Direct electrolytic dissolution of silicate minerals for air CO_2 mitigation and carbon-negative H_2 production

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We experimentally demonstrate the direct coupling of silicate mineral dissolution with saline water electrolysis and H_2 production to effect significant air CO_2 absorption, chemical conversion, and storage in solution. In particular, we observed as much as a 10^5-fold increase in OH^- concentration (pH increase of up to 5.3 units) relative to experimental controls following the electrolysis of 0.25 M Na_2SO_4 solutions when the anode was encased in powdered silicate mineral, either wollastonite or an ultramafic mineral. After electrolysis, full equilibration of the alkalized solution with air led to a significant pH reduction and as much as a 45-fold increase in dissolved inorganic carbon concentration. This demonstrated significant spontaneous air CO_2 capture, chemical conversion, and storage as a bicarbonate, predominantly as $NaHCO_3$. The excess OH^- initially formed in these experiments apparently resulted via neutralization of the anolyte acid, H_2SO_4, by reaction with the base mineral silicate at the anode, producing mineral sulfate and silica. This allowed the NaOH, normally generated at the cathode, to go unneutralized and to accumulate in the bulk electrolyte, ultimately reacting with atmospheric CO_2 to form dissolved bicarbonate. Using nongrid or nonpeak renewable electricity, optimized systems at large scale might allow relatively high-capacity, energy-efficient (<300 kJ/mol of CO_2 captured), and inexpensive (<$100 per tonne of CO_2 mitigated) removal of excess air CO_2 with production of carbon-negative H_2. Furthermore, when added to the ocean, the produced hydroxide and/or (bi)carbonate could be useful in reducing sea-to-air CO_2 emissions and in neutralizing or offsetting the effects of ongoing ocean acidification.

air capture | carbon dioxide | electrochemistry | hydrogen | mineral weathering

The abundance of silicate minerals and their ability to react with CO_2 to form stable carbonates and bicarbonates make them relevant to CO_2 mitigation efforts (e.g., refs. 1–4). The global capacity of these reactions to moderate atmospheric CO_2 is evident in the central role silicate mineral weathering plays in naturally consuming excess atmospheric CO_2 on geological time scales (5). Indeed, various methods have been proposed to accelerate this natural geochemical air CO_2 mitigation (6–9).

Although silicate weathering is extremely slow under ambient conditions, silicate mineral dissolution and subsequent reaction with CO_2 can be significantly increased in strong acids and/or bases (ref. 10 and references therein). Because very large pH gradients are produced in saline water electrolysis cells [anolyte pH < 2, catholyte pH > 12 (11)], it was reasoned that placing a silicate mineral mass in direct contact with such solutions would facilitate their dissolution to metal and silicate ions. Once formed, the positively charged metal ions could migrate to the negatively charged catholyte to form metal hydroxide, whereas the negatively charged silicate ions would react with the H^+-rich anolyte to form silicic acid, silica, and/or other silicon compounds (Fig. 1A).

Alternatively or additionally, the metal silicate could react with and neutralize the intermediate acid normally formed in the anolyte of a saline electrolysis cell, thus allowing the intermediate hydroxide (produced at the cathode via salt and water splitting) to go unneutralized and accumulate in the bulk electrolyte (Fig. 1B).

In either case, contacting of the produced hydroxide solution with CO_2 would lead to CO_2 capture and storage as metal bicarbonate or carbonate (Fig. 1).

Previously, it was proposed that the dissolution of silicate minerals be indirectly coupled to an electrolytic chloralkali-type process to effect air CO_2 capture and storage (7). Here, the splitting of NaCl and H_2O would produce $NaOH_{(aq)}$, $Cl_{2(g)}$, and $H_{2(g)}$ (aq, aqueous; g, gaseous). The NaOH would be contacted with air to capture and convert ambient CO_2: $NaOH + CO_2 \rightarrow NaHCO_{3(aq)}$, whereas the H_2 and Cl_2 would be exothermically reacted in a fuel cell to produce electricity and HCl. The latter would then be neutralized via spontaneous reaction with silicate minerals to form metal chlorides that, together with the $NaHCO_{3(aq)}$, could presumably be safely stored in the ocean.

Subsequently, it was demonstrated (12) that significantly elevated pH and hydroxide concentrations (relative to controls) can be attained in bulk electrolyte during the electrolysis of seawater (naturally containing 0.48 M NaCl) when the anode is encased in a porous carbonate mineral ($CaCO_3$) mass. Then equilibration of the electrolyte with air neutralized the pH via the reaction of air CO_2 with the excess hydroxide, forming dissolved bicarbonates. This scheme allowed the direct participation of a mineral carbonate in saline water electrolysis and hydroxide formation without the need for separate fuel cell acid production. It is this basic scheme that we sought to test in the context of accelerating silicate mineral dissolution and air CO_2 capture as an adjunct to conventional saline water electrolysis. Details of the experiments conducted are described in *Materials and Methods*.

Such approaches have the potential to be more energy-efficient and less environmentally risky than more widely discussed chemical air CO_2 capture and concentration methods (e.g., refs. 13–18). This is because they avoid: (*i*) energy-inefficient base/sorbent regeneration and production of highly concentrated molecular CO_2 and (*ii*) the need to guarantee long-term sequestration of the latter volatile compound. Methods of cost-effectively producing and using hydroxides in once-through schemes also allow the use of the massive air contacting offered by natural water bodies (e.g., the ocean, as opposed to reliance on expensive, engineered air contactors) to effect air CO_2 absorption and chemical conversion to environmentally beneficial marine (bi)carbonates in solution at global scales (7, 12, 19, 20). Perhaps more significantly, the strategic addition of chemical base to the surface ocean in locations when/where the dissolved CO_2 concentration exceeds that in the overlying atmosphere [e.g., upwelling regions (21)] would consume some of the excess dissolved CO_2, and thus avoid its degassing to the atmosphere. This would then reduce some of the ocean's >300 gigatonnes (Gt) of gross CO_2 emissions per year (22), and hence proportionately reduce the CO_2 burden in the atmosphere without the need of performing the more difficult task of directly removing CO_2 from air. Furthermore, excess ocean CO_2 removal is required

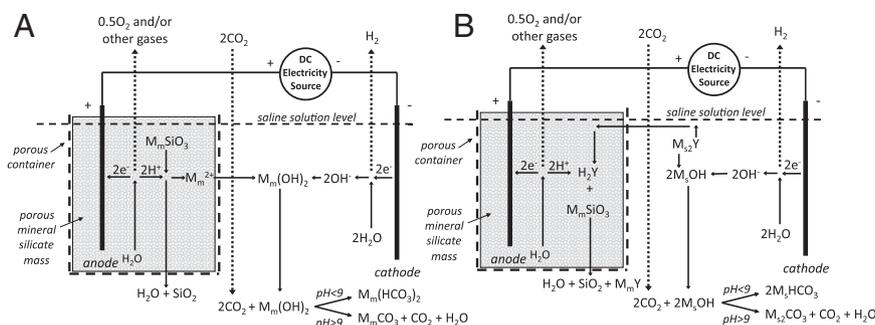EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES

Fig. 1. Schemes for the enhanced production of hydroxide and subsequent air CO_2 capture and storage in a saline water electrolysis cell in the presence of a metal silicate mineral. (*A*) Metal silicate is split, with the divalent mineral metal (M_m) forming the hydroxide. Only silicate mineral and water are consumed. (*B*) Both the metal silicate and the metal salt electrolyte are permanently split, with the monovalent salt metal (M_s) forming the hydroxide and the M_m and electrolyte anions forming a stable metal salt (M_mY). Here, silicate mineral, electrolyte salt, and water are consumed.

for any effective air CO_2 capture scheme because removal of air CO_2 alone will simply reduce air CO_2 concentration relative to that in the ocean. This leads to an increase in the ocean-to-air CO_2 flux, largely replacing the air CO_2 removed (23). Schemes that consume/remove and sequester excess ocean CO_2 (e.g., refs. 24, 25) therefore effectively address both excess ocean and air CO_2, sidestepping the need for direct air CO_2 capture.

Results and Discussion

The experimental procedures are discussed in *Material and Methods*, and results are reported in Table 1. Relative to non-silicate controls, dramatic increases in solution pH were observed at the end of electrolysis of 0.25 M Na_2SO_4 solutions when silicate minerals were present in the anolyte, with pH reaching as high as 11.1 in the ultramafic rock (UM-4) treatment after 1.5 h of electrolysis. This represented as much as a 3 mM increase in [OH^-] relative to the control solution, <0.02 mM. Overnight aeration of the solutions [i.e., full air–solution equilibration (*Materials and Methods*)] led to significantly lower and stable solution pH and as much as a 1.6-mM increase in total dissolved inorganic carbon (DIC) concentration. Such base neutralization and DIC increase presumably occurred via $CO_{2(air)} + OH^- \rightarrow HCO_3^-$, the reaction that would have dominated at the pH values observed.
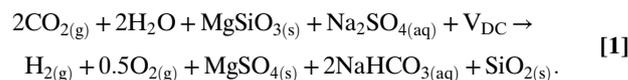
Unexpectedly, solution Ca^{2+} and Mg^{2+} concentrations in mineral treatments were not consistently elevated relative to the control, and these concentrations could only account for <16% of that required to charge-balance the HCO_3^- produced (Table 1). We suspect that variable leaching of Ca^{2+} and Mg^{2+} from the paper filters used in the experiments may have contributed to the concentrations and variability observed. In any case, the paucity of these cations relative to the hydroxide and bicarbonate produced (Table 1) suggests that the bulk of these anions were instead balanced by the primary electrolyte cation, Na^+. Lack of visible precipitation on the exposed cathode and in the electrolyte in all experiments provides further evidence that more soluble $NaHCO_3$, rather than relatively insoluble calcium or magnesium (bi)carbonates, dominated the DIC produced.

The preceding scenario would have occurred if the H_2SO_4 produced at the anode and normally the neutralizer of cathodically generated NaOH had instead reacted with the silicate mineral mass, therefore allowing the NaOH to accumulate in the bulk electrolyte (e.g., Fig. 1*B*). The mineral silicate/sulfuric acid reaction would result in the formation of a metal sulfate and hydrated silica; e.g., $MgSiO_3 + H_2SO_4 \rightarrow MgSO_4 + H_2SiO_3$. Alternatively, the highly acidic anolyte could promote alteration of the silicate mineral mass as H_3O^+ exchanged for the mineral's metal cations, leaving behind a silica-rich layer similar to amorphous, solid silica, $SiO_{2(s)}$ (26). Metal sulfate precipitation would then remove Ca/Mg ions from solution. The reaction rate in this scenario would likely be governed by diffusion and H_3O^+/metal
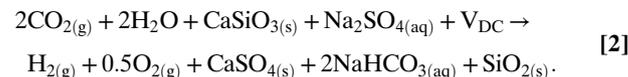
ion exchange kinetics of the fast-reacting chain silicates studied here (e.g., refs. 26, 27).

In any case, formation of silica, $SiO_{2(s)}$, is presumed to be the ultimate fate of the original mineral silicate moiety. If silica and/or sulfates precipitated onto or around the anode, it could potentially reduce conductivity and depress current flow within the cell over time; however, this was not observed within the time frame of the experiments conducted.

From the available evidence, the following primary net reaction for the UM-4 experiments is thus inferred:

$$2CO_{2(g)} + 2H_2O + MgSiO_{3(s)} + Na_2SO_{4(aq)} + V_{DC} \rightarrow$$
$$H_{2(g)} + 0.5O_{2(g)} + MgSO_{4(s)} + 2NaHCO_{3(aq)} + SiO_{2(s)}. \quad [1]$$

For the wollastonite experiments:

$$2CO_{2(g)} + 2H_2O + CaSiO_{3(s)} + Na_2SO_{4(aq)} + V_{DC} \rightarrow$$
$$H_{2(g)} + 0.5O_{2(g)} + CaSO_{4(s)} + 2NaHCO_{3(aq)} + SiO_{2(s)}. \quad [2]$$

V_{DC} means direct current voltage. Although the details of the reactions involved remain to be further elucidated, the ability to significantly enhance atmospheric CO_2 absorption into a salt solution with the strategic addition of silicate minerals and the application of dc electricity has been demonstrated.

One implication of the preceding observations is that globally abundant and relatively inexpensive silicate minerals and saline water (seawater, as well as natural or artificial brines) could be reacted using nongrid and/or nonpeak renewable energy to effect spontaneous capture of air CO_2 and its long-term storage as bicarbonate or possibly carbonate (Fig. 2). The cogeneration of valuable carbon-negative H_2 and O_2 or Cl_2 could help offset costs or could allow some energy recovery, for example, via fuel cell conversion to electricity with the production of fresh water or acid. Although further research is clearly needed, the following sections explore the possibility of conducting such a process at globally significant scales.

Issues for Large-Scale Application. *Thermodynamics and energy expenditure.* In the case of the UM-4 experiments, the theoretical minimum required energy expenditure for reaction 1 is 137 kJ/mol of CO_2 (ΔG^o, Gibbs free energy at a concentration of 1 M at standard temperature and pressure). The reaction scheme for wollastonite (reaction 2) has a ΔG^o of 110 kJ/mol of CO_2. These minimum energies are comparable to a ΔG^o of 237 kJ/mol of H_2 or 118.5 kJ/mol of OH^- generated (i.e., 118.5 kJ/mol of CO_2 potentially reacted with the OH^-) in the catholyte during conventional water electrolysis. The actual energy expenditure observed in our experiments ranged from 426 to 481 kJ of electricity (kJ_e)/mol of CO_2, implying an energy efficiency ranging from 23% to 32% (Table 2).

Table 1. Relevant chemical and electrical measurements before, during, and after electrolysis, and after electrolyte aeration

Mineral treatment	Initial pH	Electrolysis time, h	Mean voltage, V	Mean current, mA	Energy, mWh$_e$	End of electrolysis		End of aeration			
						pH	[OH$^-$], μM	pH	Ca^{2+}, μM	Mg^{2+}, μM	DIC, μM
None	6.5	1.5	3.5	8.8	46.1	5.8	0.016	6.8	67.1	22.3	43
Wollastonite	6.5	0.5	3.6	7.1	12.8	10.4	697	7.6	36.6	3.2	418
	(0.05)		(0.02)	(0.6)		(0.1)	(139)	(0.1)	(8.0)	(0.02)	(1.5)
UM-4	6.5	0.5	3.5	9.5	16.8	10.6	1,000	8	51.3	24.5	597
UM-4	6.3	1.5	3.6	8.7	46.7	11.1	3,162	8	92.2	72.9	1,614

Numbers in parentheses are SDs of the results of replicate experiments.

Because chemical work can typically be performed in industrial electrolysis systems at $\geq 50\%$ energy efficiency (28, 29), the potential realized energy cost of the electrolysis would then be <274 kJ$_e$/mol of CO$_2$ (Table 2). In support of these estimates, realized energy costs in commercial alkaline water electrolyzers are roughly 385–500 kJ$_e$/mol of H$_2$ (28) or 190–250 kJ$_e$/mol of OH$^-$ internally generated (or 190–250 kJ$_e$/mol of CO$_2$ potentially consumed).

Although we have not considered a full system design in detail, we can estimate additional energy demands for major components. Adding nonpassive air contacting to these systems could add about 30 kJ/mol of CO$_2$ to the energy requirement (16). Further ancillary liquid, gas, and solids handling/pumping might add an additional 30 kJ/mol of CO$_2$, bringing the total energy expenditure to <334 kJ/mol of CO$_2$ captured and stored. This estimate is lower than that of previously described air capture systems based on the NaOH/Ca(OH)$_2$ reaction with air CO$_2$ (14, 16, 17) (Table 2), primarily because energy-intensive, low-efficiency thermal regeneration of NaOH/Ca(OH)$_2$ and the concentration of molecular CO$_2$ are avoided.

To maximize CO$_2$ mitigation benefits, the electricity for the electrochemical process must come from nonfossil sources (Fig. 2). These are globally abundant, and in some cases, the delivered electricity can be cheaper than conventional grid electricity if (*i*) it is produced and used locally, hence reducing energy transmission costs, and/or (*ii*) off-peak, renewable grid electricity is used (30). Assuming an extractible wind energy density of 10.8 terrajoules of electricity km$^{-2}\cdot$y^{-1} (30) then implies a land or ocean area requirement of $<7 \times 10^5$ km$^2\cdot$Gt^{-1} of CO$_2$ captured per year for energy harvesting alone, or, at most, about 0.13% of the earth's surface to effect 1 Gt of CO$_2$ removal per year. This footprint would be reduced if higher density energy sources were used (e.g., geothermal, solar, nuclear).

Also, rather than deploying new, nonfossil energy production for this proposed carbon-negative hydrogen production, would a more cost-effective carbon benefit accrue by simply plugging this energy into the grid, thereby supplanting fossil energy use and CO$_2$ emissions? Assuming that 300 kJ$_e$ is required per mol of CO$_2$ captured and stored (or 0.147 g of CO$_2$ removed per kJ$_e$ used), this can then be compared with an average 0.155 g of CO$_2$ emitted per kJ$_e$ produced in generation of electricity in the United States (31). By this calculation, simply adding renewable energy to the grid would have a slight advantage over silicate electrolysis with respect to carbon management. A much greater advantage would be obtained if the renewable electricity were specifically substituted for more carbon-intensive, coal-fired electricity generation. However, these calculations ignore the added benefits of silicate electrolysis, which include: (*i*) carbon-negative H$_2$ production and use in potentially offsetting gasoline use and emissions (see below), and (*ii*) ocean alkalinity production in helping neutralize or offset the effects of ocean acidification.

Silicate minerals. Many common silicate rocks have appropriate compositions to provide alkalinity needed for CO$_2$ conversion to (bi)carbonate. A given mass of basalt can convert about one-third its weight of CO$_2$ into bicarbonate, based on reaction equilibria for typical basalt compositions and allowing for the formation of appropriate clay alteration phases (7). Basalts are also the most common rock type in the Earth's crust, with their global mass dwarfing that needed for conversion of all present and future anthropogenic CO$_2$. For example, the mass of the Columbia River basalts in the United States alone is estimated at over 500 million Gt (32), or 10^4 times that needed to remove possible total cumulative anthropogenic emissions of 20,000 Gt of CO$_2$. If basalts could be used for the process, they would provide a virtually unlimited supply both in terms of overall mass and geographic availability (33).

Less alkaline igneous rocks, such as andesites and granites, are also abundant and could readily supply the needed alkalinity for acid/CO$_2$ neutralization. In addition, many immature clastic rocks, such as greywackes and arkoses, could be used. Greater rock reactivity could be realized by selecting more glassy volcanic rocks as source material because they are known to dissolve much faster than their crystalline equivalents (27). The use of alkaline earth aluminosilicate minerals is likely to be less advantageous because their dissolution rates are several orders of magnitude lower than those of the minerals used in the above experiments. Here, the exchange of H$_3$O$^+$ for Na, Ca, or Mg in aluminosilicates will be limited eventually by much slower breaking of the framework silicate bonds at the mineral–solution interface (e.g., refs. 34–36).

Regarding the energy and carbon penalty for mineral extraction, grinding, and transportation, several studies (2, 9, 37) indicate that depending on the circumstances, these costs will be small relative to other system energy expenditures (e.g., electrolysis) and relative to the system's CO$_2$ removal potential. This is predicated on the assumption that grinding silicate minerals to extremely small particles (e.g., 1 μm) will not be required for the process (9). Significant amounts of preexisting waste silicate mineral particles and fragments are also available at little or no cost at certain locations (2). The most cost-effective silicate mineral sources/types, particle sizes, and siting remain to be determined for the proposed process.
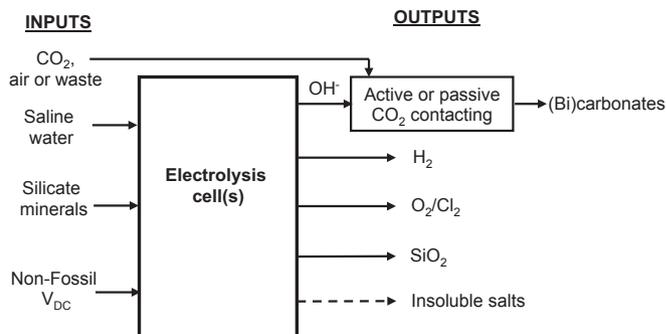

Fig. 2. Schematic of inputs and outputs of saline water electrolysis in the presence of silicate minerals to effect hydrogen and oxygen or chlorine generation and to produce hydroxide for the net removal of CO$_2$ and storage as (bi)carbonate. The dashed line denotes the possibility of avoiding salt removal from the electrolyte by the formation and harvesting of insoluble carbonates whose metal atoms are derived from the silicate mineral (Fig. 1*A*). This would then allow nonchloride salt/electrolyte recycling. V$_{DC}$, direct current voltage.

Table 2. Energy expended per mole of CO_2 captured and stored in the experiments

Mineral treatment	Total electricity applied, kJ_e	Net CO_2 captured and stored, mol	Observed energy cost, kJ_e/mol of CO_2	Observed efficiency, %	Energy cost at >50% efficiency, kJ_e/mol of CO_2	Energy expenditure previously reported for chemical air capture, kJ/mol of CO_2
None	0.166	1.84×10^{-6}	90,146	—	—	
Wollastonite	0.046	9.54×10^{-5}	481	23	<220	400–1,000
UM-4	0.061	1.40×10^{-4}	431	32	<274	
UM-4	0.168	3.95×10^{-4}	426	32	<274	

Data are derived from Table 1. Observed energy efficiency is the theoretical minimum work for the presumed respective chemical reactions (described in main text) multiplied by 100 and divided by the observed energy expenditure. The potential energy expenditure in optimized systems is based on the theoretical minimum work and assuming >50% energy efficiency in performing chemical work, which is typical of industrial electrochemical systems. Previous energy estimates for chemical air capture are from Zeman (14), Socolow et al. (16), and House et al. (17).

Electrolytes and chlorine generation. Natural chloride solutions, such as seawater, inland brines, and underground saline groundwater, represent the most abundant, and therefore the lowest cost electrolytes, but Cl_2, rather than O_2, is typically generated in the electrolysis of such solutions. If not safely consumed or used, large-scale Cl_2 release would pose serious environmental risks. It may be possible to avoid such emissions via the following: (*i*) use of oxygen-selective anodes (11), (*ii*) use of high- or low-electrode current densities (11), (*iii*) use of ion-selective membranes to exclude chloride ion from entering the anolyte, (*iv*) diversion of the H_2 produced at the cathode to a gas diffusion anode, or (*v*) use of less abundant nonchloride salts as in the experiments described here. Prevention of some or all gas evolution would reduce the overall electrical energy required, but would then forgo benefits/revenue from gas production.

Other concerns with the use of natural chloride solutions include the possible production of harmful halogenated organic compounds, as well as precipitation of inorganic compounds, and fouling of the electrodes, particularly the cathode (7). To avoid these issues, purer artificial chloride electrolytes could be formed from commercial minerals or evaporative NaCl (7), assuming a cost-effective source of water is available. Brief reversal of electrode polarity might be useful in removing electrode scale/precipitates, and/or periodic physical cleaning of the electrodes may be necessary.

Barring abundant low-cost sources, the use of nonchloride electrolytes would appear to dictate that these be conserved and recycled rather than used in a once-through fashion. One way to achieve this is to precipitate and harvest the captured carbon as a solid carbonate whose metal constituent is derived from the mineral silicate (Fig. 1*A*) rather than from electrolyte cations (Fig. 1*B*). This would then avoid loss of electrolyte in the once-through removal of dissolved bicarbonate, but it would also necessitate water recharge. It would also reduce the carbon capture and storage efficiency of the system: Only 1 mol of carbon could be stored (as carbonate) per mol of metal cations vs. 2 mol of carbon stored per mol of metal cations if metal bicarbonates are formed. The ability to precipitate metal carbonates whose metal is derived from mineral silicates, although theoretically possible (Fig. 1*A*), has yet to be demonstrated.

Air contacting. Although the absorption of CO_2 by the hydroxide produced could occur within the electrolysis cell, to increase air-contacting efficiency and capacity the hydroxide-enriched solution would more likely be periodically or continuously removed from the cell and used in air-contacting devices (e.g., refs. 14, 16, 17). This could include adding the solution to large bodies of water in contact with air, the ocean (70% of the Earth's surface: 3.61×10^8 km^2, excluding surface roughness) being the ultimate example of a planetary-scale, passive CO_2 absorber (7, 12, 19, 20). It would be necessary to add hydroxide to the ocean in dilute enough form to avoid potential negative environmental impacts, including keeping the pH below that which would negatively affect biota and below levels that trigger abiotic precipitation of seawater constituents, such as $CaCO_3$ and $Mg(OH)_2$. On the other hand, if safely achievable, such addition of alkalinity could be useful in countering ocean acidification and its biotic effects (7, 12).

Additionally, as discussed in the Introduction, adding hydroxide to the large regions of the surface ocean where seawater CO_2 concentration is higher than that of the overlying air would help mitigate atmospheric CO_2 by reducing natural ocean CO_2 emissions, and thus avoiding the necessity and complexity of directly capturing CO_2 from air.

Fate of silicon and other constituents. If solid silica formation in the anolyte is the ultimate fate of the mineral silicate moiety (see above), a means of removing and storing or using the silica would need to be considered in large-scale applications. A build-up of silica directly on the anode could compromise its functioning and would require periodic electrode polarity reversal and/or other cleaning methods. To the extent that soluble silica remains in solution, it would accompany the removal of the dissolved metal hydroxide or bicarbonate produced in the cell. If this solution were added to the ocean, this potential addition of soluble silica could enhance marine phytoplankton growth and additional air CO_2 consumption in regions where silicon is a limiting nutrient (9, 38). Biotic effects (positive or negative) could also occur with the addition of soluble metals (e.g., Fe, Cr, Mn) that are present in small quantities in many mineral silicates and whose local abundance in seawater can significantly influence marine biogeochemistry (39). Similarly, the fate, impact, or use of any metal salts formed from the electrolysis, for example, Mg or Ca sulfates or chlorides, would need to be considered in large-scale applications.

Siting. To minimize costs, large-scale air capture would best be located where capital, energy, and delivered reagent costs are minimized (7, 13). For example, systems using seawater as an electrolyte would be optimally sited at coastal locations, where solar-, wind-, or ocean-derived electricity would also be locally available and where silicate mineral resources and H_2 markets are in close proximity. The electrolysis could, in fact, be done directly in brine or seawater reservoirs or in the ocean, where the electrodes and silicate would penetrate the water surface from either stationary or mobile platforms (e.g., modified or specially designed ships). This would preclude the need and expense of pumping seawater into electrochemical facilities on land but would also require sea-going infrastructure, maintenance, and resupply. The electrochemical dissolution of the mineral silicate could then proceed in situ, generating hydroxide alkalinity and CO_2 absorption potential directly into the water body. However, as previously mentioned, the consequences or avoidance (or use) of various side reactions and byproducts produced during the electrolysis of seawater (e.g., Cl_2, chlorinated organics) would need to be carefully considered (7).

At inland sites, waste water, groundwater, or natural or artificial brine of appropriate salinity could be used for the process, with above- or below-ground reservoirs providing a storage area for the solution once reacted with CO_2. Alternatively, as mentioned above, it may be possible to precipitate, harvest, and store the carbon as a solid carbonate whose metal component is derived from the silicate mineral (Fig. 1*A*). This could then potentially allow the salt electrolyte to be recycled (with water recharge) rather than consumed or discarded, permitting the use of less abundant and more expensive nonchloride salts as electrolytes (Fig. 2).

Potential Economics. Lacking a demonstration of an optimized system at scale precludes a precise estimation of costs and revenues. Nevertheless, the following might be illustrative.

If a total energy requirement of 300 kJ$_e$/mol of CO_2 (see above) is assumed, this would equate to 1.9 megawatt hours of electricity (MWh$_e$) per metric ton (t) of CO_2 captured. Assuming an electricity cost of \$60/MWh$_e$ [e.g., unsubsidized wind-derived electricity (30)], the electricity cost of the system would be 1.9 × \$60 = \$114/t of CO_2 consumed. The advanced alkaline electrolyzer capital cost is reportedly \$600/t of H$_2$ produced (29, 40). Assuming a similar capital cost for the electrolyzer envisioned here yields a CO_2-equivalent capital cost of \$600 × 1 t of H$_2$ produced per 44 t of CO_2 captured = \$14/t of CO_2 captured. Nonelectrical and nonmineral operation and maintenance charges are assumed to be 3% of capital expenditure (29) or \$0.42/t of CO_2 captured.

Assuming that about 1.2 t of crushed silicate mineral will be consumed per t of CO_2 captured and converted to bicarbonate (reactions 1 and 2, and considering molecular weights) at a cost of \$20 per t of extracted, ground, and delivered silicate (2, 41) adds \$24/t of CO_2 captured. A total of 0.4 t of water is consumed per t of CO_2 captured, at an assumed cost of \$2/t of CO_2, which includes the pumping cost (if required; see in situ option above). The use of natural brine is assumed both for the electrolyte and for the water source, assuming that Cl$_2$ emission and other issues can be safely dealt with (see above). Passive air/solution contacting of the hydroxide once placed in the ocean or other large reservoir is assumed at a cost of \$0. The total gross cost of such a system is then \$114 + \$14 + \$0.42 + \$24 + \$2 ≈ \$154/t of CO_2 captured.

Assuming the market value of the H$_2$ produced is \$1,500 per t of H$_2$ (29), the revenue is then \$1,500 × 1/44 = \$34 per t of CO_2 consumed. This reduces the CO_2 capture cost to \$154 − \$34 = \$120/t of CO_2 captured. Other potential cost offsets (not monetarily valued here) might include the following: (*a*) energy storage and recovery, including load leveling and peak shaving via H$_2$ storage/oxidation, especially in the context of time-variable electricity production from renewable sources like solar and wind; (*b*) subsequent freshwater production via H$_2$ oxidation; (*c*) the value of O$_2$ or other gases produced; and (*d*) ocean acid mitigation via alkalinity addition (e.g., local or regional preservation or enhancement of economically important marine shellfish) (12, 42–44).

If 9 t of CO_2 are avoided per t of H$_2$ produced [via this carbon-negative electrolysis vs. carbon-positive natural gas reforming (29)], and if 44 t of CO_2 are captured from air per t of H$_2$ produced (Fig. 1, considering mole weights), a total of 9 + 44 = 53 t of CO_2 is then mitigated per t of H$_2$ produced, or 53 t × 1/44 = 1.2 t of CO_2 mitigated per t of CO_2 captured. This increases to 1.4 t of CO_2 mitigated per t of CO_2 captured if the H$_2$ produced is used to replace the use of conventional gasoline. The net cost per t of CO_2 mitigated is then \$120/1.4 = \$86/t of CO_2 mitigated. Additional CO_2 mitigation would occur if soluble silicon and/or trace metals, possibly derived from the electrolyzed solution, were added to the ocean to subsequently stimulate CO_2 capture and storage via enhanced marine photosynthesis (see above).

A net cost of <\$100/t of CO_2 mitigated is well below the \$600–\$1,000/t of CO_2 previously estimated for chemical/thermal air CO_2 capture that excludes storage costs (16, 17) and is even within the cost range of more conventional capture and geological storage of molecular CO_2 from point-source waste streams (45). However, lacking an optimized prototype system, the true cost-effectiveness and environmental benefit of this mineral/electrolysis-based CO_2 mitigation scheme at scale remain to be determined.

Conclusions

A method has been demonstrated at laboratory scale that uses the anolyte acidity normally produced in saline water electrolysis to accelerate silicate mineral dissolution in the course of producing H$_2$ and other gases. The resulting electrolyte solution was shown to be significantly elevated in hydroxide concentration, which was, in turn, strongly absorptive and retentive of CO_2. When powered by nonfossil electricity and consuming globally abundant minerals and saline solutions, such systems at scale might provide a relatively efficient high-capacity means to consume and store excess air CO_2 as environmentally beneficial seawater bicarbonate or carbonate while also producing a carbon-negative "super green" fuel or chemical feedstock, H$_2$. Notably, such electrochemical methods avoid the need for inefficient and costly thermal/mechanical processes required in concentrating CO_2 from air and in recycling of reagents, as inherent in most previously described chemical air capture systems (e.g., 13–17). Use of the produced hydroxide to consume excess ocean CO_2 would preclude the need for the equivalent amount of more technically complex direct air CO_2 capture and concentration while performing the same net atmospheric CO_2 mitigation. Chemical base/alkalinity addition to the ocean would also help neutralize or offset the effects of ocean acidification.

Further research is needed to determine optimum designs and operating procedures, cost-effectiveness, and the net environmental impact/benefit of electrochemically mediated air CO_2 capture and H$_2$ production using base minerals. We concur with Lackner et al. (18): "There is abundant R&D to be undertaken with regard to the various possible materials, components, and workings of air capture technology. Given the enormity of the global climate challenge…this R&D needs to be scaled up urgently." Methods that do not require concentrating molecular CO_2 from air (or from waste streams), as exemplified here, could point the way to more cost-effective, environmentally beneficial, and safer air CO_2 management with, in the present case, the added benefits of renewable fuel production and ocean alkalinity addition.

Materials and Methods

Three hundred milliliters of 0.25 M (0.5 N) Na$_2$SO$_4$ in deionized water was added to a 400-mL glass beaker into which was vertically suspended a graphite anode and cathode (each was 2 mm in diameter and 16.5 cm long, and was submerged to a depth of 5.5 cm) horizontally separated by a distance of 5.7 cm. Both the anode and cathode were contained and vertically centered in separate porous plastic tubes (perforated Falcon 15-mL centrifuge tubes, 1.5-cm outer diameter × 12 cm) that facilitated the support and placement of the electrodes, as well as their contact with the electrolyte. The inside wall and bottom of the anode container had been lined with a paper filter, and depending on the experiment conducted, the inside of the anode container was filled with ~12 g of either powdered wollastonite (CaSiO$_3$, NYAD 325; NYCO Minerals, Inc.) or a powdered ultramafic silicate rock standard (UM-4; Canada Centre for Mineral and Energy Technology), or it was left unfilled. The UM-4 material is a serpentenized hornblende metaperidotite from the Canadian Shield containing 38.8% SiO$_2$, 22.6% MgO, 12.5% FeO, 9.23% Al$_2$O$_3$, and smaller quantities of other constituents (46). The quantity of silicate added was such that the upper surface of the silicate mass was ~2.5 cm above the surface of the electrolyte, whereas about 5.5 cm of the mass and the vertically and centrally positioned electrode were submerged. The pH of the electrolyte was then measured using a calibrated Thermo Scientific Orion 8203BN pH probe (precision of ±0.01 units). A 40-mL solution sample was also taken via syringe and stored in a sealed vial in darkness at room temperature. The OH$^-$ concentration was calculated from pH: [OH$^-$] = $10^{(pH - 7.6)}$ μM.

The electrodes were then connected to a dc power source that produced a closed-circuit voltage averaging 3.5–3.6 V and a mean current of 7.1–9.5 mA (Table 1). Electrolysis ensued in all experiments, as evidenced by very gentle gas (H$_2$) bubbling from the cathode. The electrolysis was allowed to proceed for up to 1.5 h with the solution's pH periodically measured. At the end of electrolysis, pH was measured, the electrodes were removed, and a 40-mL solution sample taken and stored as above. The remaining solution was then gently bubbled (0.4 L/min) overnight with air. After at least 18 h of bubbling, the solution's pH was again measured and another 40-mL sample taken and stored. The duration of air bubbling was chosen for convenience and to ensure that air/solution equilibrium was attained as indicated by the final temporal stability of solution pH. In fact, the majority of the total pH depressions observed occurred within the first few hours of air bubbling.

Selected water samples taken in the preceding experiments were then analyzed for total DIC concentration using an OI Analytical 1030W carbon

analyzer that used phosphoric acid to convert DIC to $CO_{2(g)}$, followed by N_2 sparging and CO_2 quantification using a solid-state, nondispersive IR detector. Analytical precision was $\pm 5\%$. Na^+, Ca^{2+}, and Mg^{2+} concentrations were measured using a Thermo Electron XSeries inductively coupled plasma quadrupole mass spectrometer. Samples were diluted volumetrically with an internal standard solution in 2% nitric acid. A fully quantitative analysis using a linear calibration curve based on known National Institute of Standards and Technology traceable standards was performed. The internal standard was corrected for instrument drift and suppression from the digest matrix. Analytical uncertainty was about $\pm 5\%$. The raw DIC, Ca^{2+}, and Mg^{2+} concentrations were corrected for water loss by multiplying by the ratio of the initial to the final Na^+ concentrations in each experiment.

1. Lackner KS (2002) Carbonate chemistry for sequestering fossil carbon. *Annual Review of Energy and the Environment* 27:193–232.
2. Mazzotti M, et al. (2005) *IPCC Special Report on Carbon Dioxide Capture and Storage*, eds Metz BO, et al. (Cambridge Univ Press, Cambridge, UK), pp 319–337.
3. Stephens JC, Keith DW (2008) Assessing geochemical carbon management. *Clim Change* 90:217–242.
4. Kelemen PB, Matter J (2008) In situ carbonation of peridotite for CO_2 storage. *Proc Natl Acad Sci USA* 105:17295–17300.
5. Archer D, et al. (2009) Atmospheric lifetime of fossil fuel carbon dioxide. *Annu Rev Earth Planet Sci* 37:117–134.
6. Schuiling RD, Krijgsman P (2006) Enhanced weathering: An effective and cheap tool to sequester CO_2. *Clim Change* 74:349–354.
7. House KZ, House CH, Schrag DP, Aziz MJ (2007) Electrochemical acceleration of chemical weathering as an energetically feasible approach to mitigating anthropogenic climate change. *Environ Sci Technol* 41(24):8464–8470.
8. Köhler P, Hartmann J, Wolf-Gladrow DA (2010) Geoengineering potential of artificially enhanced silicate weathering of olivine. *Proc Natl Acad Sci USA* 107(47):20228–20233.
9. Köhler P, et al. (2013) Geoengineering impact of open ocean dissolution of olivine on atmospheric CO2, surface ocean pH and marine biology. *Environ Res Lett*, 10.1088/1748-9326/8/1/014009.
10. White AF, Brantley SL, eds (1995) Chemical weathering rates of silicate minerals. *Reviews in Mineralogy* 31:1–583.
11. Bennett JE (1980) Electrodes for generation of hydrogen and oxygen from seawater. *Int J Hydrogen Energy* 5:401–408.
12. Rau GH (2008) Electrochemical splitting of calcium carbonate to increase solution alkalinity: Implications for mitigation of carbon dioxide and ocean acidity. *Environ Sci Technol* 42(23):8935–8940.
13. Keith DW, Ha-Duong M, Stolaroff JK (2006) Climate strategy with CO_2 capture from the air. *Clim Change* 74:17–45.
14. Zeman F (2007) Energy and material balance of CO_2 capture from ambient air. *Environ Sci Technol* 41(21):7558–7563.
15. Keith DW (2009) Why capture CO_2 from the atmosphere? *Science* 325(5948):1654–1655.
16. Socolow R, et al. (2011) *Direct Air Capture of CO_2 with Chemicals* (American Physical Society, College Park, MD).
17. House KZ, et al. (2011) Economic and energetic analysis of capturing CO2 from ambient air. *Proc Natl Acad Sci USA* 108(51):20428–20433.
18. Lackner KS, et al. (2012) The urgency of the development of CO_2 capture from ambient air. *Proc Natl Acad Sci USA* 109(33):13156–13162.
19. Kheshgi HS (1995) Sequestering atmospheric carbon dioxide by increasing ocean alkalinity. *Energy* 20:915–922.
20. Harvey LDD (2008) Mitigating the atmospheric CO2 increase and ocean acidification by adding limestone powder to upwelling regions. *J Geophys Res Oceans* 113, 10.1029/2007JC004373.
21. Takahashi T, et al. (2009) Climatological mean and decadal change in surface ocean pCO2 and net sea-air CO_2 flux over the global oceans. *Deep Sea Res Part 2 Top Stud Oceanogr* 56:554–577.
22. Prentice IC, et al. (2001) *Climate Change 2001: The Scientific Basis: Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, ed Houghton JT (Cambridge Univ Press, Cambridge, UK), pp 183–237.
23. Cao L, Caldeira K (2010) Atmospheric carbon dioxide removal: Long-term consequences and commitment. *Environ Res Lett*, 10.1088/1748-9326/5/2/024011.
24. Lampitt RS, et al. (2008) Ocean fertilization: A potential means of geoengineering? *Phil Trans R Soc London A* 366:3919–3945.
25. Eisaman MD, et al. (2012) CO_2 extraction from seawater using bipolar membrane electrodialysis. *Energy Environ Sci* 5:7346–7352.
26. Schott J, et al. (2012) Formation, growth and transformation of leached layers during silicate minerals dissolution: The example of wollastonite. *Geochim Cosmochim Acta* 98:259–281.
27. Brantley SL, Chen Y (1995) Chemical weathering rates of pyroxenes and amphiboles. *Reviews in Mineral Chemistry* 31:119–172.
28. Ivy J (2004) *Summary of Electrolytic Hydrogen Production Milestone Completion Report NREL/MP-560-36734* (National Renewable Energy Laboratory, US Department of Energy, Golden, CO).
29. Committee on Alternatives and Strategies for Future Hydrogen Production and Use, National Research Council and National Academy of Engineering (2004) *The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs* (National Academy Press, Washington, DC).
30. Schmidt TS, Born R, Schneider M (2012) Assessing the costs of photovoltaic and wind power in six developing countries. *Nat Clim Change* 2:548–553.
31. Energy Information Agency (2013) *Electric Power Annual* (EIA, US Department of Energy, Washington, DC).
32. Tolan TL, et al. (1989) Revisions to the estimates of the areal extent and volume of the Columbia River Basalt Group. *Geological Society of America Special Papers* 239:1–20.
33. Raymond LA (2007) *Petrology: The Study of Igneous, Sedimentary, and Metamorphic Rocks* (Waveland Press, Long Grove, IL), 2nd Ed.
34. Blum AE, Stillings LL (1995) Feldspar dissolution kinetics. *Reviews in Mineral Geochemistry* 31:291–351.
35. Oelkers EH (2001) A general kinetic description of multi-oxide silicate mineral and glass dissolution. *Geochim Cosmochim Acta* 65:3703–3719.
36. Carroll SA, Knauss KG (2005) Dependence of labradorite dissolution kinetics on $CO_{2(aq)}$, $Al_{(aq)}$, and temperature. *Chem Geol* 217:213–225.
37. Hangx SJ, Spiers CJ (2009) Coastal spreading of olivine to control atmospheric CO_2 concentrations: A critical analysis of viability. *Int J Greenhouse Gas Control* 3:757–767.
38. Tréguer PJ, De La Rocha CL (2013) The world ocean silica cycle. *Annu Rev Mar Sci* 5:477–501.
39. Morel FMM, Price NM (2003) The biogeochemical cycles of trace metals in the oceans. *Science* 300(5621):944–947.
40. Bourgeois R (2006) *Alkaline Electrolysis Final Technical Report, DOE Award DE-FC36-04GO14223* (General Electric Global Research Center, Niskayuna, NY).
41. Steen B, Borg G (2002) An estimation of the cost of sustainable production of metal concentrates from the earth's crust. *Ecol Econ* 42:401–413.
42. Rau GH (2011) CO_2 mitigation via capture and chemical conversion in seawater. *Environ Sci Technol* 45(3):1088–1092.
43. Hollier W, Rau GH, Andrew Dicks A, Bainbridge S (2011) Reef climate adaptation research and technology. *International Journal of Climate Change: Impacts and Responses* 2:127–142.
44. Rau GH, McLeod EL, Hoegh-Guldberg O (2012) The need for new ocean conservation strategies in a high-carbon dioxide world. *Nat Clim Change* 2:720–724.
45. Rubin ES, Zhai H (2012) The cost of carbon capture and storage for natural gas combined cycle power plants. *Environ Sci Technol* 46(6):3076–3084.
46. Tetley NW, Turek A (1974) Chemical analyses of ultramafic rock standards: UM-1, UM-2, UM-4. *Chem Geol* 14:135–139.