Viability of greenhouse gas removal via the artificial addition of volcanic ash to the ocean

Jack Longmana,[b,c*,] Martin R. Palmer[b], Thomas M. Gernon[b]

[a] Marine Isotope Geochemistry, Institute for Chemistry and Biology of the Marine Environment (ICBM), University of Oldenburg, PO Box 2503, 26111 Oldenburg, Germany

[b] School of Ocean and Earth Sciences, University of Southampton, Southampton SO14 3ZH, UK

[c] School of Geography and the Environment, University of Oxford, South Parks Road, Oxford, OX1 3QY, UK

[*]Corresponding Author: jack.longman@uni-oldenburg.de

Abstract

Attempts to mitigate human contributions to climate change have become a highly debated topic, as it becomes evident that optional global emission reductions are not being adhered to by many nations. Therefore, substantial research is taking place into negative carbon technologies that actively reduce the amount of atmospheric carbon dioxide (CO_2), via greenhouse gas removal (GGR). Various GGR methods have been proposed, from reforestation to ocean fertilisation. Here, we discuss the advantages of an approach based on the enhanced input of tephra to the ocean, to increase the drawdown of atmospheric CO_2. Natural addition of tephra to the ocean results in enhanced organic matter preservation in sediment; hence augmenting its delivery should raise the level of sequestration. Our calculations indicate offshore tephra addition could sequester 2750 tonnes of CO_2 per 50,000 tonnes of ash delivered (a typical bulk carrier's capacity). The cost is estimated to be ~$55 per tonne of CO_2 sequestered and is an order of magnitude cheaper than many other proposed GGR technologies. Further advantages include; tephra addition is simply an augmentation of a natural Earth process, it is a low technology approach that requires few developments, and it may sequester carbon for thousands of years. Hence, we suggest offshore tephra addition warrants further investigation to assess its viability.

Keywords

29 Greenhouse Gas Removal, geoengineering, offshore tephra addition, volcanic ash, diagenesis,
30 climate change

31 Introduction

32 Proposals have recently been made to remediate human contributions to climate change
33 through geoengineering, leading to considerable discussion of the topic (Royal Society, 2018).
34 To ensure the world stays below the IPCC upper limit to "safe" warming (IPCC, 2018),
35 additional measures other than non-binding agreements will be required (Haszeldine et al.,
36 2018; Tollefson, 2018). Hence, Greenhouse Gas Removal (GGR), via geoengineering, has
37 been posited to reduce levels of anthropogenic carbon dioxide (CO_2) in the atmosphere, thus
38 avoiding large-scale impacts of climate change such as ecosystem collapse and major changes
39 in ocean circulation (Lomax et al., 2015; Steffen et al., 2018).

40 A variety of GGR methods have been proposed, from reforestation and habitat restoration (e.g.
41 (e.g. Bastin et al., 2019), to infrastructural changes, such as low-carbon concrete production
42 (Ghouleh et al., 2017) and the use of biomass in building materials (e.g. Ramage et al., 2016).
43 Other GGR proposals involve enhancing the rate at which the Earth's natural carbon cycle
44 sequesters atmospheric CO_2 in natural sinks (Royal Society, 2018). Examples of natural cycle
45 manipulation include increasing the alkalinity of the ocean (i.e., reversing ocean acidification
46 (Renforth and Henderson, 2017)), enhancing mineral carbonation (i.e., converting silicate
47 rocks into carbonates (Matter et al., 2016)) and ocean fertilization (i.e., enhancing
48 photosynthetic carbon removal (Boyd et al., 2007)).

49 All proposed GGR interventions have associated risks, and face scientific, economic and
50 societal barriers to implementation. For example, repurposing terrestrial biomass for carbon
51 sequestration necessarily requires the utilization of agricultural land currently used to produce
52 food. Manipulation of natural cycles also suffer from an unpalatable image due to perceived
53 meddling with the natural world, and potential impacts on ecosystems (Royal Society, 2018).

No single mechanism of emissions reduction or GGR can feasibly halt the rise in atmospheric CO_2 levels (Royal Society, 2018), so it is beneficial to consider a range of emissions reduction and GGR strategies that have lesser risks and implementation barriers, rather than adoption of a single big impact, high-risk strategy. Hence, we present a potential GGR mechanism based on enhanced input of the products of explosive volcanism (Figure 1) into the oceans. This approach builds on the role that natural tephra deposition in the oceans plays in the carbon cycle (Figure 2) (Longman et al., 2019) and examines the potential enhancement of these natural processes to achieve GGR. Based on real-world data, we calculate the potential of the proposed method to sequester atmospheric carbon, and provide an estimate of likely costs.

The Approach

It is estimated that the global amount of organic carbon (C_{org}) reaching the seafloor is equivalent to 8.4 Gt CO_2 a^{-1}, of which ~13% is buried and 87% returned to the ocean-atmosphere (Burdige, 2007). The variety of processes controlling the C_{org} burial efficiency (CBE) lead to wide geographical variations in this value, from >70% to <0.3%; (Dunne et al., 2007). Within these processes there are four distinct mechanisms by which tephra deposition enhances CBE (Longman et al., 2019), outlined below.

Fertilization

Tephra releases nutrients, such as dissolved Iron (Fe), to surface waters when it falls into the oceans, and may thus stimulate biological productivity where availability of nutrients limits phytoplankton growth (Olgun et al., 2011). This process has been the subject of extensive study (e.g., see Olgun et al. (2011) and Duggen et al. (2010) for reviews). For example, phytoplankton blooms occurred when tephra was deposited in the nutrient-poor NE Pacific Ocean following eruption of Kasatochi volcano (Langmann et al., 2010; Olgun et al., 2011), in the vicinity of the Mariana Islands following the 2003 Anatahan eruption (Lin et al., 2011), after the eruption of Miyake-jima in 2000 (Uematsu et al., 2004), and potentially in the

Southern Pacific after the eruption of Pinatubo in 1991 (Siegenthaler and Sarmiento, 1993). Other research suggests subduction zone-related ash deposition may play a role in controlling productivity (Duggen et al., 2007). In each case, the increased productivity sequestered CO_2 from the ocean-atmosphere. For example, the 2008 eruption of Kasatochi led to the export of ~0.01 Pg carbon from the upper ocean (Hamme et al., 2010). Carbon was removed from the upper oceans when phytoplankton (and their consumers) settled out of the upper ocean and into the deep ocean (the 'biological pump'; Sarmiento and Gruber, 2006). In addition to accelerating the rate of the biological pump (Fig. 2), tephra deposition in the surface oceans also likely enhances the transport of organic carbon (C_{org}) from surface oceans into deeper water because plankton debris may become physically associated with the negatively buoyant particles (e.g., Rubin et al., 2011). This leads to the incorporation of dense, Fe-rich dust (and by analogy tephra) in algal colonies, ballasting the tephra and enhancing sinking rates (Pabortsava et al., 2017).

Dissolved Oxygen (O_2) consumption

Much of the Fe contained within tephra is in the form of Fe^{II} (Maters et al., 2017), which is highly reactive and rapidly oxidized to Fe^{III} through pore water O_2 consumption. This process also occurs during tephra transport through the water column, but due to ballasting tephra settling rates are too fast for this to be significant, leading to the export of a large proportion of Fe^{II} to the sediment (Hembury et al., 2012). Once sufficient tephra (i.e., a layer >0.5 cm thick) accumulates on the ocean floor, oxidation of Fe^{II} in the tephra causes dissolved O_2 concentrations fall to zero within sediment pore waters, reducing the exposure of the newly deposited C_{org} to oxidative processes (Haeckel et al., 2001; Hembury et al., 2012). Because the oxidation of labile C_{org} in marine sediments is critically dependent on dissolved O_2 levels in pore water (Hartnett et al., 1998), the presence of tephra likely enhances C_{org} preservation in sediments and further sequesters CO_2 from the ocean-atmosphere system (Fig. 2).

Colloidal association

Tephra contains high concentrations of reactive Fe Mn and Al (Homoky et al., 2011). These reactive phases form stable colloids with C_{org} (Lalonde et al., 2012), inhibiting C_{org} oxidation and enhancing preservation (Fig. 2). Notably, the colloid–C_{org} complexes are sufficiently stable to protect C_{org} from oxidation even if they are transported from shelf environments to the deep sea (Dunne et al., 2007).

Authigenic carbonate formation

Tephra is also rich in divalent cations released into sediment pore waters during diagenesis (Gieskes, 1983; Murray et al., 2018). One proposed method of GGR is to increase ocean alkalinity, through artificial addition of divalent cations to the ocean (Kheshgi, 1995; Renforth and Henderson, 2017). Within marine sediments, cations released from tephra react with the enhanced alkalinity created by C_{org} oxidation, resulting in the precipitation of authigenic calcium carbonate and calcium-magnesium carbonate ($Ca(Mg)CO_3$). Again, this process effectively locks carbon derived from C_{org} into a form that may be stable for millennia (Schrag et al., 2013).

Technology readiness

Addition of tephra to the oceans requires no new technology and ocean fertilization experiments have proven feasible (Boyd et al., 2007). In mesoscale experiments, artificial Fe addition enhances phytoplankton productivity in high nutrient, low chlorophyll environments by alleviating Fe-related nutrient limitation (Martin and Fitzwater, 1988). Phytoplankton blooms as a result of natural tephra addition to HNLC regions have also been observed, confirming the fertilizing potential of tephra in these environments (Langmann et al., 2010; Olgun et al., 2011). The mechanisms relating to the impact of tephra within seafloor sediments indicate that sequestration of plankton-produced C_{org} may occur over millennial timescales, but

128 an assessment of the amount of tephra deposition required to enable significant levels of carbon
129 sequestration is required.

130 Most active terrestrial volcanoes produce tephra and, with the exception of Australia, it is
131 produced on every continent (Fig. 3). Tephra is one of the most common components of global
132 oceanic sediments, such that it comprises ~25% of Pacific Ocean sediments (Scudder et al.,
133 2016), and with an estimated yearly flux of ash to the Pacific Ocean of $0.13 – 0.22 \times 10^{15}$ g a^{-1}
134 (Olgun et al., 2011). Quarrying of recent tephra (optimal for this proposed method) provides
135 aggregate for cement works and road surfaces, but supplies are not limiting. Large recent
136 deposits of basaltic tephra are located across the globe (Fig. 3). In addition, bentonite clay
137 (diagenetically altered tephra) mining is well-established (Eisenhour and Brown, 2009), so
138 novel, energy-intensive, extraction techniques are not required. Most tephra extraction occurs
139 in open pits using bucket loaders so would only require sorting of the unconsolidated tephra to
140 grain size <63μm, the fraction containing most Fe-rich minerals (Homoky et al., 2011).

141 **Storage potential and longevity of storage**

142 The gross storage potential is defined here as the increase in CO_2 storage resulting from tephra
143 addition to the oceans. The net storage potential is the gross storage minus the CO_2 requirement
144 of delivering the tephra to the oceans; although the latter value is not included in most methods
145 evaluated in the GGR Royal Society report (Royal Society, 2018).

146 Here, we provide an estimate of the potential carbon storage using the Peru margin as an
147 example due to its naturally high primary productivity, resulting from upwelling of nutrient-
148 rich Pacific bottom waters (Pennington et al., 2006). The high productivity leads to depletion
149 of O_2 in the water column, and an oxygen minimum zone (OMZ) bathing sediment to depths
150 of 400m (Bohlen et al., 2011). As a result, the sediments contain up to 15% C_{org} below the
151 OMZ (Arthur et al., 1998). CBE increases from 18% on the inner shelf (with no OMZ) to
152 average of 47% below the OMZ (Dale et al., 2015) due to the reduced oxidant exposure.

153 Table 1 contains an estimate of the key parameters required to assess gross and net potential
154 storage of C_{org} on the inner shelf through the addition of tephra to these sediments. In these
155 calculations, we assume that reduced oxidant exposure in the sediments resulting from tephra
156 addition, yields a similar increase in CBE to that resulting from the OMZ. As with all GGR
157 strategies, there are large uncertainties in evaluating these parameters, in particular CBEs.
158 Nevertheless, this exercise is useful for provide a comparison with other GGR strategies with
159 similar uncertainties (Royal Society, 2018) (Table 2).

160 The calculated net potential removal is ~2300 t of CO_2 per 50,000 t of tephra delivered to the
161 oceans per year. The impact of Fe fertilization has a limited duration, but each addition of
162 tephra to the seafloor will impact C_{org} storage for hundreds to thousands of years. Table 1
163 assumes a tephra layer of 5 mm is required to achieve the calculated increase in CBE, but
164 microelectrode studies of tephra deposited on the seafloor reveal that pore water dissolved O_2
165 concentrations can fall to <50% of bottom water levels within 1 mm of the sediment-water
166 interface (Hembury et al., 2012). Thus, the dependence of CBE on dissolved O_2 exposure
167 times (Hartnett et al., 1998) would likely lead to enhanced CO_2 storage even under minimal
168 tephra loading. Note also, that the natural CBEs observed on the Peru margin are not typical
169 of shelf sediments. The average CBE in sandy sediments, that represent 70% of the global
170 area of continental shelves with water depths <200 m, is ~1% (Burdige, 2007). Hence,
171 selection of optimal seafloor sites for large increases in gross potential storage (i.e. large C_{org}
172 fluxes, but low CBE, delivery of optimum amounts of tephra to achieve maximum increase in
173 C_{org} preservation) and net potential storage (i.e. close to readily accessible tephra deposits) may
174 yield potential CO_2 storage rates similar to those described in Table 1. In addition, timing
175 tephra loading to coincide with the maximum rate of C_{org} deposition at the sediment surface
176 (e.g. following phytoplankton blooms) would further enhance the scale of C_{org} preservation.
177 During seasonal upwelling, there is high C_{org} production in surface waters and fluxes to the

seafloor, but it is largely remineralised in oxygenated nature of the bottom waters, yielding low CBEs (Dale et al., 2015). Timing tephra delivery to just after the upwelling period may result in large absolute carbon burial.

Resources required

The only processing of the tephra prior to its use would be light crushing and sorting. Spreading tephra over the ocean would require infrastructure, including loading terminals and adapted ships (i.e. with mechanisms for tephra release), but land transport costs would be low because most volcanoes are located close to the oceans (Fig. 3). Marine vessels require an energy source, but the use of redundant coal barges could reduce CO_2 emissions. Freshly deposited tephra is unconsolidated and can be removed and loaded into transport using conventional excavators and trucks. In comparison to a number of other proposed GGR methods, this approach is uncomplicated (Table 2). Ocean fertilization, for example, requires the processing of Fe^{II}-rich solution (Boyd et al., 2000), and other proposals require entirely new approaches to infrastructural development (e.g. carbon capture and storage; Royal Society, 2018). In contrast, offshore tephra addition would require; i) loading of ash onto barges; ii) travel to site of optimal loading as determined via study of seafloor environment and ocean currents (see Boyd et al., 2000); and iii) release of ash in a steady manner along prescribed paths.

Environmental benefits and challenges

Ocean-wide changes in bottom water and deep-sea oxygenation levels have been invoked as one of the causes of benthic foraminiferal extinction at the Cretaceous-Tertiary boundary (e.g., Coccioni and Galeotti, 1994). Hence, it has been suggested that tephra deposition on the seafloor may have a similar on benthic communities. For example, ash fall associated with the 1991 Mt. Pinatubo eruption caused mass mortality of benthic foraminifers over a large area of the South China Sea (Hess and Kuhnt, 1996), with mortality of all benthic foraminifers at sites receiving 6-8 cm of tephra. In addition, there was a reduction in species diversity at sites

receiving ~2 cm of tephra (Hess et al., 2001; Hess and Kuhnt, 1996). However, whereas recovery of the benthic community from the K-T extinction took several thousand years (Coccioni and Galeotti, 1994), recovery of South China Sea sediments was largely complete less than 10 years after tephra deposition, even in the areas that received the thickest deposits (Hess et al., 2001; Kuhnt et al., 2005). Tephra may leach some toxic elements into the water column (Jones and Gislason, 2008), and in some circumstances can lead to a drop in the pH of seawater as acids are released (Frogner Kockum et al., 2006; Frogner et al., 2001). Other impacts of tephra deposition are unknown, including potential impacts on planktic, and larger organisms. However, while large scale tephra input to surface waters in the immediate vicinity of volcanoes may be harmful, there is no evidence that the initial mortality is long-lasting or widespread (Hoffmann et al., 2012; Jones and Gislason, 2008; Wall-Palmer et al., 2011). There are also examples from the geologic record showing that pre-deposition benthic ostracod species survived at least 6 cm of tephra deposition (Perrier et al., 2012). Nevertheless, environmental impact assessments would be required to examine ecosystem responses to enhanced tephra loading.

Tephra extraction will lead to environmental impacts on-shore, but most types of tephra are of low toxicity and the risks can be mitigated by standard procedures such as cast-back mining adopted during industrial bentonite extraction (Eisenhour and Brown, 2009).

Scalability and engineering challenges

As with ocean fertilization through iron addition, tephra fertilization should be scalable without significant cost increases. The financial cost/benefit ratio depends on the scale of operations and the site selection. Typical charter rates for 50,000 t bulk carriers are ~\$10,000 d^{-1} which, for a 2000 km deployment at 20 km hr^{-1} and 2 days loading (UNCTAD, 2018), yields a cost of ~\$70,000 per deployment. Terrestrial transport costs will increase this estimate. If we assume ~\$600 d^{-1} to hire a 44-tonne truck, and ten 60-km round journeys are possible per day, then

~$68,000 will be necessary per deployment. Even so, the estimated cost of $55 per tCO_2 deployed, based on the estimates in Table 1, is an order of magnitude lower than many other GGR technologies (Table 2, Royal Society, 2018).

Monitoring and evaluation

Many of the risks to implementation and optimization of tephra dispersal can be investigated in laboratory studies. Both natural (e.g. Hamme et al., 2010; Langmann et al., 2010; Olgun et al., 2011) and laboratory studies (e.g. Hoffmann et al., 2012; Mélançon et al., 2014) have shown that ash fertilizes phytoplankton productivity, so the primary risk is that the approach does not sufficiently raise CBEs. This question may be tackled by undertaking experiments to measure C_{org} degradation rates under various conditions of tephra loading and over a range of sediment types. The responses of benthic biota to tephra loading can also be investigated in laboratory studies (cf. Brown et al., 2017). Once laboratory tests are completed, small-scale *in situ* studies would be necessary to test the concept, with several years of monitoring.

Social factors

Natural volcanic processes transport millions of tonnes of tephra to the oceans every year, with an estimated 2.2×10^8 t yr deposited in the Pacific Ocean alone (Olgun et al., 2011). Hence, unlike most other proposed GGR interventions, the mechanism outlined here is an augmentation to a naturally occurring process. In addition, tephra addition to the ocean does not require changes to land use, such as reforestation of agricultural land. Freshly deposited tephra frequently creates a barren landscape in volcanic areas, and following eruptions governments may have to invest funds to clear tephra from local infrastructure. Hence, tephra deposits can be seen as a problem that requires a solution. Nevertheless, public opinion regarding any GGR initiative is likely to be mixed (Royal Society, 2018), and it would be important to undertake public engagement to communicate the positive aspects of the approach.

Policy factors

The ‘dumping’ of material in international waters is currently banned under the London Convention and Protocol, but the restriction of tephra loading to shallow waters within territorial waters of individual nations is less clear and would require clarification.

Conclusions

We have outlined how artificial addition of tephra to the ocean may lead to C_{org} sequestration and GGR, and have discussed its positive and negative aspects. The advantages of tephra dispersal in this regard are:

- tephra addition to the oceans is a natural process
- tephra is widely distributed around the world
- the technology is simple and readily available
- no repurposing of valuable land resources is required
- tephra is not a scarce resource

The key factors required to transform this hypothesis into a potentially viable GGR method are:

- optimization to achieve maximum GGR for minimal tephra loading
- identification of optimal oceanic sites
- determination of potential ecological impacts
- assessment of prime locations for sourcing tephra and optimal approaches for transporting tephra to the ocean
- assessment of the scalability and economics required to have a significant GGR impact

Based on this analysis, we suggest there is a prima facie case for further study of tephra addition to the oceans as part of the palette of strategies to achieve GGR.

References

Arthur, M.A., Dean, W.E., Laarkamp, K., 1998. Organic carbon accumulation and preservation in surface sediments on the Peru margin. Chem. Geol. 152, 273–286. https://doi.org/10.1016/S0009-2541(98)00120-X

Bastin, J.-F., Finegold, Y., Garcia, C., Mollicone, D., Rezende, M., Routh, D., Zohner, C.M., Crowther, T.W., 2019. The global tree restoration potential. Science (80-.). 365, 76–79. https://doi.org/10.1126/SCIENCE.AAX0848

Bohlen, L., Dale, A.W., Sommer, S., Mosch, T., Hensen, C., Noffke, A., Scholz, F., Wallmann, K., 2011. Benthic nitrogen cycling traversing the Peruvian oxygen minimum zone. Geochim. Cosmochim. Acta 75, 6094–6111. https://doi.org/10.1016/j.gca.2011.08.010

Boyd, P.W., Jickells, T., Law, C.S., Blain, S., Boyle, E.A., Buesseler, K.O., Coale, K.H., Cullen, J.J., de Baar, H.J.W., Follows, M., Harvey, M., Lancelot, C., Levasseur, M., Owens, N.P.J., Pollard, R., Rivkin, R.B., Sarmiento, J., Schoemann, V., Smetacek, V., Takeda, S., Tsuda, A., Turner, S., Watson, A.J., 2007. Mesoscale iron enrichment experiments 1993-2005: synthesis and future directions. Science 315, 612–7. https://doi.org/10.1126/science.1131669

Boyd, P.W., Watson, A.J., Law, C.S., Abraham, E.R., Trull, T., Murdoch, R., Bakker, D.C.E., Bowie, A.R., Buesseler, K.O., Chang, H., Charette, M., Croot, P., Downing, K., Frew, R., Gall, M., Hadfield, M., Hall, J., Harvey, M., Jameson, G., LaRoche, J., Liddicoat, M., Ling, R., Maldonado, M.T., McKay, R.M., Nodder, S., Pickmere, S., Pridmore, R., Rintoul, S., Safi, K., Sutton, P., Strzepek, R., Tanneberger, K., Turner, S., Waite, A., Zeldis, J., 2000. A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. Nature 407, 695–702.

https://doi.org/10.1038/35037500

Brown, A., Thatje, S., Hauton, C., 2017. The Effects of Temperature and Hydrostatic Pressure on Metal Toxicity: Insights into Toxicity in the Deep Sea. Environ. Sci. Technol. 51, 10222–10231. https://doi.org/10.1021/acs.est.7b02988

Burdige, D.J., 2007. Preservation of organic matter in marine sediments: Controls, mechanisms, and an imbalance in sediment organic carbon budgets? Chem. Rev. 107, 467–485. https://doi.org/10.1021/cr050347q

Coccioni, R., Galeotti, S., 1994. K-T boundary extinction: geologically instantaneous or gradual event? Evidence from deep-sea benthic foraminifera. Geology 22, 779–782. https://doi.org/10.1130/0091-7613(1994)022<0779:KTBEGI>2.3.CO;2

Dale, A.W., Sommer, S., Lomnitz, U., Montes, I., Treude, T., Liebetrau, V., Gier, J., Hensen, C., Dengler, M., Stolpovsky, K., Bryant, L.D., Wallmann, K., 2015. Organic carbon production, mineralisation and preservation on the Peruvian margin. Biogeosciences 12, 1537–1559. https://doi.org/10.5194/bg-12-1537-2015

Duggen, S., Croot, P., Schacht, U., Hoffmann, L., 2007. Subduction zone volcanic ash can fertilize the surface ocean and stimulate phytoplankton growth: Evidence from biogeochemical experiments and satellite data. Geophys. Res. Lett. 34, L01612. https://doi.org/10.1029/2006GL027522

Duggen, S., Olgun, N., Croot, P., Hoffmann, L., Dietze, H., Delmelle, P., Teschner, C., Skolen, A.P.M., 2010. The role of airborne volcanic ash for the surface ocean biogeochemical iron-cycle: a review, Biogeosciences.

Dunne, J.P., Sarmiento, J.L., Gnanadesikan, A., 2007. A synthesis of global particle export from the surface ocean and cycling through the ocean interior and on the seafloor.

322 Global Biogeochem. Cycles 21, n/a-n/a. https://doi.org/10.1029/2006GB002907

323 Eisenhour, D.D., Brown, R.K., 2009. Bentonite and its impact on modern life. Elements.
324 https://doi.org/10.2113/gselements.5.2.83

325 Falkowski, P., Scholes, P.J., Boyle, E., Canadell, J., Canfield, D., Elser, J., Gruber, N.,
326 Hibbard, K., Högberg, P., Linder, S., Mackenzie, F.T., Moore III, B., Pedersen, T.,
327 Rosenthal, Y., Seitzinger, S., Smetacek, V., Steffen, W., 2000. The Global Carbon
328 Cycle: A Test of Our Knowledge of Earth as a System. Science (80-.). 290, 291–296.
329 https://doi.org/10.1126/science.274.5291.1346

330 Frogner Kockum, P.C., Herbert, R.B., Gislason, S.R., 2006. A diverse ecosystem response to
331 volcanic aerosols. Chem. Geol. 231, 57–66.
332 https://doi.org/10.1016/j.chemgeo.2005.12.008

333 Frogner, P., Reynir Gíslason, S., Óskarsson, N., 2001. Fertilizing potential of volcanic ash in
334 ocean surface water. Geology 29, 487. https://doi.org/10.1130/0091-
335 7613(2001)029<0487:FPOVAI>2.0.CO;2

336 Ghouleh, Z., Guthrie, R.I.L., Shao, Y., 2017. Production of carbonate aggregates using steel
337 slag and carbon dioxide for carbon-negative concrete. J. CO2 Util. 18, 125–138.
338 https://doi.org/10.1016/j.jcou.2017.01.009

339 Gieskes, J.M., 1983. The chemistry of interstitial waters of deep sea sediments: interpretation
340 of deep sea drilling data, in: Riley, J.P., Chester, R. (Eds.), Chemical Oceanography.
341 Academic Press, London, pp. 221–269.

342 Gudmundsson, M.T., Thordarson, T., Höskuldsson, Á., Larsen, G., Björnsson, H., Prata, F.J.,
343 Oddsson, B., Magnússon, E., Högnadóttir, T., Petersen, G.N., Hayward, C.L.,
344 Stevenson, J.A., Jónsdóttir, I., 2012. Ash generation and distribution from the April-May

2010 eruption of Eyjafjallajökull, Iceland. Sci. Rep. 2, 572. https://doi.org/10.1038/srep00572

Haeckel, M., van Beusekom, J., Wiesner, M.G., König, I., 2001. The impact of the 1991 Mount Pinatubo tephra fallout on the geochemical environment of the deep-sea sediments in the South China Sea. Earth Planet. Sci. Lett. 193, 151–166. https://doi.org/10.1016/S0012-821X(01)00496-4

Hamme, R.C., Webley, P.W., Crawford, W.R., Whitney, F.A., DeGrandpre, M.D., Emerson, S.R., Eriksen, C.C., Giesbrecht, K.E., Gower, J.F.R., Kavanaugh, M.T., Peña, M.A., Sabine, C.L., Batten, S.D., Coogan, L.A., Grundle, D.S., Lockwood, D., 2010. Volcanic ash fuels anomalous plankton bloom in subarctic northeast Pacific. Geophys. Res. Lett. 37, n/a-n/a. https://doi.org/10.1029/2010GL044629

Hartnett, H.E., Keil, R.G., Hedges, J.I., Devol, A.H., 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. Nature 391, 572–575. https://doi.org/10.1038/35351

Haszeldine, R.S., Flude, S., Johnson, G., Scott, V., 2018. Negative emissions technologies and carbon capture and storage to achieve the Paris Agreement commitments. Philos. Trans. R. Soc. A Math. Eng. Sci. 376, 20160447. https://doi.org/10.1098/rsta.2016.0447

Hembury, D.J., Palmer, M.R., Fones, G.R., Mills, R.A., Marsh, R., Jones, M.T., 2012. Uptake of dissolved oxygen during marine diagenesis of fresh volcanic material. Geochim. Cosmochim. Acta 84, 353–368. https://doi.org/10.1016/J.GCA.2012.01.017

Hess, S., Kuhnt, W., 1996. Deep-sea benthic foraminiferal recolonization of the 1991 Mt. Pinatubo ash layer in the South China Sea. Mar. Micropaleontol. 28, 171–197. https://doi.org/10.1016/0377-8398(95)00080-1

Hess, S., Kuhnt, W., Hill, S., Kaminski, M.A., Holbourn, A., de Leon, M., 2001. Monitoring the recolonization of the Mt Pinatubo 1991 ash layer by benthic foraminifera. Mar. Micropaleontol. 43, 119–142. https://doi.org/10.1016/S0377-8398(01)00025-1

Hoffmann, L.J., Breitbarth, E., Ardelan, M.V., Duggen, S., Olgun, N., Hassellöv, M., Wängberg, S.-Å., 2012. Influence of trace metal release from volcanic ash on growth of Thalassiosira pseudonana and Emiliania huxleyi. Mar. Chem. 132–133, 28–33. https://doi.org/10.1016/J.MARCHEM.2012.02.003

Homoky, W.B., Hembury, D.J., Hepburn, L.E., Mills, R.A., Statham, P.J., Fones, G.R., Palmer, M.R., 2011. Iron and manganese diagenesis in deep sea volcanogenic sediments and the origins of pore water colloids. Geochim. Cosmochim. Acta 75, 5032–5048. https://doi.org/10.1016/J.GCA.2011.06.019

IPCC, 2018. Summary for Policymakers, in: Masson-Delmotte, V., Zhai, P., Pörtner, H.O., Roberts, D., Skea, J., Shukla, P.R., Pirani, A., Chen, Y., Connors, S., Gomis, M., Lonnoy, E., Matthews, J.B.R., Moufouma-Okia, W., Péan, C., Pidcock, R., Reay, N., Tignor, M., Waterfield, T., Zhou, X. (Eds.), Global Warming of 1.5°C. An IPCC Special Report on the Impacts of Global Warming of 1.5°C above Pre-Industrial Levels and Related Global Greenhouse Gas Emission Pathways, in the Context of Strengthening the Global Response to the Threat of Climate Change,. World Meteorological Organization, Geneva, p. 32. https://doi.org/10.1017/CBO9781107415324

Jones, M.T., Gislason, S.R., 2008. Rapid releases of metal salts and nutrients following the deposition of volcanic ash into aqueous environments. Geochim. Cosmochim. Acta 72, 3661–3680. https://doi.org/10.1016/j.gca.2008.05.030

Kheshgi, H.S., 1995. Sequestering atmospheric carbon dioxide by increasing ocean alkalinity. Energy 20, 915–922. https://doi.org/10.1016/0360-5442(95)00035-F

392 Kuhnt, W., Hess, S., Holbourn, A., Paulsen, H., Salomon, B., 2005. The impact of the 1991
393 Mt. Pinatubo eruption on deep-sea foraminiferal communities: A model for the
394 Cretaceous–Tertiary (K/T) boundary? Palaeogeogr. Palaeoclimatol. Palaeoecol. 224,
395 83–107. https://doi.org/10.1016/J.PALAEO.2005.03.042

396 Lalonde, K., Mucci, A., Ouellet, A., Gélinas, Y., 2012. Preservation of organic matter in
397 sediments promoted by iron. Nature 483, 198–200. https://doi.org/10.1038/nature10855

398 Langmann, B., Zakšek, K., Hort, M., Duggen, S., 2010. Volcanic ash as fertiliser for the
399 surface ocean, Atmos. Chem. Phys.

400 Lin, I.I., Hu, C., Li, Y.H., Ho, T.Y., Fischer, T.P., Wong, G.T.F., Wu, J., Huang, C.W., Chu,
401 D.A., Ko, D.S., Chen, J.P., 2011. Fertilization potential of volcanic dust in the low-
402 nutrient low-chlorophyll western North Pacific subtropical gyre: Satellite evidence and
403 laboratory study. Global Biogeochem. Cycles 25.
404 https://doi.org/10.1029/2009GB003758

405 Lomax, G., Workman, M., Lenton, T., Shah, N., 2015. Reframing the policy approach to
406 greenhouse gas removal technologies. Energy Policy 78, 125–136.
407 https://doi.org/10.1016/j.enpol.2014.10.002

408 Longman, J., Palmer, M.R., Gernon, T.M., Manners, H.R., 2019. The role of tephra in
409 enhancing organic carbon preservation in marine sediments. Earth-Science Rev.
410 https://doi.org/10.1016/J.EARSCIREV.2019.03.018

411 Martin, J.H., Fitzwater, S.E., 1988. Iron deficiency limits phytoplankton growth in the north-
412 east pacific subarctic. Nature 331, 341–343. https://doi.org/10.1038/331341a0

413 Maters, E.C., Delmelle, P., Gunnlaugsson, H.P., 2017. Controls on iron mobilisation from
414 volcanic ash at low pH: Insights from dissolution experiments and Mössbauer

spectroscopy. Chem. Geol. 449, 73–81. https://doi.org/10.1016/J.CHEMGEO.2016.11.036

Mathers, J., Craft, E., Norsworthy, M., Wolfe, C., 2014. Green Freight Handbook. Enironmental Defense Fund, New York.

Matter, J.M., Stute, M., Snæbjörnsdottir, S.Ó., Oelkers, E.H., Gislason, S.R., Aradottir, E.S., Sigfusson, B., Gunnarsson, I., Sigurdardottir, H., Gunnlaugsson, E., Axelsson, G., Alfredsson, H.A., Wolff-Boenisch, D., Mesfin, K., Fernandez de la Reguera Taya, D., Hall, J., Dideriksen, K., Broecker, W.S., 2016. Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. Science 352, 1312–4. https://doi.org/10.1126/science.aad8132

Mélançon, J., Levasseur, M., Lizotte, M., Delmelle, P., Cullen, J., Hamme, R.C., Peña, A., Simpson, K.G., Scarratt, M., Tremblay, J.-É.É., Zhou, J., Johnson, K., Sutherland, N., Arychuk, M., Nemcek, N., Robert, M., 2014. Early response of the northeast subarctic Pacific plankton assemblage to volcanic ash fertilization. Limnol. Oceanogr. 59, 55–67. https://doi.org/10.4319/lo.2014.59.1.0055

Murray, N.A., McManus, J., Palmer, M.R., Haley, B., Manners, H., 2018. Diagenesis in tephra-rich sediments from the Lesser Antilles Volcanic Arc: Pore fluid constraints. Geochim. Cosmochim. Acta 228, 119–135. https://doi.org/10.1016/J.GCA.2018.02.039

Olgun, N., Duggen, S., Croot, P.L., Delmelle, P., Dietze, H., Schacht, U., Óskarsson, N., Siebe, C., Auer, A., Garbe-Schönberg, D., 2011. Surface ocean iron fertilization: The role of airborne volcanic ash from subduction zone and hot spot volcanoes and related iron fluxes into the Pacific Ocean. Global Biogeochem. Cycles 25, n/a-n/a. https://doi.org/10.1029/2009GB003761

Pabortsava, K., Lampitt, R.S., Benson, J., Crowe, C., McLachlan, R., Le Moigne, F.A.C.,

Mark Moore, C., Pebody, C., Provost, P., Rees, A.P., Tilstone, G.H., Woodward, E.M.S., 2017. Carbon sequestration in the deep Atlantic enhanced by Saharan dust. Nat. Geosci. 10, 189–194. https://doi.org/10.1038/ngeo2899

Pennington, J.T., Mahoney, K.L., Kuwahara, V.S., Kolber, D.D., Calienes, R., Chavez, F.P., 2006. Primary production in the eastern tropical Pacific: A review. Prog. Oceanogr. 69, 285–317. https://doi.org/10.1016/j.pocean.2006.03.012

Perrier, V., Meidla, T., Tinn, O., Ainsaar, L., 2012. Biotic response to explosive volcanism: Ostracod recovery after Ordovician ash-falls. Palaeogeogr. Palaeoclimatol. Palaeoecol. 365–366, 166–183. https://doi.org/10.1016/j.palaeo.2012.09.024

Ramage, M.H., Burridge, H., Busse-Wicher, M., Fereday, G., Reynolds, T., Shah, D.U., Wu, G., Yu, L., Fleming, P., Densley-Tingley, D., Allwood, J., Dupree, P., Linden, P.F., Scherman, O., 2017. The wood from the trees: The use of timber in construction. Renew. Sustain. Energy Rev. https://doi.org/10.1016/j.rser.2016.09.107

Renforth, P., Henderson, G., 2017. Assessing ocean alkalinity for carbon sequestration. Rev. Geophys. 55, 636–674. https://doi.org/10.1002/2016RG000533

Royal Society, T., 2018. Greenhouse Gas Removal. Royal Society, London.

Rubin, M., Berman-Frank, I., Shaked, Y., 2011. Dust- and mineral-iron utilization by the marine dinitrogen-fixer Trichodesmium. Nat. Geosci. 4, 529–534. https://doi.org/10.1038/ngeo1181

Sarmiento, J.L., Gruber, N., 2006. Ocean biogeochemical dynamics. Princeton University Press.

Schrag, D.P., Higgins, J.A., Macdonald, F.A., Johnston, D.T., 2013. Authigenic carbonate and the history of the global carbon cycle. Science (80-.). 339, 540–3.

https://doi.org/10.1126/science.1229578

Scudder, R.P., Murray, R.W., Schindlbeck, J.C., Kutterolf, S., Hauff, F., Underwood, M.B., Gwizd, S., Lauzon, R., McKinley, C.C., 2016. Geochemical approaches to the quantification of dispersed volcanic ash in marine sediment. Prog. Earth Planet. Sci. 3, 1. https://doi.org/10.1186/s40645-015-0077-y

Siegenthaler, U., Sarmiento, J.L., 1993. Atmospheric carbon dioxide and the ocean. Nature. https://doi.org/10.1038/365119a0

Steffen, W., Rockström, J., Richardson, K., Lenton, T.M., Folke, C., Liverman, D., Summerhayes, C.P., Barnosky, A.D., Cornell, S.E., Crucifix, M., Donges, J.F., Fetzer, I., Lade, S.J., Scheffer, M., Winkelmann, R., Schellnhuber, H.J., 2018. Trajectories of the Earth System in the Anthropocene. Proc. Natl. Acad. Sci. 115, 8252–8259. https://doi.org/10.1073/pnas.1810141115

Tollefson, J., 2018. IPCC says limiting global warming to 1.5 °C will require drastic action. Nature 562, 172–173. https://doi.org/10.1038/d41586-018-06876-2

Uematsu, M., Toratani, M., Kajino, M., Narita, Y., Senga, Y., Kimoto, T., 2004. Enhancement of primary productivity in the western North Pacific caused by the eruption of the Miyake-jima Volcano. Geophys. Res. Lett. 31, n/a-n/a. https://doi.org/10.1029/2003gl018790

UNCTAD, 2018. Review of Maritime Transport. United Nations, New York and Geneva.

Wall-Palmer, D., Jones, M.T., Hart, M.B., Fisher, J.K., Smart, C.W., Hembury, D.J., Palmer, M.R., Fones, G.R., 2011. Explosive volcanism as a cause for mass mortality of pteropods. Mar. Geol. 282, 231–239. https://doi.org/10.1016/J.MARGEO.2011.03.001

Zahariev, K., Christian, J.R., Denman, K.L., 2008. Preindustrial, historical, and fertilization

simulations using a global ocean carbon model with new parameterizations of iron limitation, calcification, and N2 fixation. Prog. Oceanogr. 77, 56–82. https://doi.org/10.1016/j.pocean.2008.01.007

Figures

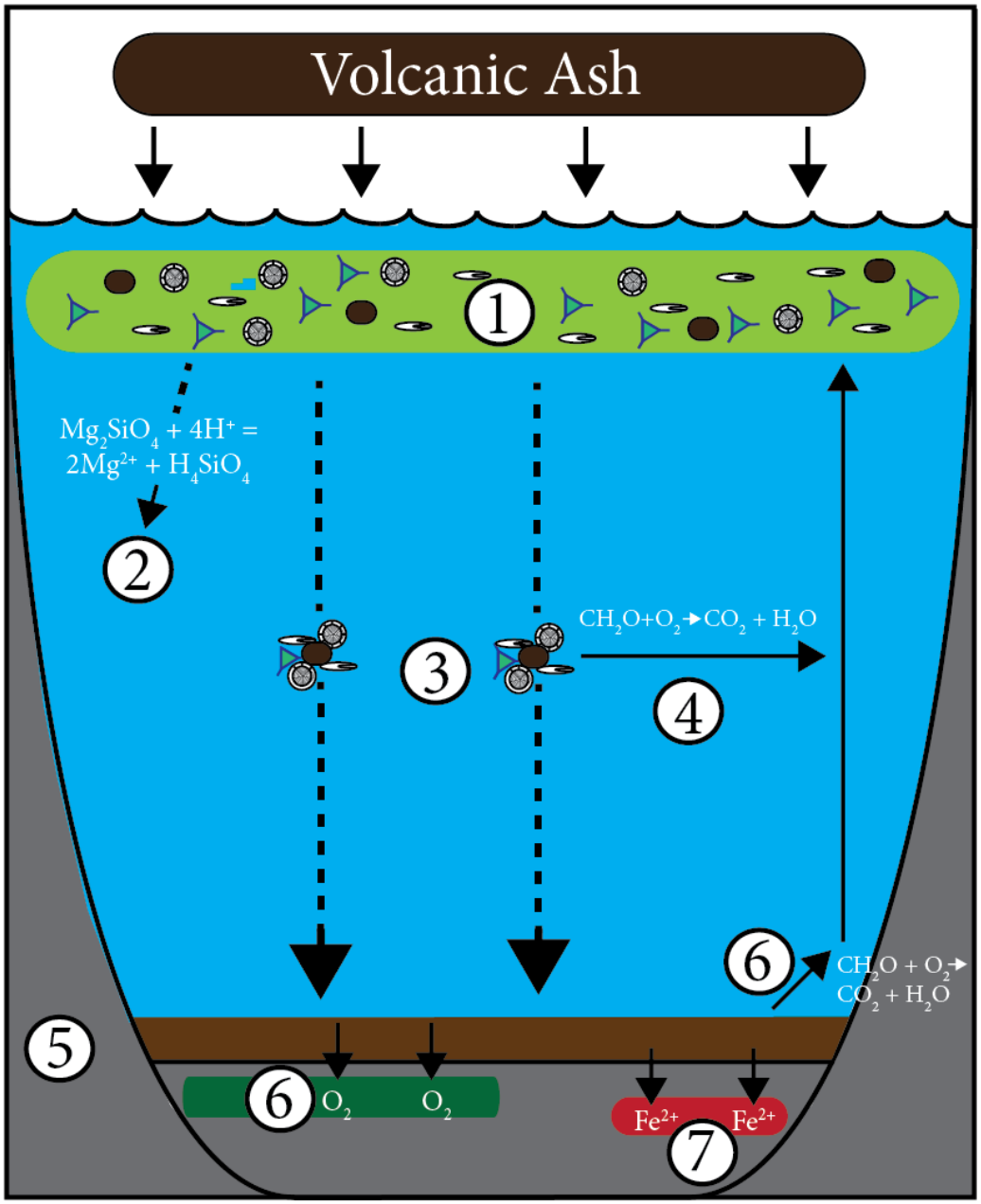

Figure 1: Schematic image detailing the processes which may occur to enhance carbon sequestration and greenhouse gas removal via the addition of volcanic ash to the ocean. 1) The fertilization of phytoplankton blooms in the upper ocean. 2) The release of Mg^{2+} (and Ca^{2+}) ions to the ocean, via the dissolution of minerals contained in the ash. Here we use the dissolution of olivine as an example. Mg^{2+} are released during this process which consumes H^+ ions, thus increasing alkalinity. 3) The transfer of organic carbon from the upper to lower ocean (the biological pump), enhanced by the

association of phytoplankton to ash particles. 4) The remineralization of some organic matter during transport through an oxygenated water column 5) The formation of a volcanic ash layer at the sediment-water interface. 6) Removal of O_2 from organic-rich sediments and formation of anoxic conditions, reducing organic carbon oxidation and remineralization. 7) The release of reactive species of Fe, Mn and Al, available to bind to organic carbon and reduce oxidation.

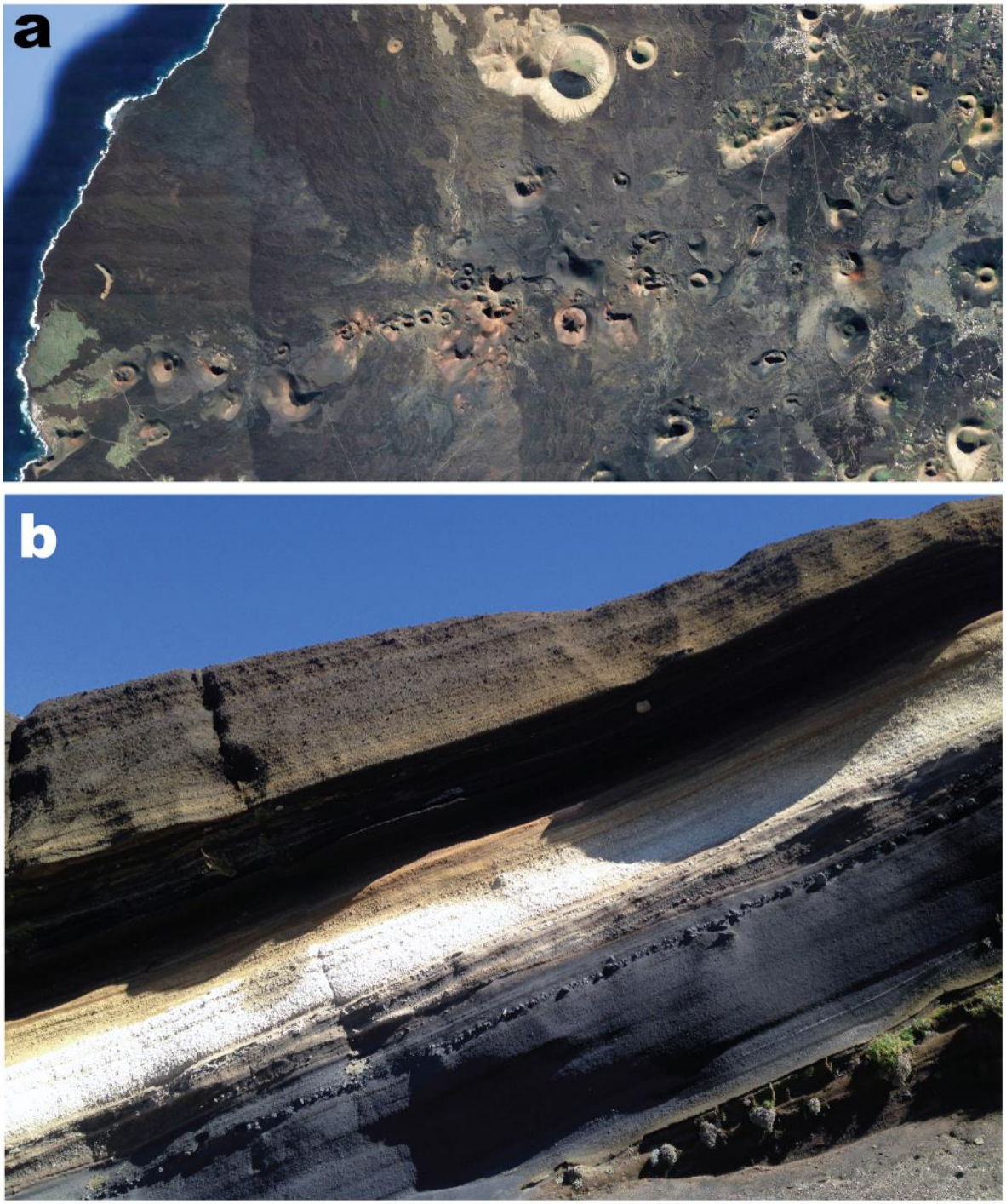

Figure 2: Examples of Holocene-age tephra in the natural environment. Panel a is an aerial image of cinder cone volcanoes in Lanzarote (Canary Islands), displaying both the extensive tephra fields surrounding them and their proximity to the ocean. Panel b is an example of bedded tephra deposits from Tenerife (also Canary Islands).

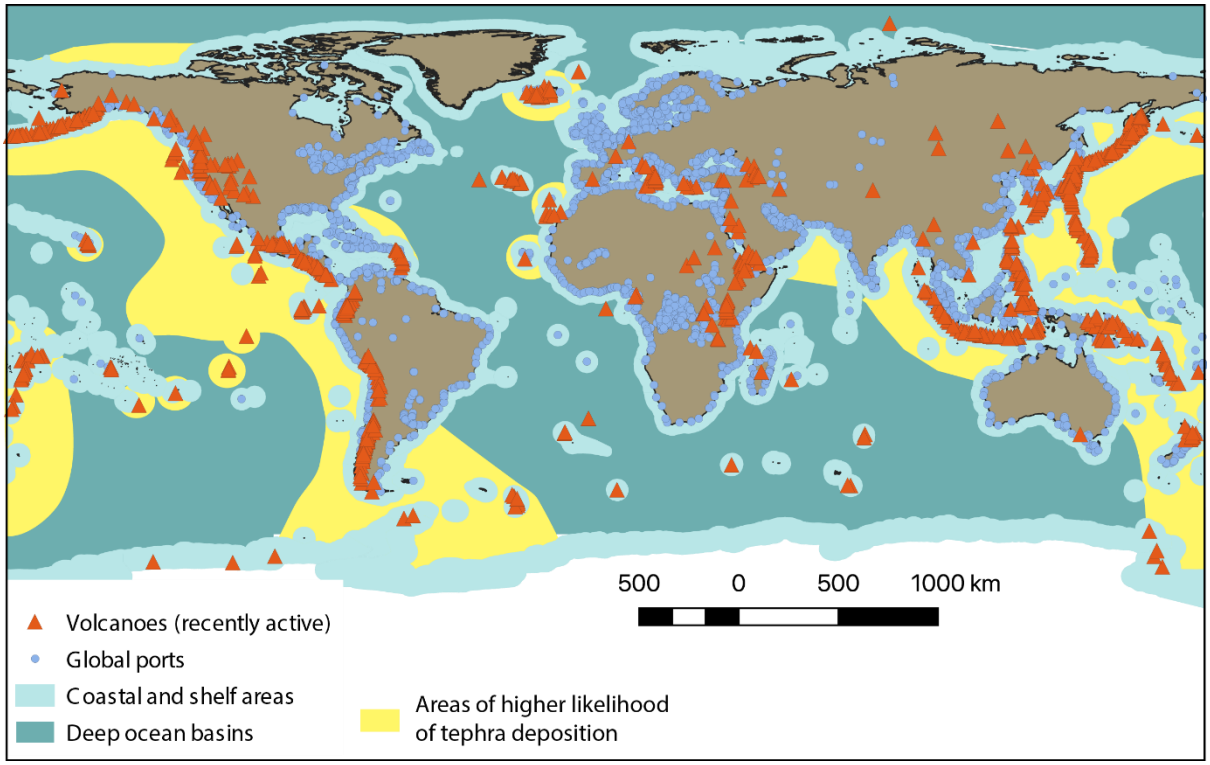

Figure 3: Global map displaying the location of all active (and recently active) volcanoes (red triangles), and of global ports (blue circles) Also indicated is regions in which tephra deposition is considered highly likely (yellow), from Olgun et al., 2011. Most volcanoes are located either on, or close to the ocean, and very few are a significant distance from major ports. Also displayed are the extent of coastal and shelf seas (those which are <200 m in depth), which would be the target for offshore tephra addition.

Table 1: Estimates of gross and net potential CO_2 storage. [a] Typical CO_2 equivalent fluxes are calculated from the POC rain rate of Site 1 from the inner Peruvian shelf (Dale et al., 2015). [b] Burial efficiencies are taken from the average carbon burial efficiency of sites 1 and 2 of the inner Peru shelf, with OMZ carbon burial efficiencies an average of sites 6-8 (Dale et al., 2015). [c] Mass of tephra with a density of 1400 kg m^3 (a typical value of tephra; Gudmundsson et al., 2012) and 50 % porosity (Hembury et al., 2012) required per square meter of seafloor. [d] Bulk carrier capacity from Freese, 2017. [e] Yearly CO_2 equivalent flux to the area covered by tephra. [f] Gross increase in CO_2 preserved in sediment achieved by reducing remineralization by 29%. [g] Estimate of onshore CO_2 emissions, calculated assuming truck size of 44 tonnes (typical articulated lorry load size) an average distance of 30km from tephra source to port, 1140 journeys necessary to carry 50,000 tonnes of tephra, and using the EDF's green freight calculator (Mathers et al., 2014). [h] Estimate of offshore CO_2 emissions, calculated from values in Freese, 2017. [j] Net CO_2 storage calculated via subtraction of onshore and offshore CO_2 emissions from gross storage.

Gross potential CO_2 storage	**Value**
Typical inner Peru shelf C_{org} burial rate	79.5 mmol m^{-2} d^{-1} [a]
Yearly C_{org} flux to sediments	348.52 gC m^{-2} yr^{-1} [a]
CO_2 equivalent flux to sediments	1277 gCO_2 m^{-2} yr^{-1} [a]
Typical Peru shelf burial efficiency	18% [b]
Typical Peru shelf burial efficiency below Oxygen Minimum Zone	47 % [b]
Likely increase in burial efficiency as a result of O_2 depletion	29% [b]
Resource requirement	
Thickness of tephra applied to sediment	0.5 cm
Volume of tephra required per square meter	5 x 10^3 cm^3 m^{-2}
Mass of tephra (50% porosity)	6.7 x 10^3 g m^{-2} [c]
Assumed bulk carrier capacity	50,000 t [d]
Area covered per carrier load	7.5 x 10^6 m^2 [c]
Yearly supply of carbon to this area before remineralization	2.61 x 10^9 gC yr^{-1} [e]
Gross CO_2 storage per load per year for 29% reduction of remineralization	**2777 t CO_2 [f]**
CO_2 emissions associated	
CO_2 emitted by 44 tonne truck (per tonne load and km travelled)	91.2 gCO_2 t^{-1} km^{-1} [g]
Distance from tephra source to port	30 km [g]
Number of journeys	~1140 [g]
CO_2 emitted per 50,000 tonnes tephra transported to port	136 t CO_2 [g]

CO_2 emitted by carrier (per tonne load and km travelled)	3 gCO_2 t^{-1} km^{-1} [h]
CO_2 emitted by 50,000 t bulk carrier	150 x 10^3 gCO_2 km^{-1} [h]
Distance to and from load port, and tephra spreading	2000 km [i]
CO_2 emitted per carrier load	300 t CO_2 [h]
Net CO_2 storage per load	**2341 t CO_2 [j]**

529

530 Table 2: Comparison of removal potential and costs, alongside technology readiness levels (TRLs) of
531 other proposed GGR methods, and enhanced tephra loading. Table adapted from Royal Society
532 (2018), with additional data from this study. [a] Estimates of global potential for CO_2 removal from
533 tephra loading taken from Longman et al. (2019). There are 9 TRLs describing maturity of
534 technology: TRL1 basic principles, TRL2 invention and research, TRL3 proof of concept, TRL4
535 bench scale research, TRL5 pilot scale, TRL6 large scale, TRL7 inactive commissioning, TRL8 active
536 commissioning and TRL9 operations.

GGR Method	**Global CO_2 removal potential (Gt CO_2 a^{-1})**	**Cost per tCO_2 (US$)**	**Technology readiness level (TRL)**
Afforestation, reforestation and forest management	Afforestation/reforestation: 3-20, forest management: 1-2	3-30	8-9
Wetland, peatland and coastal habitat restoration	0.4-20	10-100	5-6
Soil carbon sequestration	1-10	10 profit, 3 cost	8-9
Biochar	2-5	0-200	3-6
Ocean fertilization	1-3	10-500	1-5
Enhanced terrestrial weathering	0.5-4	50-500	1-5
Mineral carbonation	–	50-300 (*ex situ*), 20 (*in situ*)	3-8
Ocean Alkalinity	40	70-200	2-4
Offshore tephra loading	**0.88 [a]**	**~55**	**2-4**

537

538

539