unit of material.

An additional challenge will be posed by the difficulty of finding places where coal deposits and magnesium silicates are collocated. In North America, for example, ultramafic deposits are found along both coasts rather than in the interior where most coal deposits and coal-fired power plants are located. Systematic analyses of

¹This figure is the cost per ton avoided, a value larger than the cost per ton carbonated because it accounts for the carbon emissions arising from energy used in the process.

the availability of co-located deposits of coal and ultramafic rocks and of the costs and environmental impacts of the mining activities required for large scale industrial carbonation are needed to judge the extent to which these factors might constrain the use of industrial carbonation.

Despite the seemingly insurmountable challenges of mineral carbonation, it has been suggested that some fine-sized industrial byproducts including asbestos-mining tailings, cement-kiln dust, and coal fly ash could be used for industrial carbonation, drastically reducing the cost because the size reduction step would be eliminated (Gerdemann et al. 2007). More research is needed to define the quantities of these industrial byproducts to understand the scale of this potential niche opportunity for industrial carbonation. If the costs could be reduced, industrial carbonation could be valuable in some regions of the world where there are no underground carbon storage reservoirs.

3.2 Increasing the store of dissolved carbon in the oceans by increasing alkalinity

As described in Section 2.2.1, increasing atmospheric CO₂ has resulted in an increase in oceanic uptake of CO₂. Due to the relatively constant ocean alkalinity during this period of atmospheric CO₂ increase, surface bicarbonate ion concentrations have increased while carbonate ion concentrations have decreased resulting in a reduction of surface-ocean pH. If the alkalinity of the oceans was increased, the ocean's capacity to store dissolved inorganic carbon would increase and the associated increase in acidity would be reduced. Increasing the ocean's alkalinity, therefore, has the potential to simultaneously reduce atmospheric CO₂ by increasing the ocean's store of dissolved carbon while also reducing the ocean acidification that is occurring.

Two distinct strategies of increasing the store of dissolved carbon in the oceans by increasing the alkalinity of the oceans have evolved: (1) accelerating CaCO₃ mineral dissolution and adding the dissolution products to the surface oceans (Caldeira and Rau 2000; Kheshgi 1995; Rau and Caldeira 1999), a set of approaches that manipulates the ten-thousand-year time scale marine carbon chemistry process and (2) adding alkalinity directly to the oceans without adding additional carbon either from non-carbonate sources or from carbonate dissociation with CO₂ capture (Kheshgi 1995; Lackner 2002). This second strategy is an attempt to accelerate both the million-year weathering time scale by enhancing the release of alkalinity from minerals, and the ten-thousand-year carbonate chemistry processes, by mitigating against the increasing acidity of the surface oceans and its impact on the distribution of inorganic dissolved carbon.

The first strategy, adding the dissolution products of either CaCO₃ or MgCO₃ to the oceans, would contribute two units of alkalinity for each unit of carbon, allowing a net increase in the ocean's uptake of atmospheric CO₂. Although this approach has more favorable kinetics than silicate mineral dissolution, which is associated with the second strategy, to achieve the same amount of additional oceanic carbon storage twice as many moles of carbonate material as silicate material would be required.

3.2.1 Accelerated calcium carbonate dissolution

Rau and Caldeira (1999) have proposed a scheme in which CaCO₃ is dissolved in a carbonic acid solution produced by contact with flue gas from power plants

containing high partial pressure CO_2 (flue gas from coal-fired power plants are generally 13–15% CO_2). The products of this reaction (reaction 6 in reverse), the dissolved CaCO_3 along with the dissolved carbon, would be discharged to the ocean as a solution of bicarbonate and Ca^{2+} ions. This proposal eliminates the requirement for separating and capturing CO_2 .

Because the bicarbonate solution is necessarily dilute, very large quantities of water are required for CaCO_3 dissolution and subsequent transport of bicarbonate solution into the oceans. The energy costs associated with pumping the water and with the flue gas to water contactors suggest that the process will probably be restricted to power plants located near the ocean. Roughly 12% of US CO_2 emissions from electricity generation comes from coastal power plants, and most of these coastal power plants are within several hundred kilometers of major carbonate deposits (Rau et al. 2004).

The effective dispersion of the products of the reaction in the CaCO_3 supersaturated surface waters of the oceans is another potential constraint. The ocean injection scheme would have to be designed to prevent re-precipitation of calcium carbonate and the degassing of CO_2 as the solution is introduced to the already supersaturated ocean water. This might be achieved by injecting the solution at depth rather than at the surface or diluting the outflow solution with seawater and equilibrating this diluted solution with the atmosphere before dispersing in the surface ocean, but the engineering and costs of managing dissolution have not been evaluated (Caldeira and Rau 2000). Another potential constraint would include ensuring that the circulation of the receiving ocean allowed for rapid exchange with the total volume of water.

Potential impacts to marine ecosystems of increasing the bicarbonate and Ca^{2+} concentrations are varied. Firstly, the additional alkalinity will increase the buffering capacity of the surface oceans reducing the current trend of ocean acidification. In addition, studies have shown that enrichment of seawater with Ca^{2+} and bicarbonate enhances the calcification and growth rate of marine corals (Langdon et al. 2000). Given the already high concentrations of both of these dissolved constituents in seawater, adding them to the surface oceans is not likely to have extensive negative impacts. It is possible, however, that other constituents would need to be removed from the flue gas prior to contacting seawater to avoid negative environmental impacts. The effluent oxygen concentration could also be reduced by partial equilibration with the flue gas (Rau et al. 2004).

3.2.2 Adding alkalinity without additional carbon

Another way to increase the amount of dissolved carbon stored in the oceans is to directly add alkalinity in the form of base cations to the surface oceans, an idea first proposed by Kheshgi (1995), and further developed by Lackner (2002). If a cost-effective means of adding alkalinity were to be identified, this technique has potential to remove large quantities of CO_2 from the atmosphere while simultaneously reducing the anthropogenic perturbation of oceanic pH. If the base cations (alkalinity) are derived from silicate minerals then two approaches are possible: (1) the minerals could be ground up, dispersed in the ocean, and allowed to dissolve or (2) an industrial process could be designed that mimics the weathering process by disassociating silicate minerals into silicates and metal ions or oxides to be added to the ocean.

The base cations could also be derived from carbonates if the carbonate is disassociated and the carbon is captured and separately stored (Kheshgi 1995). CaCO_3 minerals could be disassociated by an industrial process (calcined) to produce CaO and CO_2 ; the CaO (lime) might then be added to the ocean where it will increase alkalinity eventually removing almost twice as much CO_2 from the atmosphere as was emitted in the calcination step (Kheshgi 1995). On long time-scales the net effect could be equivalent to accelerating the dissolution of CaCO_3 .

Any base cations could be added to alter the alkalinity but Ca and Mg are the most abundant. Of these two, Mg is particularly interesting for two reasons: (1) Large quantities of Mg are available as Mg -silicates which do not add carbon when dissolved or disassociated, whereas Ca is primarily available as CaCO_3 for which the associated CO_2 must be managed; (2) the surface oceans are generally supersaturated with respect to Ca so additions of Ca may result in precipitation of CaCO_3 which removes only one mole of C for each Ca whereas since Mg -carbonates are not precipitated in the modern ocean, a mole of Mg added to the surface ocean would contribute two units of alkalinity that would stay in solution with potential to buffer close to two moles of bicarbonate.

Silicate mineral dissolution is extremely slow particularly at the conditions of temperature and pressure of ocean surface water. Pretreating the mineral fragments to increase their solubility in seawater could increase the dissolution. One approach would be to simply grind up minerals and disperse them to dissolve in the surface oceans. Within this approach, calcium carbonate would not dissolve due to its supersaturation, magnesium carbonates are close to saturation and have slow dissolution kinetics, while sodium carbonates dissolve rapidly. Based upon published dissolution rates derived from laboratory experiments (Pokrovsky and Schott 2000) it would take more than 8,000 years for a micron size particle of olivine to dissolve in the surface ocean.

In addition to the major challenges associated with preparing minerals for dissolution, some mechanism, presumably dispersal from ships, would be required to distribute the minerals. The rate of dissolution and the impacts of high local concentrations of dissolved minerals would determine the requirements for dispersal. If the solid being dispersed dissolves slowly, the distribution pattern may not be as critical because the material will have time to move with the ocean currents, but if the dissolution is rapid the material will have to be more evenly and widely distributed in order to maximize the impact of the additional alkalinity while minimizing side effects.

The potential success and impact of adding alkalinity to the oceans as a means of reducing atmospheric CO_2 concentrations would be dependent on the interaction of three very different time scales, (1) the anthropogenic CO_2 emissions pulse, (2) oceanic mixing, and (3) the dissolution of the solid that delivers the metal ions. Ocean circulation models could help to determine effective distribution strategies. It might be possible, for example, to disperse materials that dissolved at mid-ocean depths in upwelling regions. The natural ocean circulation pattern could then carry the alkalinity up to the surface in a distributed way, perhaps reducing the requirements for even dispersal. Incorporating ocean circulation into distribution strategies could reduce the implementation challenges of using ships to evenly distribute alkalinity throughout the surface oceans. Dispersal methods that rely on ocean mixing to

spread the alkalinity pulse will be slower and will, therefore, require a longer time-frame to impact either atmospheric CO₂ concentrations or ocean acidification.

While no current technologies allow the addition of alkalinity to the oceans at acceptable cost and sufficiently low environmental risk, the availability of materials and thermodynamic barriers suggest that such a technology could be plausible. Moreover, there is some reason to believe that extensions of current research might address the most obvious barriers standing in the way of acceptable technology for alkalinity addition.

To accelerate the extremely slow dissolution of silicate minerals in ocean water and to reduce the amount of material required, a preceding extraction technique could be used to separate Mg and Ca oxides and hydroxides from silicate minerals (Goff and Lackner 1998). The challenge, however, is balancing the additional energy cost of breaking down the silicate minerals into oxides.

Consider, for example, the addition of Mg derived from Mg-silicates into surface ocean waters. The challenge might be divided into four phases: (1) mining, (2) processing, (3) transport and (4) ocean dispersal. Known resources of the appropriate minerals combined with current commercial technologies for large-scale mining and transport suggest that, assuming that high dissolution efficiencies could be achieved, the mining and transport phases are possible at costs of well under \$100 per ton of carbon. The crux of the challenge, therefore, is defining and developing a system of processing and ocean dispersal that has acceptable financial and energy costs as well as a low CO₂ profile.

As a reference case, consider a process using olivine with no processing other than pulverization. If particles were ground to a 50 μm size, for example, sink rates would be approximately 10⁻³ m/s and particles would take a few months to sink through the full ocean depth. The energy required to grind particles to 50-μm size is on the order of 10 kJ/mol-C, a small number compared to the carbon content of readily available energy sources. Combustion of natural gas, for example, yields about 700 kJ/mol-C, so if the grinding process were fueled by gas, the carbon emissions from grinding would be only a few percent of the carbon captured by alkalinity addition.

At the pH of seawater, the kinetics of olivine dissolution are so slow that even 50 μm particles would experience only partial dissolution over the time it would take to sink through the ocean depth (Hanchen et al. 2006). Alkalinity addition would be completely uneconomic with such a low dissolution efficiency.

The process could be improved either by pretreatment that increases the reaction rate or by finer pulverization. As particle size is decreased, the energy required for grinding increases and the sink rate decreases, decreasing the required reaction rates and therefore decreasing the energy required for the thermal pretreating necessary to achieve the desired reaction rate. Using current grinding technologies, finer pulverization alone will not succeed because the energy and financial costs of grinding increase much faster than the surface-area-to-volume ratio. Research on pretreatment would build on prior research directed at accelerating mineral carbonation in an industrial setting in which a CO₂ stream would be reacted with a magnesium silicates. This work has focused on combinations of fine grinding and heat treatment to accelerate the reaction of magnesium silicates with CO₂.

Recent mineral carbonation studies have demonstrated that reaction rates for 75 micron particles of olivine and serpentine can be accelerated using heat treatment

and elevated reaction temperatures (Gerdemann et al. 2007; O'Connor et al. 2002, 2004c). Although the required energy inputs for heat pretreatment are still several times too large to achieve industrial carbonation at reasonable costs, it seems promising to pursue similar methods to explore the possibility of reduced energy inputs while achieving much lower reaction rates needed for dissolution of small particles dispersed in the ocean. The regime to be explored for pretreatment for ocean dissolution is very different from that examined by current mineral carbonation studies which are aiming to achieve reaction times on the order of hours. Moreover, the industrial mineral carbonation studies must address simultaneous dissolution and carbonation which is a more difficult process than simple oceanic dissolution because the formation of carbonates forms coatings that hinder further dissolution.

In summary, there is ample room to improve the economics of alkalinity addition by building on current research directed at industrial mineral carbonation to optimize the trade off between use of pretreatment and finer pulverization.

3.2.3 Barriers to increasing ocean alkalinity

The manipulation of ocean chemistry is controversial as the implications and disruptions to marine systems are complex and potentially severe (Buesseler et al. 2008; Chisholm et al. 2001), and strong public opposition demonstrated in other ocean manipulation projects (Figueiredo et al. 2002; Sagarin et al. 2007) is likely. Acknowledging these critical and fundamental environmental and social challenges, this section reviews a few technical barriers to increasing ocean alkalinity.

Among the many challenges associated with increasing ocean alkalinity is designing an effective dispersion mechanism that maintains ions in solution at the point of injection; sudden increases in the local concentration of base cations, carbonate, or hydrogen ion (pH) could result in mineral precipitation, particularly carbonate formation, which would remove alkalinity from the water. The addition of rapidly dissolving sodium carbonates, for example, would cause a spike in the carbonate ion concentration, which in the already supersaturated surface waters, could lead to significant carbonate formation. With carbonate formation the intended alkalinity increase would not occur, although some enhanced carbon storage capacity could still be achieved (as discussed in Section 3.2.2). Given the saturation conditions of the surface ocean, alkalinity addition in the form of Mg rather than Ca could be more effective. These challenges of maintaining ions in solution at the point of injection could be minimized with well-designed injection and dispersion methods, but no systematic analysis has yet been done on alkalinity dispersion options.

The environmental impacts of increasing surface alkalinity are uncertain near the point of alkalinity addition; the sensitivity of marine organisms to pH changes might require the engineering of systems that avoid sudden large perturbations in pH. In addition to pH changes, another local impact associated with adding alkalinity would be the increase in particulate solid material raining down through the ocean that would affect seawater turbidity and perhaps organic carbon export.

On a larger scale, the addition of base cations might be expected to provide an environmental benefit since it would tend to increase ocean pH counteracting the decline in pH due to atmospheric CO₂ and, therefore, contribute to a shift in the oceanic acidity back toward pre-industrial pH. It is not clear, however, that all of the environmental impacts of the current reductions in pH could be mitigated by a

corresponding increase in pH. Magnesium has been shown to inhibit the formation of CaCO_3 by organisms, so it is possible that an increase in oceanic magnesium would further reduce calcification rates.

3.3 In situ geochemistry

Facilitating these same geochemical reactions in situ, i.e. in locations where the minerals exist naturally, defines another set of geochemical carbon management approaches that involve identifying locations for direct injection that have conditions favoring the chemical reactions that immobilize CO_2 . Enhanced carbonate formation in calcium and magnesium silicate rich aquifers and carbonate dissolution in submarine carbonate deposits are both potentially promising approaches that harness the combined effectiveness of physical trapping of the CO_2 gas and the geochemical reactions that transform the CO_2 gas into dissolved or solid carbon.

Expanding upon Dunsmore's idea of using cation-rich evaporitic brines, a recent focus has been on injecting CO_2 underground into cation-rich brines where some of the CO_2 will dissolve in the brine and some will form carbonates (Matter 2005; NRC 2003). Deep brine formations have received a lot of attention in discussions of physical underground storage options because they have the largest potential storage capacity of all the candidate underground storage sites (Blencoe et al. 2001; IPCC 2005). Incorporating brine-water chemistry and the potential for carbonate formation into the underground site selection process could allow for maximized chemical storage reducing leakage risks associated with physical storage alone. It has been long acknowledged that the formation of carbonates will occur to some degree during the direct injection of CO_2 gas into underground aquifers with Ca and Mg silicates mineralogy (Bachu et al. 1994), but the potential extent and scale of dissolution of underground rocks and subsequent formation of carbonates are not well understood.

Several research groups that have been focusing on the development of a useful aboveground engineered carbonation process have recently begun to expand the application of their knowledge of the kinetics of these reactions to consider below ground carbonation (O'Connor et al. 2004b; Rush et al. 2004; Wolf et al. 2004). The formation of carbonates may be utilized to increase the integrity of underground reservoirs by sealing faults where CO_2 may escape (McKelvy 2004). Recent studies aimed at understanding the kinetics of olivine dissolution and magnesium carbonate precipitation in the conditions of deep aquifers demonstrate that Mg-silicate dissolution increases with increasing pressure and temperature, and magnesite precipitation exhibits slow kinetics and requires a critical degree of supersaturation (Giammar et al. 2005). Injection of CO_2 into aquifers dominated by serpentine mineralogy has been suggested as an effective carbon storage strategy because both the mineralogy will result in the formation of both solid carbonates and dissolved bicarbonate (Cipolli et al. 2004; Giammar et al. 2005).

One challenge associated with carbonate formation in aquifers is the reduction of effective porosity of the aquifer and the armoring of the remaining surface area to prevent future dissolution (Cipolli et al. 2004). This armoring may reduce further carbonation, but could minimize the leakage potential of the gaseous CO_2 escaping from the underground reservoir. Techniques to measure and observe in

situ carbonation have also been recently developed to facilitate understanding and quantification of the potential for this approach (Wolf et al. 2004).

Each of these in-situ reactions in an aquifer is dependent on the rate of dissolution of CO₂ in the pore water. How much of the CO₂ gas will be dissolved into the groundwater depends on the specific chemistry of the groundwater, as well as the hydrological flow. Indeed, increasing the flow of brines by groundwater pumping could be a way to accelerate CO₂ dissolution (Keith et al. 2004).

Another in situ scheme that relies on a combination of geochemical reactions and physical trapping of CO₂ gas is the injection of CO₂ into carbonate sediments on the ocean floor at depths sufficient to ensure that the CO₂ is negatively buoyant (House et al. 2006). (N.B. In geological reservoirs and in the ocean the density of CO₂ increases with increasing depth/pressure. In geologic reservoirs the increasing temperature means that the density of CO₂ is always less than that of water, whereas in the ocean in which temperatures are cold and roughly independent of depth below the thermocline there is a depth, typically about 3.5 km, below which the density of CO₂ exceeds that of water). Sediment deposits on the abyssal plain are relatively thin and poorly consolidated, if they were located at shallow depths they would be poor candidates for geologic storage as CO₂ would probably leak to the sediments into the ocean, but at depths below which CO₂ is negatively buoyant the risk of leakage is greatly reduced as CO₂ would tend to migrate downwards through the porous media.

Leakage from such sediments is still possible, however, because the sediments are unconsolidated and would probably be fractured by injection of CO₂ which could then migrate upwards. In carbonate sediments, however, dissolution and subsequent addition of alkalinity to the pore fluid would tend to neutralize CO₂ that was released, providing a second trapping mechanism. Finally, release of CO₂ to the oceans will be impeded by a third trapping mechanism, the formation of CO₂ hydrates with pore waters. Recent research exploring this approach of CO₂ storage in deep-sea sediments suggests that the permanence guaranteed by the double cap of buoyancy and the formation of CO₂ hydrates might minimize the need for investment in monitoring and verification technology (House et al. 2006).

4 Comparisons with other mitigation strategies and research prioritization

The urgency of the carbon-climate problem and the lack of progress in slowing emissions (Canadell et al. 2007; Raupach et al. 2007) provides justification for research on seemingly far-fetched approaches, but research management decisions need to prioritize among many options because all potential areas cannot be covered equally. There is a risk that investing in low-probability options may distract or take away from investments in and societal commitment to other more immediately applicable carbon management approaches. But there is also the potential that research in far-fetched ideas could accelerate societal commitment to emissions reductions by demonstrating the severity and scale of the climate change-carbon problem.

Tools for research prioritization are needed to enable more rational prioritization of limited research funds. Attempting systematic prioritization is particularly critical among the “fringe” or high-risk options that have a unique potential for carbon management yet have a low probability of near-term implementation. Allocation of research effort occurs continuously and necessarily involves decision-making under

substantial uncertainty. Structured discussion of research prioritization is therefore valuable even when it is necessarily imprecise and subjective.

To compare the value and potential of these geochemical approaches and develop a framework within which to prioritize R&D needs, it is useful to consider geochemical carbon storage options within the context of the more conventional CO₂ capture and storage (CCS) in geologic formations (Anderson and Newell 2004; Herzog 2001; Holloway 2001; IPCC 2005; Parson and Keith 1998). Given the varied and serious obstacles to developing and implementing geochemical approaches to carbon management in the context of the increasing attention and advancement of CCS, geochemical approaches are most likely to be important in the next half century if they (1) reduce the risks associated with CCS storage in underground reservoirs, (2) extend the geographic or economic scope of applicability beyond that of conventional CCS, or (3) reduce the costs associated with reducing atmospheric CO₂ compared to CCS.

Farther in the future, chemical approaches might be important if they substantially increase available storage capacity, but only under scenarios in which (1) the burning of fossil fuels with CCS supplies a significant fraction of energy beyond this century, or (2) CCS with geologic storage is judged too risky or otherwise restricted in capacity. Total storage capacity limitations is not likely to be relevant within a reasonable time-horizon for applied research, so potential contributions to increasing the global capacity of carbon storage should not be a significant driver of such research. Overall global storage capacity for geologic storage is large compared to estimates of total CO₂ emissions over the next half-century, however distribution of storage reservoirs is uneven throughout the world (Bradshaw and Cook 2001; Bradshaw and Dance 2004; IPCC 2005).

Research on geochemical approaches, therefore, should be prioritized according to its likely contribution to one or more of the three attributes listed above: risk reduction, extending scope, and reducing costs.

Although research on all of these methods is of lower priority than research on more immediately practical means of mitigation, research on these alternative approaches should be sustained to maintain a portfolio of options and to improve the chance of discoveries that might yield a low-probability, high-payoff result. Recognizing the reality of limited funding, particularly for these long-shot proposals, we provide our perspective on prioritization among the ideas presented above.

Table 2 compares each of the major options discussed with the more immediately available approach of CCS in geologic formations. The various criteria that are compared include the integrity of the CO₂ storage, the local environmental risks and impacts, the geographic scope, the economic scope, the costs, and the implementation time-frame.

With respect to integrity of carbon storage, industrial carbonation and in situ geochemistry could provide improved carbon storage security by providing an option with a lower likelihood than CCS of CO₂ re-entering the atmosphere. Geochemical approaches that involve increasing dissolved oceanic carbon are likely to store carbon on the ten-thousand year time scale which is comparable to that predicted for conventional CCS.

Comparing the local environmental risks of these geochemical storage methods with local risks of conventional CCS is difficult due to the complexity, uncertainty, and variation in the risks. Nevertheless it can be said that the methods that

Table 2 Assessment of each of the major geochemical approaches compared with CO₂ capture and storage (CCS) in geologic formations

Geochemical approaches		Risks		Scope		Costs
		Integrity	Environmental risks	Geographic scope	Economic scope	
Carbonation	Silicate minerals	+	~ /?	+	-	-
	Brines	+	+	+	~	-
Increasing dissolved oceanic carbon	Carbonate dissolved (Rau and Caldeira)	~	?	+	~	+
	Adding alkalinity without carbon	~	?	+	+	?
In situ geochemistry	Cation-rich groundwater	+	+	~	~	~
	Carbonate sediments	+	?	+	~	~

Comparative evaluation of criteria assumes the proposed approaches are implemented as currently envisioned without major unanticipated consequences. Criteria-defining questions: (1) Integrity—How does the global risk of CO₂ leakage back to the atmosphere compare with CCS? (2) Environmental risks—How do local environmental risks/impacts compare to CCS? (3) Geographic scope—Does this approach extend the geographic scope of carbon management beyond that of CCS? (4) Economic scope—Does this approach extend the economic scope beyond that of CCS? That is, does it extend the set of technologies or economic sectors to which CCS might be applied? (5) Costs—How do predicted overall costs compare to CCS?

Metrics for answering criteria-defining questions:

+ improved

~ same

- worse

? difficult to predict.

incorporate CO₂ dissolution in groundwater or carbonation using groundwater would have a lower level of local risk associated with CO₂ gas leakage compared to CCS.

Each of these approaches, with the exception of facilitating in situ geochemistry with cation rich groundwater in geologic formations already deemed appropriate for CCS, provides opportunities to extend the geographic potential for carbon management. Given that regional potential for geologic storage is varied, geographic limitations are likely to become a major obstacle to conventional CCS so the potential to extend the possibilities for carbon management in otherwise limited areas may become increasingly valuable. The abundance of potential geologic reservoirs for carbon storage within the USA has undoubtedly contributed to the current US focus on CCS with geologic storage, and the associated decline in research interests in these geochemical approaches.

Among these geochemical approaches, only alkalinity addition, in our view, provides a significant improvement beyond conventional CCS with respect to broadening the economic scope of carbon storage options, i.e. only alkalinity addition significantly expands the economic sectors and technological activities (e.g. power generation, personal transportation, etc.) whose carbon emissions could be removed from the atmosphere.

With respect to costs, the carbonation approaches are currently much more expensive than CCS, the in situ geochemistry approaches are likely to be equivalent to CCS, the carbonate dissolution approach proposed by Rau and Caldeira could cost less, while it is difficult to predict the costs associated with adding alkalinity to the oceans. Each set of potential engineering constraints associated with each approach, including dispersion, mining, location, etc. could add cost to the option, but more research is needed to assess each of these constraints to effectively compare the economic viability of the different approaches.

With respect to the timescale required to implement and achieve carbon reductions, none of the geochemical approaches provide advantages in this regard.

The in situ approaches discussed above that involve integrating knowledge of carbonate chemistry into underground physical storage provide potential for improving conventional CCS. While improving CCS is generally worthwhile, incremental improvements in this area are unlikely to significantly increase the overall scope and potential for CCS, or carbon storage options more generally. The current major challenges for CCS involve the high cost of capture (Rubin et al. 2007), regulatory and legal limitations (Wilson and Figueiredo 2006; Wilson et al. 2003), and skepticism among the public (Alphen et al. 2007; Huijts et al. 2007; Palmgren et al. 2004). In summary, gross storage capacity does not appear to be a critical limiting step to the development of CCS so investing in enhancing in-situ geochemical carbon storage in a CCS system does not address the major challenges of CCS; investments in this area, therefore, are unlikely to alter the overall potential of CCS to contribute to near-term reductions in atmospheric CO₂ concentrations.

This assessment, simplistic though it is, allows several interesting conclusions. First, the various industrial ex situ carbonation schemes do not offer improvements in cost or economic scope nor do they offer an unequivocal reduction in environmental risk. These schemes rely upon a supply of separated CO₂ requiring a preceding CO₂ capture step, so the applicability of these techniques is limited by the cost and applicability of CO₂ capture which will likely be restricted to large point sources of CO₂. Carbonation does provide an improvement in integrity of the long-term storage, however, and also broadens the geographic potential beyond CCS. The carbonate dissolution approach offers cost benefits and the alkalinity addition scheme could provide valuable additional scope, both geographic and economic.

The approaches involving a manipulation of ocean alkalinity provide several other potential advantages over CCS. First, these approaches offer the possibility of an absolute cap on the cost of mitigating CO₂ emissions due to the complete independence from existing unequally distributed infrastructure. Like the enhancement of biological sinks, the addition of alkalinity provides mitigation at a fixed cost across the economy. This point can be understood by considering that conventional mitigation technologies must be integrated into existing energy systems, and current CO₂ capture technology, for example, is only practically for certain large point sources. For any carbon management technology there will be niches where it is particularly cheap to apply and other sectors where it is prohibitively expensive. Even when many technologies are combined there will be some sectors in the economy for which mitigation will be very expensive. Like the enhancement of biological sinks, therefore, the addition of alkalinity provides mitigation at a fixed cost across the economy because enhanced oceanic uptake of CO₂ would occur regardless of economic or infrastructure distribution. Immobilization of carbon emitted from non-

point CO₂ sources will not be possible without some mechanism for capturing CO₂ directly from the air, so this potential for CO₂ uptake is valuable.

Second, altering ocean alkalinity to enhance oceanic uptake of CO₂ offers the possibility of reducing the impact of higher atmospheric pCO₂ on surface waters. By increasing the ocean's buffering capacity, the acidification of the oceans will be minimized. Lastly, these approaches also offer the possibility of cost reductions, a consequence of the first point.

Notwithstanding these potential advantages no practical method now exists for adding alkalinity to the ocean at reasonable cost and there are serious environmental implications of manipulating the marine system in this way. Two central challenges stand in the way of a practical method: (1) the development of cost effective and environmentally benign methods of extracting cations from silicate minerals, and (2) the development of an effective ocean dispersion mechanism with sufficient dilution that the alkalinity does not adversely affect the local environment. There does not appear to be an inherent physical barrier to designing cost and energy-efficient systems for adding alkalinity to the oceans, so we suggest that such methods merit funding as a low-probability, high-payoff research area.

Addition of alkalinity to the ocean is a means of geoengineering: the intentional large-scale manipulation of the environment applied with the aim of counteracting rather than abating a source of pollution. It is unlike the best known geoengineering schemes in that it manipulates CO₂ concentrations directly rather than attempting to compensate for the climatic effects of increased CO₂ by altering global albedo or some other climate forcing. Also, unlike some other geoengineering proposals, because altering ocean alkalinity is dependent on ocean-atmosphere mixing the change will be slow, not immediate, so the addition of alkalinity would not be useful to mitigate immediate effects of abrupt climate changes that might arise from high peak atmospheric concentrations. This approach, therefore, is associated with the ethical challenges associated with other geoengineering proposals.

5 Conclusions

Proposed carbon management approaches that rely primarily on the acceleration of the chemical neutralization of CO₂ gas through interactions with minerals have potential to play an important role in managing carbon. Among the three broad categories of geochemical approaches reviewed herein, mineral carbonation, altering ocean alkalinity, and in-situ geochemical processes, current research is focusing primarily on in-situ geochemical processes. Given the unique potential of geochemical approaches to contribute to atmospheric CO₂ reductions, we believe that increased support for research on mineral carbonation and ocean alkalinity alteration are justified.

While accelerating the formation of carbonate minerals in industrial processes does not currently look like a promising approach (Gerdemann et al. 2007), the major obstacles to industrial carbonation may be overcome by the application of finely ground industrial byproducts for the mineral requirements. More research to assess the potential scale of the use of industrial byproducts is needed. In addition, in some regions of the world where there are no geologic storage reservoirs appropriate for carbon storage, mineral carbonation has potential to become a valuable process

if the costs and energy requirements can be reduced even slightly. Recent research on the use of concentrated solar energy to thermally decompose CaCO_3 into CaO for CO_2 air capture (Nikulshina et al. 2007, 2006) and other innovative technologies could be expanded and applied to the challenges of mineral carbonation.

Increasing the alkalinity of the surface oceans to increase the ocean's carbon storage capacity is an approach that is worthy of more research for two critical reasons: (1) this approach relies on the ocean's natural CO_2 uptake mechanism so non-point sources of CO_2 could be incorporated and (2) the costly CO_2 capture process would not be required. In addition, ocean alkalinity addition could simultaneously mitigate against ocean acidification. In some respects, addition of alkalinity to the oceans serves as a kind of long timescale method of remediation rather than a means of geoengineering; a means to reduce the climatic and geochemical impacts of anthropogenic CO_2 on century to millennial time scales.

Although the geochemical carbon management approaches reviewed here appear unlikely to contribute substantially to the imminent need for reducing atmospheric concentrations within the next decade or two, sustaining research in these alternative approaches is prudent as we continue upon a dangerous and uncertain path of increasing atmospheric CO_2 concentrations.

Acknowledgements The authors thank Ken Caldeira, Asher Siebert, Frank Zeman, and Anne Johansen for helpful review of the manuscript, and three anonymous reviewers for comments and suggestions that greatly improved this paper.

References

- Albany Research Center (2003) Albany Research Center, US Department of Energy. <http://www.alrc.doe.gov/>
- Alphen KV, Voorst QVVT, Hekkert MP, Smits REHM (2007) Societal acceptance of carbon capture and storage technologies. *Energy Policy* 35:4368–4380
- Anderson S, Newell R (2004) Prospects for carbon capture and storage technologies. *Ann Rev Environ Resour* 29:109–142
- Aresta M (ed) (2003) Recovery and utilization of carbon dioxide. Kluwer, The Netherlands
- Bachu S, Gunter WD, Perkins EH (1994) Aquifer disposal of CO_2 : hydrodynamic and mineral trapping. *Energy Convers Manag* 35(4):269–279
- Bengtsson (2006) Geo-engineering to confine climate change: is it at all feasible? *Clim Change* 77:229–234
- Berner RA, Lasaga AC, Garrels RM (1983) The carbonate-silicate geochemical cycle and its effects on atmospheric carbon dioxide over the past 100 million years. *Am J Sci* 283:641–683
- Blencoe JG, Cole DR, Horita J, Moline GR (2001) Experimental geochemical studies relevant to carbon sequestration, first national conference on carbon sequestration. NETL
- Bradshaw J, Cook P (2001) Geological sequestration of carbon dioxide. *Environ Geosci* 8(3):149–151
- Bradshaw J, Dance T (2004) Mapping geological storage prospectivity of CO_2 for the world's sedimentary basins and regional source to sink matching. In: 7th International conference on greenhouse gas control technologies. Vancouver, Canada
- Broecker WS (2007) CO_2 arithmetic. *Science* 315:1371
- Buesseler KO et al (2008) Ocean iron fertilization—moving forward in a sea of uncertainty. *Science* 319(5860):162–
- Caldeira K, Rau G (2000) Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: Geochemical implications. *Geophys Res Lett* 27(2):225–228
- Canadell JG et al (2007) Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks. *Proc Natl Acad Sci USA* 104(47):18866–18870
- Chester R (1990) Marine geochemistry. Chapman and Hall, London

- Chisholm SW, Falkowski PG, Cullen JJ (2001) Dis-crediting ocean fertilization. *Science* 294(5541):309–310
- Cicerone R (2006) Geoengineering: encouraging research and overseeing implementation. *Clim Change* 77:221–226
- Cipolli F, Gambardella B, Marini L, Ottonello G, Zuccolini MV (2004) Geochemistry of high-pH waters from serpentinites of the Gruppo di Voltri (Genova, Italy) and reaction path modeling of CO₂ sequestration in serpentine aquifers. *Appl Geochem* 19:787–802
- Crutzen PJ (2006) Albedo enhancement by stratospheric sulfur injections: a contribution to resolve a policy dilemma? *Clim Change* 77:211–220
- Deleuze M, Brantley SL (1997) Inhibition of calcite crystal growth by Mg²⁺ at 100°C and 100 bars: influence of growth regime. *Geochim Cosmochim Acta* 61:1475–1485
- Dunsmore HE (1992) A geological perspective on global warming and the possibility of carbon dioxide removal as calcium carbonate mineral. *Energy Convers Manag* 33(5–8):565–572
- Feely RA et al (2004) Impact of anthropogenic CO₂ on the CaCO₃ system in the oceans. *Science* 305(5682):362–366
- Figueiredo MAD, Reiner DM, Herzog HJ (2002) Ocean carbon sequestration: a case study in public and institutional perceptions, sixth international conference on greenhouse gas control technologies. Kyoto, Japan
- Gerdemann SJ, Dahlin DC, O'Connor WK (2003) Carbon dioxide sequestration by aqueous mineral carbonation of magnesium silicate minerals. In: Gale J, Kaya Y (eds) *Greenhouse gas technologies*. Elsevier Science, Amsterdam, The Netherlands
- Gerdemann SJ, O'Connor WK, Dahlin DC, Penner LR, Rush H (2007) Ex situ aqueous mineral carbonation. *Environ Sci Technol* 41:2587–2593
- Giammar DE, Robert G, Bruant J, Peters CA (2005) Forsterite dissolution and magnesite precipitation at conditions relevant for deep saline aquifer storage and sequestration of carbon dioxide. *Chem Geol* 217:257–276
- Goff F, Lackner KS (1998) Carbon dioxide sequestration using ultramafic basic rock. *Environ Geosci* 5(3):89–101
- Goff F et al (2000) Evaluation of ultramafic deposits in the Eastern United States and Puerto Rico as sources of magnesium for carbon dioxide sequestration. LA-13694-MS, Los Alamos National Laboratory, Los Alamos, New Mexico
- Goldberg P, Chen Z-Y, O'Connor W, Walters R, Ziock H (2001) CO₂ mineral sequestration studies in US. *J Energy Environ Res* 1(1):117–126
- Hanchen M, Prigiobbe V, Storti G, Seward TM, Mazzotti M (2006) Dissolution kinetics of forsteritic olivine at 90–150°C including effects of the presence of CO₂. *Geochim Cosmochim Acta* 70(17):4403–4416
- Herzog H (2001) What future for carbon capture and sequestration? *Environ Sci Technol* 35(7):148A–153A
- Herzog H (2002) Carbon sequestration via mineral carbonation: overview and assessment. MIT Laboratory for Energy and the Environment, Cambridge, MA
- Holdren JP (2006) The energy innovation imperative, addressing oil dependence, climate change, and other 21st century energy challenges. innovations, technology, governance & globalization. *Innov Technol Govern Global* 1:3–23
- Holloway S (2001) Storage of fossil fuel-derived carbon dioxide beneath the surface of the earth. *Annu Rev Energy Environ* 26:145–166
- House KZ, Shrag DP, Harvey CF, Lackner KS (2006) Permanent carbon dioxide storage in deep-sea sediments. *Proc Natl Acad Sci U S A* 103(33):12291–12295
- Houston EC, Kerr HJ (1945) Magnesium from olivine by hydrochloric acid extraction followed by electrolysis: pilot plant studies. Tennessee Valley Authority, Report 586
- Huijts NMA, Midden CJH, Meijnders AL (2007) Social acceptance of carbon dioxide storage. *Energy Policy* 35:2780–2789
- IEA (1999) CO₂ storage as carbonate minerals. Study prepared by CSMA Minerals, Ltd. Commissioned by IEA
- IEA (2002) Solutions for the 21st century, zero emissions technologies for fossil fuels. Technology Status Report, International Energy Agency, Committee on Energy Research and Technology, Working Party on Fossil Fuels, Paris
- IPCC (ed) (2001) *Climate change 2001: mitigation*. Cambridge University Press, Cambridge, United Kingdom, and New York, NY USA
- IPCC (2005) IPCC special report on carbon dioxide capture and storage, intergovernmental panel on climate change. Working Group III

- IPCC (2007) Mitigation of climate change. Working Group III Report, Intergovernmental Panel on Climate Change
- Jia L, Anthony EJ (2003) Mineral carbonation and ZECA. In: Gale J, Kaya Y (eds) Greenhouse gas technologies. Elsevier Science, Amsterdam, The Netherlands
- Keith DW, Hassanzadeh H, Pooladi-Darvish M (2004) Reservoir engineering to accelerate dissolution of stored CO₂ in brines. In: Proceedings of 7th international conference on greenhouse gas control technologies. IEA Greenhouse Gas Program, Cheltenham, UK, Vancouver, Canada
- Kheshgi HS (1995) Sequestering atmospheric carbon dioxide by increasing ocean alkalinity. *Energy* 20(9):915–922
- Kiehl JT (2006) Geoengineering climate change: treating the symptom over the cause? *Clim Change* 77:227–228
- Kleypas JA et al (2006) Impacts of ocean acidification on coral reefs and other marine calcifiers, a guide for future research, report of a workshop held 18–20 April 2005, Sponsored by NSF, NOAA, US Geologic Survey, St. Petersburg, Florida
- Lackner KS (2002) Carbonate chemistry for sequestering fossil carbon. *Annu Rev Energy Environ* 27:193–232
- Lackner KS, Butt DP, Wendt CH (1997) Progress on binding CO₂ in mineral substrates. *Energy Convers Manag* 38(Supplement):S259–S264
- Lackner KS, Wendt CH, Butt DP, Edward L, Joyce J, Sharp DH (1995) Carbon dioxide disposal in carbonate minerals. *Energy* 20(11):1153–1170
- Langdon C et al (2000) Effect of calcium carbonate saturation state on the calcification rate of an experimental coral reef. *Glob Biogeochem Cycles* 14(2):639–654
- MacCracken MC (2006) Geoengineering: worthy of cautious evaluation? *Clim Change* 77:235–243
- Marchetti C (1977) On geoengineering and the CO₂ problem. *Clim Change* 1(1):59–68
- Matter JM (2005) In-situ testing of geological carbon dioxide sequestration in basalt aquifers: results from a pilot study in the Palisades Sill (New York). AGU Chapman conference on the science and technology of carbon sequestration. San Diego, CA
- McKelvy M (2004) Arizona State University Center for Solid State Science (personal communication)
- Mucci A, Morse JW (1983) The incorporation of Mg²⁺ and Sr²⁺ into calcite overgrowths - Influences of growth-rate and solution composition. *Geochim Cosmochim Acta* 47(2):217–233
- Nikulshina V, Galvez ME, Steinfeld A (2007) Kinetic analysis of the carbonation reactions for the capture of CO₂ from air via the Ca(OH)₂-CaCO₃-CaO solar thermochemical cycle. *Chem Eng J* 129(1–3):75–83
- Nikulshina V, Hirsch D, Mazzotti M, Steinfeld A (2006) CO₂ capture from air and co-production of H₂ via the Ca(OH)₂-CaCO₃ cycle using concentrated solar power-thermodynamic analysis. *Energy* 31(12):1715–1725
- Nilson DN, Hundley G (1999) Preliminary feasibility study of the sequestration of carbon dioxide gas with minerals: a study of the LANL aqueous process. Albany Research Center, U.S. DoE
- NRC (2003) Novel approaches to carbon management, separation, capture, sequestration, and conversion to useful products, workshop report, committee on novel approaches to the management of greenhouse gases from energy systems. National Research Council, Irvine, CA
- O'Connor WK et al (2002) Continuing studies on direct aqueous mineral carbonation for CO₂ sequestration. In: 27th International technical conference on coal utilization and fuel systems. Clear Water, FL
- O'Connor WK, Dahlin DC, Rush GE, Gerdemann SJ, Penner LR (2004a). Energy and economic evaluation of ex situ aqueous mineral carbonation. In: 7th International conference on greenhouse gas control technologies. Vancouver, Canada
- O'Connor WK et al (2004b) Aqueous mineral carbonation, mineral availability, pretreatment, reaction parametrics, and process studies. DOE/ARC-TR-04-002, Office of Process Development, Albany Research Center, Office of Fossil Energy, US DoE
- O'Connor WK et al (2004c) Aqueous mineral carbonation, mineral availability, pretreatment, reaction parametrics, and process studies Final report, Office of Process Development, Albany Research Center, Office of Fossil Energy, US DOE
- Pacala S, Socolow R (2004) Stabilization wedges: solving the climate problem for the next 50 years with current technologies. *Science* 305(5686):968–972
- Palmgren CR, Bruin WBD, Keith DW, Morgan MG (2004) Initial public perceptions of deep geological and oceanic disposal of carbon dioxide. *Environ Sci Technol* 38(24):6441–6450
- Parson EA, Keith DW (1998) Fossil fuels without CO₂ emissions. *Science* 282(6):1053–1054

- Pelejero C et al (2005) Preindustrial to modern interdecadal variability in coral reef pH. *Science* 309(5744):2204–2207
- Pokrovsky OS, Schott J (2000) Kinetics and mechanism of forsterite dissolution at 25 degrees C and pH from 1 to 12. *Geochim Cosmochim Acta* 64(19):3313–3325
- Rau GH, Caldeira K (1999) Enhanced carbonate dissolution: a means of sequestering waste CO₂ as ocean bicarbonate. *Energy Convers Manag* 40:1803–1813
- Rau GH, Knauss KG, Langer WH, Caldeira K (2004) CO₂ mitigation via accelerated limestone weathering. *Prepr Pap Am Chem Soc Div Fuel Chem* 49(1):376
- Raupach MR et al (2007) Global and regional drivers of accelerating CO₂ emissions. *Proc Natl Acad Sci U S A* 104(24):10288–10293
- Rubin EA, Chen C, Rao AB (2007) Cost and performance of fossil fuel power plants with CO₂ capture and storage. *Energy Policy* 35:4444–4454
- Rush GE, O'Connor WK, Dahlin DC, Penner LR, Gerdemann SJ (2004) Laboratory tests of mafic, ultra-mafic, and sedimentary rock types for in-situ applications for carbon dioxide sequestration. Albany Research Center, Office of Fossil Energy, US DOE
- Sabine CL et al (2004) The oceanic sink for anthropogenic CO₂. *Science* 305(5682):367–371
- Sagarin R et al (2007) Iron fertilization in the ocean for climate mitigation: legal, economic, and environmental challenges. Nichols School of the Environment, Duke University
- Schlesinger WH (1991) Biogeochemistry. An analysis of global change. Academic, San Diego
- Seifritz W (1990) CO₂ disposal by means of silicates. *Nature* 345:486
- Stephens JC, Hering JG (2002) Comparative characterization of volcanic ash soils exposed to decade-long elevated carbon dioxide concentrations at Mammoth Mountain, California. *Chem Geol* 186(3–4):289–301
- Stolaroff JK, Lowry GV, Keith DW (2005) Using CaO- and MgO- industrial waste streams for carbon sequestration. *Energy Convers Manag* 46(5):687–699
- Wigley TML (2006) A combined mitigation/geoengineering approach to climate stabilization. *Science* 314(5798):452–454
- Wilson EJ, Figueiredo MAD (2006) Geologic carbon dioxide sequestration: an analysis of subsurface property law. *ELR* 36:10114–10124
- Wilson EJ, Johnson TL, Keith DW (2003) Regulating the ultimate sink: managing the risks of geologic CO₂ storage. *Environ Sci Technol* 37(16):3476–3483
- Wolf GH, Chizmeshya AVG, Diefenbacher J, McKelvy MJ (2004) In situ observation of CO₂ sequestration reactions using a novel microreaction system. *Environ Sci Technol* 38:932–936
- Yegulalp TM, Lackner KS, Ziock HJ (2001) A review of emerging technologies for sustainable use of coal for power generation. *Int J Surf Min Reclam Environ* 15(1):52–68