

The Role of Tephra in Enhancing Organic Carbon Preservation in Marine Sediments

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Abstract

Preservation of organic carbon (C_{org}) in marine sediments plays a major role in defining ocean-atmosphere CO_2 levels, Earth climate, and the generation of hydrocarbons (Hedges and Keil, 1995). Important controls over sedimentary C_{org} preservation include; biological productivity, C_{org} isolation from oxidants (mainly dissolved O_2) in the overlying water column and sediments, and C_{org} – mineral association in sediments (Hartnett et al., 1998; Hedges and Keil, 1995). Deposition of the products of explosive volcanism (tephra) in the oceans directly enhances C_{org} burial through all these mechanisms, and indirectly through enhanced formation of authigenic carbonate (C_{auth}) derived from sedimentary C_{org} . In the modern oceans, it is suggested that tephra deposition may account for 5-10% of the C_{org} burial flux and 10-40% of the C_{auth} burial flux. However, during certain periods in Earth's history, extensive explosive volcanism may have led to enhanced C_{auth} precipitation on a sufficiently large scale to influence the global ocean-atmosphere carbon cycle. Changes in tephra-related C_{org} preservation may also have played a role in increasing C_{org} preservation rates in local marine basins, at the oxic-anoxic boundary and enhanced the generation of hydrocarbon deposits in these settings.

Keywords

Tephra, diagenesis, carbon cycle, authigenic calcite, organic carbon

1. Introduction

Tephra is defined as “all the explosively-erupted, unconsolidated pyroclastic products of a volcanic eruption” (Lowe, 2011). Subaerial volcanic eruptions currently deliver $\sim 1 \text{ km}^3 \text{ yr}^{-1}$ ($\sim 0.48 \text{ km}^3 \text{ yr}^{-1}$ DRE) of tephra to the atmosphere (Pyle, 1995) and, because most volcanoes are located close to the oceans, a high proportion of this material falls into seawater. Tephra is also directly delivered to the oceans from submarine eruptions (Straub and Schmincke, 1998) and from the rapid erosion of tephra initially deposited on land. For example, $\sim 75\%$ of

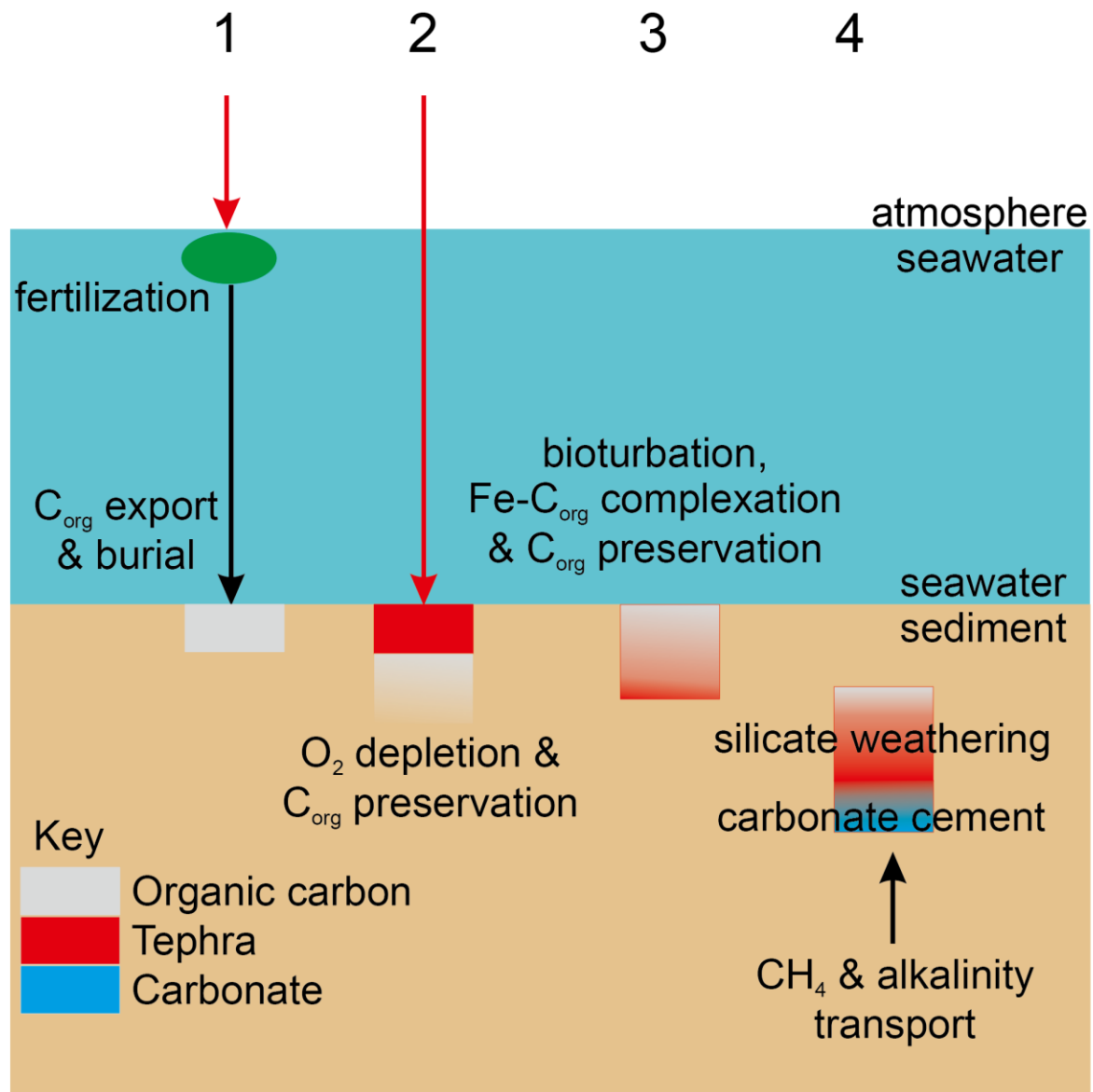


Figure 1: The role of tephra in enhancing the preservation of organic carbon in marine sediments. 1) Fe fertilization; 2) O_2 depletion; 3) reactive Fe complexation; 4) authigenic carbonate formation.

the material erupted from Soufrière Hills and deposited on the island of Montserrat during 1995-2005 was deposited in the Caribbean Sea by the end of 2005 (Le Friant et al., 2009). A measure of the scale of these processes is that Pacific Ocean sediments as a whole contain an average of ~25 wt% tephra (Straub and Schmincke, 1998). Tephra is generally fine-grained, it is in a thermodynamic state that is far from equilibrium with surface Earth conditions, and it is

highly reactive; all properties which result in a variety of methods by which tephra deposition in the oceans can enhance organic carbon (C_{org}) preservation. These mechanisms are summarized in [Figure 1](#) and discussed in more detail below, alongside the potential implications of such processes.

2. Summary of Processes

2.1. Fertilization

Marine biological productivity is limited by nutrient availability ([Moore et al., 2013](#)), with the major fertilization effect of tephra deposition in seawater observed in high-nutrient, low-chlorophyll (HNLC) regions, as a result of the release of dissolved Fe as it reacts with seawater ([Duggen et al., 2010](#); [Olgun et al., 2011](#)). These are regions of the ocean in which macronutrients (e.g. nitrate) are generally available for phytoplankton growth in high quantities, but where micronutrients (e.g. iron, zinc, cobalt) are not ([Moore et al., 2013](#)). In contrast to typical ocean environments, where nitrogen is the limiting ocean nutrient, in HNLCs it is generally iron ([Kolber et al., 1994](#)), potentially co-limiting with other micronutrients such as cobalt, manganese and zinc ([Moore et al., 2013](#)). Indeed, these elements may also be delivered to the ocean via ash deposition. In these cases, volcanic eruptions can lead to anomalously large (by biomass) phytoplankton blooms, apparent increases in the efficiency of photochemical energy conversion, and a shift in species distribution toward diatom-domination ([Boyd et al., 2007](#); [Weinbauer et al., 2017](#)). Evidence for such processes has been observed worldwide in HNLC regions; from the Iceland basin after the Eyjafjallajökull eruption ([Achterberg et al., 2013](#); [Zhang et al., 2017](#)), to the subarctic Pacific ([Mélançon et al., 2014](#)), and the Southern Ocean ([Browning et al., 2014](#)). Data from the Fe-limited, NE Pacific following deposition of tephra from the Kasatochi volcano indicate that this event led to an increase in C_{org} production of $\sim 1 \times 10^{13}$ gC over an area of $1.5\text{-}2 \times 10^6$ km²; equivalent to ~ 6 gC m⁻² ([Hamme et al., 2010](#)). The proportion of C_{org} production that is ultimately sequestered

from these stochastic fertilization events is, however, uncertain. Estimates from Kasatochi suggest a drawdown of ~ 0.01 Pg C (Hamme et al., 2010), whilst calculations from other eruptions indicate broad ranges, with Southern Ocean export as a result of ash fertilisation estimated to be $\sim 0.04 - 15$ Pg C over the past 16.5 thousand years (kyrs). The range of carbon export related to the 1991 eruptions of Pinatubo and Hudson is proposed to be $\sim 0.003 - 1$ Pg (Browning et al., 2015). Some constraints are provided by artificial iron fertilization experiments, which suggest that approximately half the biomass generated in surface waters sinks below 1000 m water depth (Smetacek et al., 2012), with the rate of carbon export being enhanced by the rapid sinking rate of diatoms compared to the majority of bloom-forming phytoplankton, including coccolithophores (Agusti et al., 2015; Tréguer et al., 2018). Further, phytoplankton will likely physically associate themselves with tephra particles, as they do with atmospheric dusts (Rubin et al., 2011), further increasing the downward transport efficiency.

It is also possible that iron from volcanic ash may fertilise low nutrient, low chlorophyll (LNLC) regions (Browning et al., 2015). These regions comprise sixty percent of the ocean, and unlike HNLC areas, are depleted in the macronutrients phosphate and nitrate, resulting in low phytoplankton concentrations (Guieu et al., 2014). It has been proposed that such a process would occur as a result of the fertilisation of nitrogen fixing bacteria by iron (Falkowski, 1997). For example, after the eruption of Anatahan volcano in 2003, there is evidence for ash fertilising both phytoplankton and diazotrophs in the North Pacific subtropical gyre (Lin et al., 2011). The impact of such processes on a larger scale is, however, unclear.

The impact on C_{org} preservation of a single tephra deposition event is, however, likely to be limited because the effect is short-lived. For example, mean chlorophyll levels in the Kasatochi affected area returned to pre-bloom values within 3 months of the event (Hamme et al., 2010; Langmann et al., 2010). Following the Eyjafjallajökull eruption, the phytoplankton bloom was similarly short-lived, and was subsumed within the prolonged bloom resulting from

the unusually negative North Atlantic Oscillation value which altered hydrological conditions (Henson et al., 2013). In addition, most HNLC regions, with the exception of the equatorial Pacific, are located over deep oxygenated oceans that do not favour C_{org} preservation. For example, a study of natural Fe fertilization in the HNLC southern Indian Ocean revealed that only ~1% of the particulate C_{org} flux observed at a depth of 150 m survived oxidation during transit through the oxygenated water column to be incorporated in core top sediments at a depth of ~4000 m (Pollard et al., 2009). Thus, application of the same preservation rates to the Kasatochi event predicts an increased C_{org} flux to the deep NE Pacific sediments of ~0.06 gC m^{-2} , compared to the average global deep (> 2 km) ocean C_{org} burial rate of 0.2 gC $m^{-2} yr^{-1}$ (Burdige, 2007); i.e. an increase on the order of 30%.

Both the Kasatochi and Eyjafjallajökull eruptions were small, discrete events (Achterberg et al., 2013; Hamme et al., 2010), but it has been suggested that prolonged large eruptions from the Middle Eocene to the Middle Miocene lowered atmospheric CO_2 as a result of oceanic Fe fertilization that promoted global cooling (Cather et al., 2009; Jicha et al., 2009). Similarly, comparison between fresh and diagenetically altered tephra indicates that there is substantial loss of Fe, Si and PO_4 from the tephra during interaction with seawater. This observation, together with the history of the intensity of arc volcanism, have also been used to suggest that an upsurge of volcanic activity in the late Cretaceous led to increased C_{org} burial in marine sediments at this time (Lee et al., 2018).

There are, however, factors that mitigate against a direct link between the size and frequencies of eruptions and their fertilization effects. In particular, heavy tephra loading in surface ocean waters leads to high levels of toxic metals and low pH values that inhibit biological activity and lead to localized plankton mortality (Hoffmann et al., 2012; Wall-Palmer et al., 2011), although it is clear that different plankton taxa and individual species within taxa have varied responses to the same degrees of tephra input (Gómez-Letona et al.,

2018). Caution must be applied to such conclusions however, as trace metal loadings experiments may be far higher than is realistic after ash fall. Hoffmann et al. (2012) measured Fe concentrations of 5.67 – 222 nmol/l in their experiments, whilst modelled iron availability after the Kasatochi eruption was generally found to be below 2 nmol/l, even proximal to the volcano (Lindenthal et al., 2013). Varied *in situ* observations of biological response to tephra input may also be related to variations in the speed and extent of Fe (and other chemical species) release from tephra. This is dependent on the variable oxidation state of Fe (and other elements) on the surface of tephra particles released during individual eruptions (Maters et al., 2017). It is also possible that tephra may attenuate light (both in the atmosphere and in the surface ocean), affecting phytoplankton productivity.

Overall, the fertilization of surface waters resulting from tephra deposition is complex and nuanced according to local oceanographic conditions, and the type and amount of tephra added during individual and successive deposition events. The greatest positive impact of sea surface fertilization on C_{org} preservation will likely occur during regular deposition of small amounts of tephra to HNLC regions (because this will see the greatest impact on productivity), and where tephra is deposited in relatively shallow seas (because this will minimize remineralization within the water column of the additional C_{org} that is produced). In contrast, it is possible intense tephra deposition may be marked by poisoning of the sea surface biota and a reduction in productivity.

2.2. Reduced Oxidant Exposure

Initial C_{org} degradation rates in anoxic sediments are similar to those within oxic sediments, but the rate of anoxic degradation decreases rapidly after the most labile organic fractions are consumed (Hedges and Keil, 1995), as evidenced by the observation that reduced exposure time to dissolved O_2 strongly increases C_{org} burial efficiency (Hartnett et al., 1998). The deposition of tephra in sediments results in the uptake of dissolved O_2 from sediment pore

waters, as a result of the oxidation of silicate-bound Fe^{II}, via coupled electron-cation transfer reactions (Hembury et al., 2012; White and Yee, 1985). This process can lead to a reduction in the O₂ levels in the pore water to zero within ~2-3 mm of the sediment-water interface in seafloor tephra layers (Haeckel et al., 2001; Hembury et al., 2012). Dissolution experiments show that Fe^{III} is preferentially released from tephra relative to Fe^{II}, most likely as a consequence of oxidation of Fe at the tephra surface followed by dissolution of Fe₂O₃. This means volcanic glass accumulating in sediments has higher Fe^{II}/Fe^{III} ratios than original volcanic glass (Maters et al., 2017).

In addition, the ratio of Fe^{III} to Fe^{II} within tephra may vary according to the nature of the volcanic activity. For example, tephra generated during divergent plate and ocean island volcanism, where hot tephra and gases may interact in the volcanic plume (Hoshyaripour et al., 2014), and basaltic tephra in general has higher Fe^{II}/Fe^{III} ratios than tephra generated from andesitic volcanism (Horwell et al., 2007). However, atmospheric processing may also act to oxidise the surface Fe, thereby reducing its ability to consume O₂ once incorporated into the sediment (Maters et al., 2017).

The presence of Fe^{II} on the surface of tephra particles may also lead to reduced levels of nitrate and nitrite within pore waters, as a result of Fe^{II}-induced catalysis of microbial nitrate reduction (Ottley et al., 1997). Experimental data also suggests Fe^{II}-bearing minerals may act to reduce nitrate to N₂ via abiotic reduction, whilst dissolved Fe^{II} can reduce NO_x⁻ to NH₄⁺ (Postma, 1990; Song et al., 2014).

The reduction in the availability of the electron acceptors for C_{org} oxidation depends on both the concentration of Fe^{II} in the tephra and the physical parameters (grain size and thickness) of the tephra layer, but models of the effects of the 1991 Pinatubo eruption in the South China Sea suggest that deposition of ~5 cm of tephra can lead to permanent exclusion of dissolved O₂ from underlying sediments (Haeckel et al., 2001), and even deposition of a few

mm of tephra leads to a reduction in dissolved O₂ pore water levels (Haeckel et al., 2001; Hembury et al., 2012). Deposition of tephra onto marine sediment also inhibits bioturbation (Lowe, 2011), with evidence from the eruption of Mount Pinatubo suggesting that tephra layers of >5 mm form a barrier to bioturbation (Wetzel, 2009). This process is important because suppression of bioturbation lowers the effective diffusion rate of electron acceptors from the overlying water that would otherwise aid C_{org} degradation.

Tephra deposited in the oceans is transported to the sea floor, with observed oceanic settling velocities of >2 cm/s (Manville and Wilson, 2004; Wetzel, 2009). As such, the impact of reducing the exposure time of C_{org} to dissolved O₂ (and other electron acceptors) in sediments commences almost immediately after tephra deposition (Ayris and Delmelle, 2012). Following the approach of Hedges and Keil (1995), the oxidation of C_{org} in marine sediments under oxygenated bottom water can be modelled by considering that (as a global average) it is composed of three fractions; 10% refractory C_{org}, preserved regardless of sedimentary conditions, 45% O₂-sensitive C_{org} and 45% fermentable C_{org}, with first order exponential decay constants of 0.03 and 0.3 yr⁻¹, respectively (Fig. 2a). If oxidation of O₂-sensitive C_{org} is completely suppressed by deposition of a tephra layer (Haeckel et al., 2001), then the additional C_{org} preservation is equal to the shaded area in Figure 2a. After the tephra has been deposited, background sedimentation resumes above the tephra layer. The interval between successive tephra deposition events thus determines the increase in C_{org} preservation at a site due to this mechanism (Fig. 2b). As such, C_{org} preservation will double at tephra deposition intervals of ~150 years (Fig. 2b). Hence, the C_{org} content of typical continental margin sediments overlain by oxic bottom water (Burdige, 2007; Lalonde et al., 2012) might rise from ~2 wt% C_{org}, to ~4 wt% under the influence tephra deposition at centennial frequencies. The eruption frequency from individual volcanic centres vary widely, but frequencies of this order (and higher), are recorded in closely-spaced volcanoes from arc settings (Rawson et al., 2015; Watt et al., 2013).

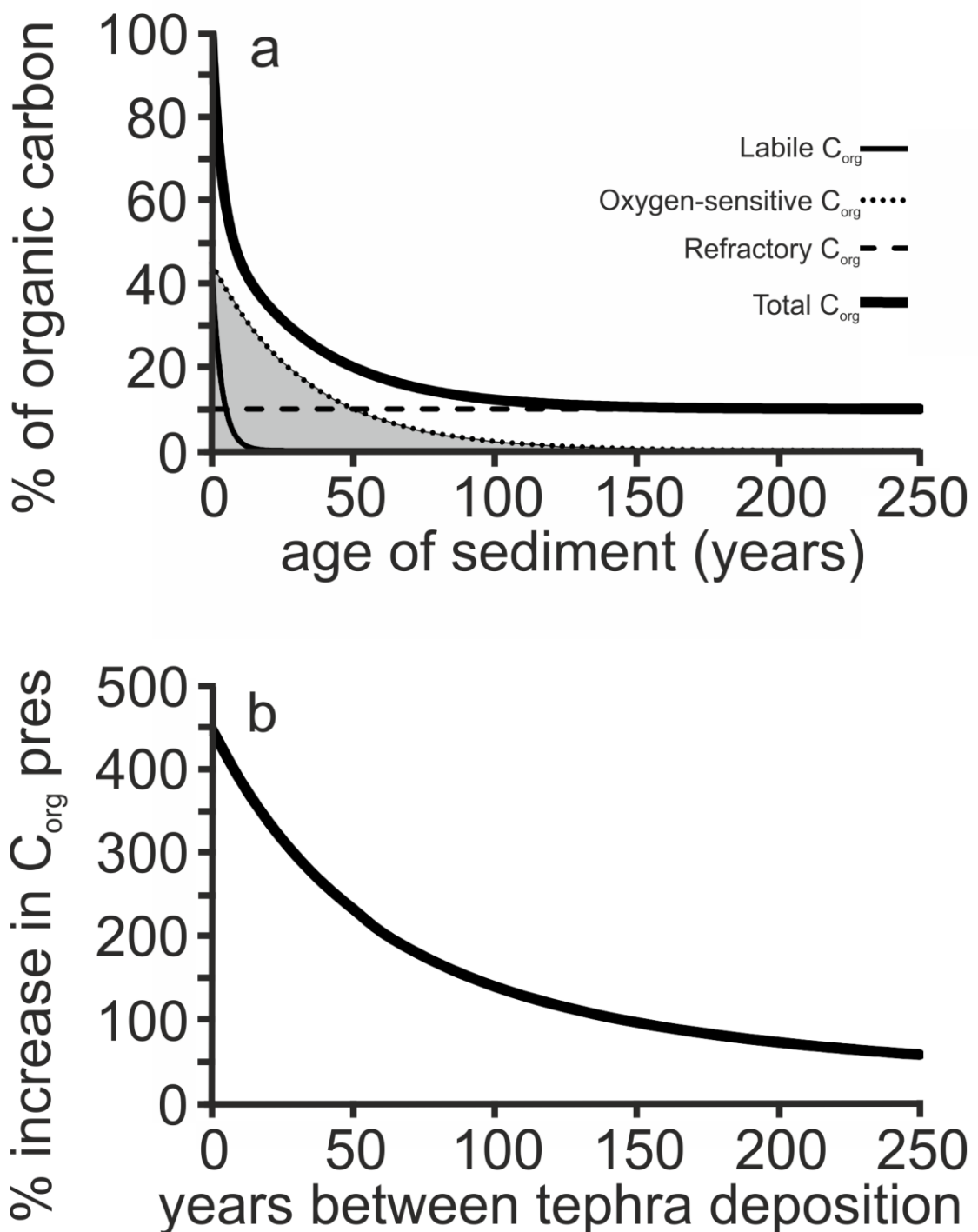


Figure 2: Role of dissolved O_2 exposure in C_{org} preservation. (a) Model-derived preservation for three different C_{org} fractions and total C_{org} as a function of sediment age after [Hedges and Keil, \(1995\)](#). Thin solid line = labile C_{org} , dotted line = oxygen-sensitive C_{org} , dashed line = refractory C_{org} and thick solid line = total C_{org} (see text for details). (b) Percentage increase

in C_{org} preservation due to decreased O_2 exposure as a function of interval between tephra deposition events.

An additional mechanism may be at play when tephra is deposited in basins with restricted circulation, which are common worldwide. For example, the Mediterranean Sea has received tephra inputs from collisional volcanic activity along its northern margin since the Late Cretaceous (Dilek & Altunkaynak, 2007). When tephra is deposited in such an environment, the depletion of dissolved O_2 in the sediment pore waters may extend into the overlying water column; further enhancing C_{org} preservation even when there are longer intervals between tephra deposition events. An example of this process is provided by studies of eastern Mediterranean sapropels (C_{org} -rich sediments) that formed by periodic increases in freshwater fluxes to the region; with the most recent sapropel forming ~6-10.5 ka (Grant et al., 2016; Rohling et al., 2015). After deposition of the sapropel, an oxidation front moves down through the C_{org} -rich layer such that C_{org} is oxidized from top to bottom (Reitz et al., 2006; Rohling et al., 2015).

The eruption of Santorini at 3.6 ka deposited tephra over some of the areas in which the last Mediterranean sapropel (S1) was deposited. At two sites where no tephra was deposited after the sapropel, 7.3-8.8 cm (~60-80%) of the C_{org} in the sapropel has been oxidized (Fig. 3). In two further sites, the sapropel was buried beneath ~40 cm and ~4 cm of tephra ~2-5 kyr after S1 formed. Beneath the thicker tephra layer, only 5.4 cm of the original 33.5 cm sapropel thickness has been oxidized, and only 6.0 cm of the original 12.1 cm sapropel thickness was oxidized beneath the thinner tephra layer (Fig. 3). The increased C_{org} preservation relative to the sites that did not receive any tephra input is not simply due to an increase in the dissolved O_2 diffusive path length by the additional layer of tephra, because deposition of the ~10-15 cm thick Augias turbidite (triggered by the Santorini eruption, but not containing tephra) above the

sapropel did not increase C_{org} preservation at either site SL139 (water depth 3293 m) or site T87-19B (water depth 3483 m) (Reitz et al., 2006).

Overall, the impact of enhanced preservation of C_{org} through reduced oxidant exposure following tephra deposition on the surface of marine sediments will be maximized under the following conditions: i) the thickness of tephra is >0.5 cm (because thinner layers of tephra are less efficient in inhibiting bioturbation); ii) the tephra is deposited on shelf sediments beneath an oxic water column (normal deep-sea sediments contain such low C_{org} concentrations (Burdige, 2007) there is no opportunity for enhanced C_{org} preservation); and iii) the tephra is deposited at centennial to sub-centennial frequencies (because longer intervals between deposition events will allow the C_{org} to be oxidized before the next tephra layer is deposited).

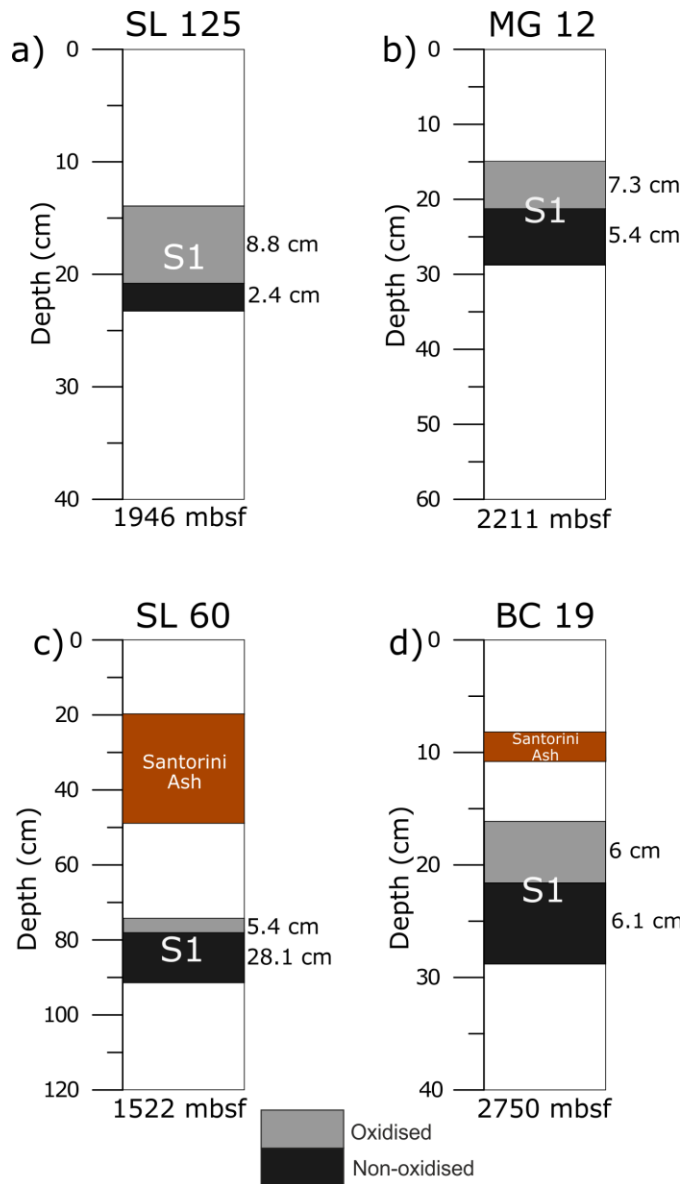


Figure 3: Impact of volcanic ash deposition on oxidation of Mediterranean sapropels (Reitz et al., 2006). Panels (a) and (b) display two cores (SL 125 and MG12) in which no volcanic ash was deposited after the formation of the sapropel. Panels (c) and (d) display two cores in which the sapropel was subsequently covered by ash from the Santorini eruption. Indicated in grey is the extent to which the sapropel has been oxidised. (1 Column)

2.3. Reactive Oxide Complexation

In addition to forming discrete layers, tephra is dispersed within background sediments. This occurs if the tephra flux either produces a layer that is too thin to inhibit bioturbation, and/or the upper surfaces of thick tephra layers are bioturbated after the seafloor is recolonized by

benthic organisms (Lowe, 2011). Under such conditions, the dispersed tephra may act to take up dissolved O₂ from pore water as outlined previously, but the act of mixing tephra with background sediments also provides an additional mechanism for enhanced C_{org} preservation, through C_{org}-mineral association.

A portion of C_{org} in marine sediments is adsorbed to mineral surfaces that inhibit its oxidation and enhances its long term preservation (Hedges and Keil, 1995). Of these interactions, the binding of C_{org} to Fe-rich reactive colloids (redox-sensitive, nano-scale Fe oxides) may be the most important, with >20% of C_{org} in average marine sediments being bound to reactive Fe (FeR) phases (Lalonde et al., 2012). Complexation can result in strong inner-sphere (or covalent) interactions (Keil and Mayer, 2014), stabilising both the reactive C_{org} and the FeR (Barber et al., 2017), and inhibiting remineralization of the C_{org}. Furthermore, it appears that the extent of FeR-C_{org} complexation increases as exposure to O₂ decreases (Barber et al., 2017), with such bonds being effectively permanent on long timescales in reduced sediments (>400 kyrs) (Haese et al., 1997). It has also been suggested FeR may act as a “synergistic ferric C_{org} shuttle”, moving C_{org} from oxic upper sediment into deeper anoxic layers (Barber et al., 2017).

The high abundance of FeR on the surface of tephra grains and the release of dissolved Fe from tephra (e.g., Maters et al., 2017) suggests that the presence of tephra within marine sediments (either as discrete layers or as dispersed grains) will enhance the production of FeR.

In addition, reactive Mn (MnR)-bearing minerals are also known to interact with dissolved organic carbon in the ocean (Stone et al., 1984; Sunda and Kieber, 1994). Studies in marine sediments indicate a strong association between MnR and C_{org} (Roy et al., 2013), possibly a consequence of carboxylate groups in the C_{org} binding to Mn oxide surfaces (Johnson et al., 2015). Subsequent studies have shown an association between various types of organic matter and MnR phases in a variety of marine and terrestrial environments (Estes et

al., 2017; Stuckey et al., 2018). Finally, reactive Al phases (AIR) may also act to enhance C_{org} preservation in both volcanic soils (Basile-Doelsch et al., 2007), and in marine sediments (Mayer, 1994). Again, tephra has been shown to be an important source of all of these reactive oxide phases within marine sediments (Homoky et al., 2011) and may thus be expected to play a role in C_{org} preservation.

Evidence for enhanced C_{org} preservation associated with tephra deposition comes from a study of sediments at site M6 south of the volcanic island of Crozet (Indian Ocean) (Homoky et al., 2011). A plot of the ratio of C_{org} to the fraction of non-volcanogenic matter versus the % of non-volcanogenic matter from site M6 indicates that there is more C_{org} present in the volcanogenic-rich sediments than would be expected from simple dilution of a biogenic source of organic matter by C_{org} -free tephra (Fig. 4a). The uppermost sample from the sediment-water interface falls off the trend defined by the rest of the data. This sample has the highest C_{org} concentration (0.52 wt%) and its deviation from the general trend likely reflects the fact that freshly deposited organic matter contains a high component of fermentable C_{org} with a high first order decay constant that has been hydrolysed in the underlying sediments (cf. Hedges and Keil, 1995). The trend defined by the sub-surface sediments indicates that the non-tephra component of the sediment (i.e., the biogenic silica and carbonate) has a C_{org} content of 0.17 wt%. If this value is assumed to be constant in the subsurface (i.e. after the fermentable C_{org} has been oxidized), an average of 69% (range 57-76%) of the C_{org} in this core appears to be associated with the volcanogenic component of the sediment. The correlation between the FeR concentration of the sediments and the percentage of volcanogenic material present (Fig. 4b) is compatible with the additional C_{org} in this sediment being associated with FeR derived from the tephra. Note that the zero intercept of Figure 4b yields a value of 0.41 wt% reactive Fe present in the non-volcanogenic portion of the sediment, which is similar to that measured in “normal” marine sediments (average 0.48 wt%; range 0.1-2.0 wt% (Lalonde et al., 2012)).

The amount of dispersed tephra is difficult to quantify in marine sediments, because it is commonly altered to authigenic clay, but it typically accounts for 20-30 wt% of the bulk sediment in the vicinity of volcanic arcs (Scudder et al., 2009). Hence, if we take the FeR/% tephra ratio of 0.006 from the Crozet data (Fig. 4b), an average of 25 wt% tephra in volcanically-influenced, continental margin sediments and a C_{org}/FeR molar ratio of 4 for such sediments (Lalonde et al., 2012), the generation of FeR by tephra diagenesis would lead to burial of an additional 0.13 wt% C_{org} for typical shelf sediments (Burdige, 2007; Lalonde et al., 2012). This represents a small increase in the total C_{org} preservation rate, but it is also associated with a change in composition of the preserved organic matter because organic compounds rich in nitrogen and/or oxygen functionalities are preferentially complexed with Fe, Mn or Al, and these types of organic compounds are generally highly labile and not well preserved in marine sediments (Lalonde et al., 2012).

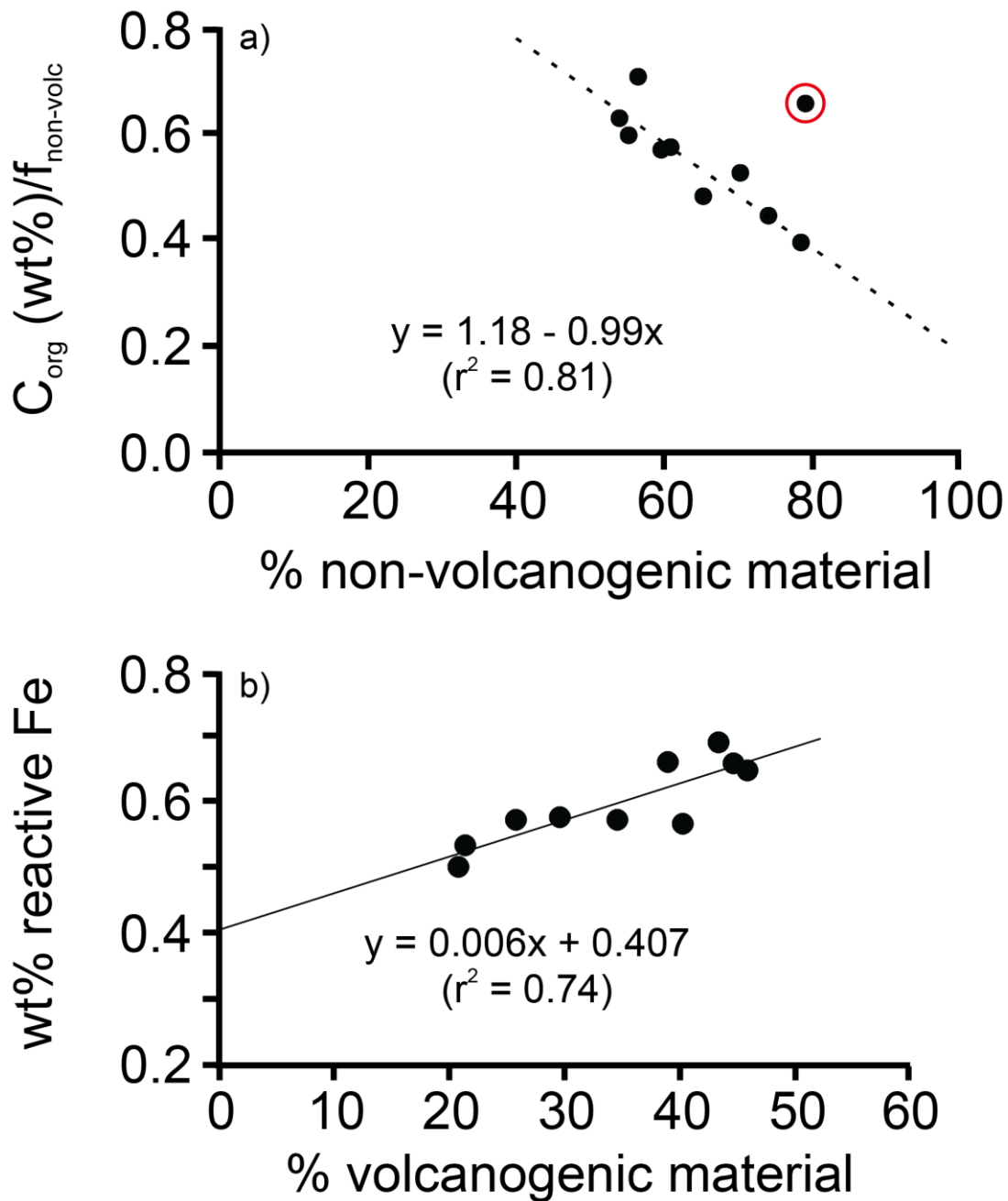


Figure 4: (a) Plot of the ratio of C_{org} to non-volcanic material versus the % of non-volcanic material within core M6 on the southern shelf of the Crozet islands (Homoky et al., 2011). (b) Plot of wt% reactive Fe versus % volcanogenic material in core M6 on the southern shelf of the Crozet Islands (Homoky et al., 2011).

Overall, the observations above suggest that FeR, MnR and AlR complexation of C_{org} due to tephra input will be maximized when there is a regular supply of small amounts of tephra that are dispersed over a wide area of the oceans (because low inputs of tephra can be readily

bioturbated and mixed with the C_{org} -bearing background sediment), and where the tephra originates from basaltic volcanism (because it has higher Fe concentrations and higher $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$ ratios). These conditions occur most commonly in the Pacific Ocean, which is ringed by arc volcanoes and contains abundant ocean island basaltic volcanoes. Paradoxically, however, the conditions under which tephra input are likely to have the greatest impact on reactive metal– C_{org} complexation are also the hardest to quantify because isolated tephra grains are difficult to distinguish visually and geochemically, particularly after they have released reactive metals during diagenesis. The estimates above suggest that while this process may only account for ~5% of global C_{org} preservation, it may influence the type of organic matter preserved, acting to preserve the sort of C_{org} typically lost early in sediment diagenesis (Hedges and Keil, 1995).

2.4. Authigenic Carbonate Formation

Formation of authigenic carbonate (C_{auth}) in marine sediments occurs when there is an increase in pore water concentrations of carbonate and/or divalent cations (mainly Ca^{2+} and Mg^{2+}) above levels required to exceed the saturation index of a carbonate mineral (mainly calcite and dolomite). C_{auth} precipitation occurs in a variety of environments (Chow et al., 2000; Schrag et al., 2013; Zhao et al., 2016), and has been invoked as a third major carbon sink in the oceans, alongside C_{org} and biogenic carbonate (Zhao et al., 2016). The most favourable conditions for C_{auth} precipitation are typically at sub-seafloor depths >1 m that are coincident with high alkalinity levels generated from diagenesis of sedimentary C_{org} during sulphate reduction and anaerobic oxidation of methane (AOM) (Lein, 2004; Schrag et al., 2013). The precipitation of C_{auth} , in which the CO_3^{2-} is derived directly or indirectly from the oxidation of C_{org} , therefore contributes to the sequestration of CO_2 that would otherwise be returned to the ocean-atmosphere. While increased pore water CO_3^{2-} concentrations favour C_{auth} precipitation, the process is enhanced by increased concentrations of dissolved Mg^{2+} and Ca^{2+} . Alteration of

volcanic material in marine sediments has long been recognized as a source of elevated Ca^{2+} levels in deep sea sediment pore water (Gieskes, 1983), including sediments adjacent to island arcs that contain high abundances of tephra (Murray et al., 2018).

By compiling DSDP/ODP/IODP pore water data, and using the Ca^{2+} flux into marine sediments, a global C_{auth} precipitation flux of $\sim 10^{13}$ gC yr⁻¹ has been calculated (Sun and Turchyn, 2014). The authors acknowledge that this likely underestimates the magnitude of this process because it only considers sites where there is a Ca^{2+} flux into sediments from the overlying seawater, whereas (as noted above) precipitation of C_{auth} also occurs when Ca^{2+} is transferred from solid phase silicates to pore waters within sediments. Hence, their estimate of global C_{auth} burial is lower than that based on modelling of anoxic marine sediments ($2\text{-}8 \times 10^{13}$ gC yr⁻¹), the sites of greatest C_{auth} formation (Wallmann et al., 2008). Importantly, in the context of this study, this latter estimate was largely based on a study of tephra-rich sediments in the Sea of Okhotsk. Wallmann et al. (Wallmann et al., 2008) concluded that much of the Ca^{2+} precipitated in C_{auth} was released from weathering of reactive silicate minerals in the tephra rather than seawater. If these two estimates of global C_{auth} burial are taken at face value, they imply that $\sim 40\text{-}85\%$ of the Ca^{2+} incorporated into C_{auth} is released from the sedimentary silicate minerals rather than from Ca^{2+} derived from seawater as buried pore water or by diffusion from the overlying water column.

In addition to acting as a source of Ca^{2+} , tephra in sediments may also enhance C_{auth} precipitation by creating anoxic conditions below the tephra that increases the amount of C_{org} available for methanogenesis and AOM. The release of Ca^{2+} into pore water during sub-seafloor tephra weathering also neutralizes the acidity generated when CH_4 oxidation takes place under aerobic conditions and would that otherwise inhibit C_{auth} precipitation (Wallmann et al., 2008).

Direct evidence for the involvement of tephra in C_{auth} precipitation is provided by the presence of ~10-30 cm thick altered tephra layers (bentonites) in sediments adjacent to the Aleutian volcanic chain that contain up to 60% calcite cement comprising carbonate derived from AOM (Hein et al., 1979). Indeed, C_{auth} cements in tephra layers are widely distributed in time and space; including in, Miocene-Quaternary sediments in the Izu-Bonin basin (Marsaglia and Tazaki, 1992), Eocene-Quaternary layers on the East Greenland margin (Chow et al., 2000), Paleocene-Eocene tephra-bearing sediments from the North Atlantic (Jones et al., 2016; Roberts et al., 1984) and North Sea Basin (Haaland et al., 2000; Obst et al., 2015), and Jurassic-Cretaceous tephra from the North Sea Basin (Jeans et al., 2000). In addition, quartz-rich sediments on continental margins previously assumed to be derived from continental weathering have been shown to be tephra in which the labile minerals have undergone intense low-temperature alteration, with calcite being a common alteration product (Smyth et al., 2008).

In assessing whether carbonate cements within tephra layers are contributing to sequestration of CO_2 derived from C_{org} , it is important to confirm that the CO_3^{2-} is derived from oxidized C_{org} and not simply the result of inclusion of CO_3^{2-} derived from the dissolution and reprecipitation of biogenic carbonate. This is evidenced by the observation that authigenic calcites typically have more depleted $\delta^{13}\text{C}$ values than biogenic carbonate (Chow et al., 2000; Zhao et al., 2016), with C_{auth} $\delta^{13}\text{C}$ values ranging from -5‰ to as low as -40‰ (Fig. 5); values indicative of formation from AOM (Hein et al., 1979; Malone et al., 2002; Schrag et al., 2013).

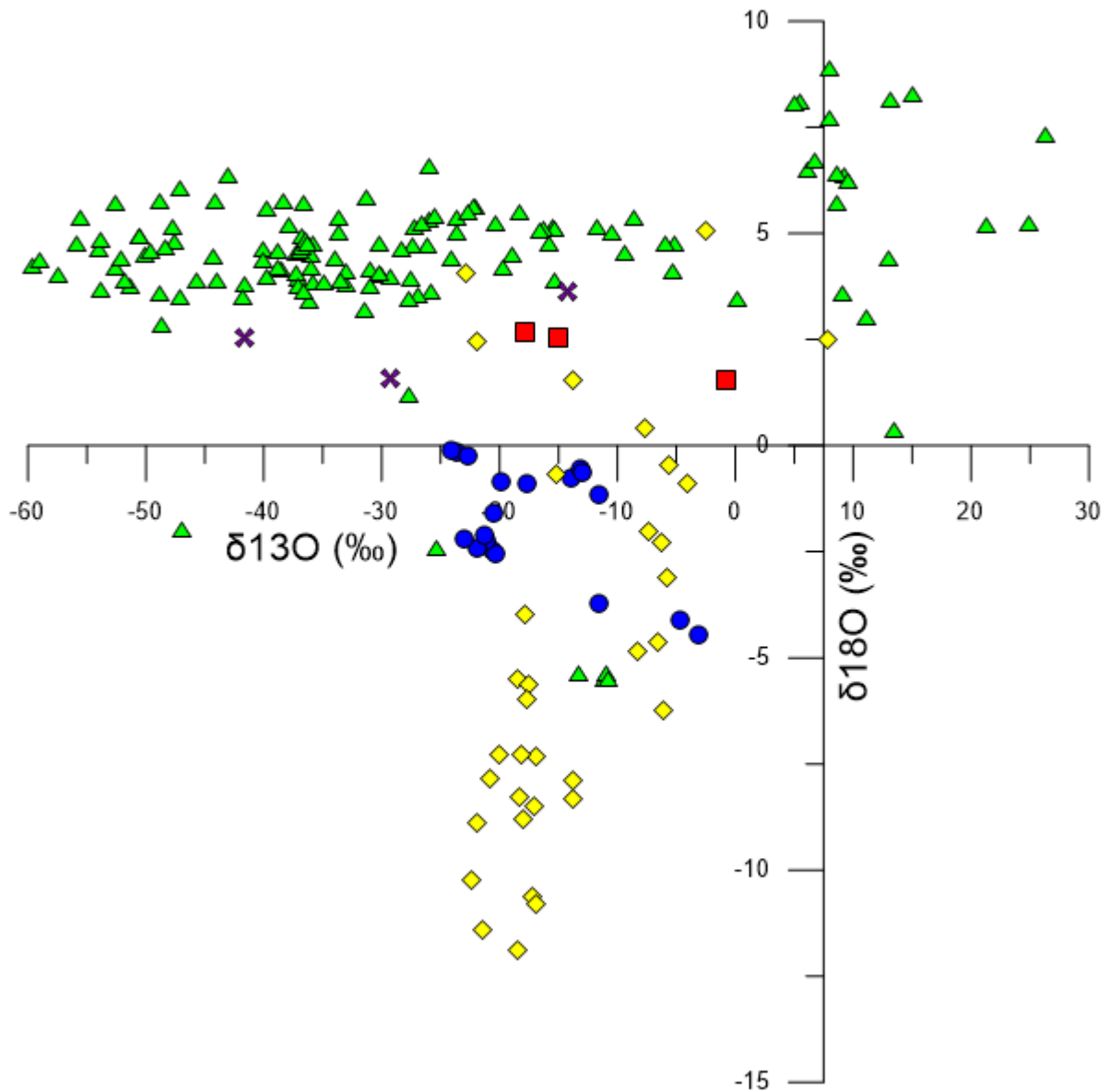


Figure 5: Carbon and oxygen isotopic composition of selected authigenic carbonates. Yellow diamonds are from authigenic Mn-Fe carbonates in Cenozoic North Sea sediments (Chow et al., 2000). Red squares are from dolomites of Quaternary age from the Peru margin (Meister et al., 2007). Purple crosses are from authigenic carbonates on the New Jersey shelf (Malone et al., 2002). Green triangles are from a selection of authigenic carbonates located at continental margin hydrocarbon seeps (Naehr et al., 2007). Blue circles are from Late Paleocene diatomites and ashes from northwestern Denmark (Pedersen and Buchardt, 1996). Most authigenic carbonates display depleted $\delta^{13}\text{C}$ values, below -5‰. Paleocene ash isotope

compositions also fall below -5‰, pointing towards an authigenic source, ~~evidence of authigenic carbonate formation in ash layers.~~

The magnitude of C_{auth} precipitation within tephra layers is dependent on the depositional environment, tephra mineralogy, grain size, pore water chemistry, temperature, pressure, and burial history (Schrag et al., 2013). These factors are highly variable and many are poorly constrained. Nevertheless, an indication of the potential scale of this process may be obtained from modelling studies of CO_2 mineralization of volcanogenic sandstones conducted for the purposes of carbon sequestration. For example, it has been calculated that ~80% of the CO_2 injected into a volcanogenic sandstone layer could be fixed as C_{auth} within 1000 years of injection; with the cement forming 1.8% of the reservoir volume (Zhang et al., 2013). Applying the same magnitude of C_{auth} formation over the same time scale to a tephra layer (with 50% porosity (Hembury et al., 2012)) in which there is diffusion of dissolved CO_3^{2-} (derived from oxidation of C_{org}) through the base of the layer, yields ~20 gC m⁻² precipitated as C_{auth} per cm thickness of tephra. Clearly, not all tephra is deposited over areas where AOM occurs sufficiently close to the sediment-water interface to impact the ocean-atmosphere carbon cycle, but these conditions most commonly occur in shelf seas (Hinrichs and Boetius, 2002), which are also the sites of greatest tephra deposition (Lowe, 2011).

The example above assumes only 1.8% of the tephra layer volume is occupied by C_{auth} , compared to up to 60% observed in buried tephra layers in the Bering Sea (Hein et al., 1979). Every 1% of porosity within a tephra layer that is filled by C_{auth} will sequester 3.24×10^{-3} gC cm⁻³ of tephra. As noted above, much of the ~1 km³ yr⁻¹ of tephra erupted into the atmosphere falls into the oceans (Pyle, 1995), with additional tephra being supplied to the oceans from dome collapse events, lahars and other post-depositional redistribution of volcanogenic material originally deposited on land (e.g. Le Friant et al., 2009).

Whereas the impacts of fertilization, reduced oxidant exposure and reactive oxide complexation occur immediately after tephra deposition, the timescale of the impact of C_{auth} precipitation on the ocean-atmosphere carbon cycle is more variable and extended. For example, within the Sea of Okhotsk, it takes ~5-50 kyr for tephra layers to be buried to the depth of C_{auth} precipitation (Wallmann et al., 2008), with precipitation taking place over kyr time periods (Hinrichs and Boetius, 2002). The depth to the AOM zone varies globally from within a few cm of the sediment-water interface in C_{org} -rich anoxic sediments, to >100 m in the deep sea (Regnier et al., 2011). Hence, a large volcanic eruption that deposits tephra over seafloor sediments spanning a range in sedimentation rates and depths to the AOM zone could reduce the flux of C_{org} to the ocean-atmosphere carbon system for up to $\sim 10^6$ years after the eruption through precipitation of C_{auth} in the tephra layer.

Overall, precipitation of C_{auth} as a consequence of tephra deposition in the oceans is favoured by deposition of tephra on C_{org} -rich sediments (because these sediments will act as a larger source of C_{org} -derived CO_3^{2-}), and deposition of sufficient tephra to form layers that are thick enough to resist bioturbation (because this will likely maximize the concentration of dissolved Ca^{2+} in tephra layer pore spaces compared to release of Ca^{2+} from dispersed tephra grains). Importantly, increased tephra deposition over a wide area is expected to result in increased C_{auth} precipitation. Thus, periods in Earth history when there were higher rates of volcanic activity and tephra deposition in the oceans are likely to have resulted in increased C_{auth} precipitation for 10^3 - 10^6 years after tephra deposition.

3. Wider Implications

3.1. Modern Oceans

The rate of C_{org} burial in the modern oceans has been calculated to be $\sim 3 \times 10^{14}$ gC yr⁻¹ (Burdige, 2007), but estimates range from 0.3 to 7.8×10^{14} gC yr⁻¹ (Dunne et al., 2007;

Palastanga et al., 2011). Tephra deposition in the oceans contributes directly to C_{org} preservation via fertilization, reduced exposure to oxidants and reactive metal complexation. The contribution of tephra deposition is implicitly included in the total estimate of global C_{org} burial because these estimates are largely obtained from compilations of C_{org} concentrations in all marine sediments (e.g. Burdige, 2007). The proportion of the total C_{org} preservation that can be ascribed to the influence of tephra deposition is difficult to quantify on the basis of the currently available data, but based on the observation that ~20% of C_{org} in sediments is associated with FeR (Lalonde et al., 2012) and the fraction of tephra in marine sediments may be as high as 25 wt. % (Scudder et al., 2009; Straub and Schmincke, 1998), it is likely that tephra deposition contributes of the order of 5-10% of the global C_{org} burial flux.

There are similarly varying estimates of the modern day burial rate of C_{auth} , between 1 to 8×10^{13} gC yr⁻¹ (Sun and Turchyn, 2014; Wallmann et al., 2008); i.e., roughly ~10% of the C_{org} burial flux. This observation is in accord with the results of modelling of deep sea sediment pore water geochemistry and isotope mass balance calculations that suggest that C_{auth} forms a minor component of the total sedimentary carbon burial rate (Mitnick et al., 2018). If, for example, it is assumed that $0.5 \text{ km}^3 \text{ yr}^{-1}$ of tephra is deposited in the oceans (i.e., half the annual airborne tephra flux (Pyle, 1995)) and that 5% of tephra layers are ultimately composed of C_{auth} , then $\sim 8 \times 10^{12}$ gC yr⁻¹ will be sequestered – i.e., ~10-40% of the annual C_{auth} sink in the modern oceans as calculated by Wallmann et al. (Wallmann et al., 2008). It has been suggested, however, that the burial rate of C_{auth} may have been higher during periods in the geologic past when oceanic dissolved O_2 levels were lower and alkalinity was higher (Schrag et al., 2013).

3.2. Ordovician

While deposition of tephra in the oceans plays a relatively minor role in the preservation of C_{org} (directly or indirectly) in the modern oceans, there have been major eruptions in Earth history that may have had a greater impact on the carbon cycle. One of the largest known

eruptions occurred 453 Ma (Sell et al., 2013) and resulted in deposition of the Millbrig K-bentonite. This eruption deposited ~800 km³ of tephra (Dense Rock Equivalent) in the Iapetus Ocean during a single event (Huff et al., 1992) – i.e., ~1000 times greater than the modern annual tephra deposition rate (Pyle, 1999). Assuming an average tephra density of 1400 kg/m³ (Gudmundsson et al., 2012), this corresponds to a volume of ~1500 km³ deposited in the ocean.

While fertilization may have occurred at the margins of this tephra deposit, the major effect of such a large eruption on marine productivity would have been deleterious, although no notable extinction events are thought to be associated with this event (Huff et al., 1992). Several million square kilometres of marine sediments would have been covered in ash layers up to 1-2 m thick (Huff et al., 1992). Hence, there would have been increased C_{org} preservation in the underlying sediments because of reduced oxidant exposure. The warmer oceans and more sluggish overturning circulation at this time would have resulted in lower water column dissolved O₂ levels compared to the modern oceans (Edwards et al., 2017; Pohl et al., 2017). Therefore, an eruption of this magnitude would also likely have led to a further reduction of dissolved O₂ concentrations in the water column because of oxidation of Fe^{II} in the tephra, reduced oxidation of C_{org} settling from the surface waters and thus increased C_{org} preservation in the immediate aftermath of the tephra deposition. The extent and depth of sediment bioturbation increased throughout the Ordovician (Droser and Bottjer, 1989), so the upper surfaces of the tephra layer would likely have been mixed into the succeeding background sediment once oxic conditions were re-established at the sediment-water interface. Given the wide areal extent of deposition of the Millbrig tephra layer in the oceans, this mixing would be expected to lead to increased reactive metal – C_{org} complexation and preservation for several thousand years after the deposition event.

The Late Ordovician is marked by both heightened explosive volcanism (Huff et al., 2010) and extensive deposition of C_{org}-rich black shales (Pohl et al., 2017). Modelling studies

and halite inclusion data suggest that seawater Ca^{2+} concentrations were ~3-4 times higher in the Ordovician than in the modern ocean (Arvidson et al., 2013; Ridgwell and Zeebe, 2005). When this is coupled with the fact that lower dissolved O_2 and higher alkalinity levels also favour C_{auth} precipitation (Schrag et al., 2013), this suggests that C_{auth} precipitation within Ordovician tephra layers would have been even more prevalent than those within the modern oceans. Indeed, many Ordovician bentonites contain such high C_{auth} concentrations in the form of calcite cements that they have been mistaken for limestone layers (Berkley and Baird, 2002). As an indication of the scale of this process, if only 5% of the pore space within the ~1500 km³ of tephra deposited into the oceans by the Millbrig event was ultimately comprised of C_{auth} , this would be equivalent to ~2.5 x 10¹⁶gC sequestered, or ~1000 times the present annual precipitation rate of C_{auth} in the modern oceans (Sun and Turchyn, 2014).

The changing ocean-atmosphere carbon cycle during the Ordovician has been linked to explosive volcanism, magmatic super plumes and outgassing from large igneous provinces (e.g., Algeo et al., 2016; Buggisch et al., 2010). Significantly, the deposition of the Millbrig bentonite took place ~100-200 kyr prior to the Guttenberg $\delta^{13}\text{C}$ excursion (GICE) which marked a sharp positive spike of ~2‰ in the $\delta^{13}\text{C}$ of biogenic marine carbonates that lasted for ~100 kyr (Buggisch et al., 2010); this is generally considered to be indicative of increased C_{org} preservation that could arise from increased precipitation of C_{auth} . Comparison of carbonate and organic carbon $\delta^{13}\text{C}$ values suggests that the early stages of the GICE were marked by rising atmospheric CO_2 levels, possibly from volcanic degassing, followed by declining CO_2 concentrations as C_{org} burial rates increased (Pancost et al., 2013). The extent to which the GICE was specifically linked with global cooling in addition to impacting the carbon cycle is contentious (e.g. Buggisch et al., 2010; Herrmann et al., 2011). Nevertheless there is considerable evidence that the Late Ordovician was marked by a long-term cooling trend

(Algeo et al., 2016), during a time of the most extensive explosive volcanic activity in the Phanerozoic (Huff et al., 2010).

3.3. Jurassic

The Middle-Late Jurassic sedimentary basins of northwest Europe contain C_{org}-rich sediments that were deposited in shallow basins with restricted circulation to the open ocean and are recognized as important source rocks for large hydrocarbon fields in the region (Hallam, 1987). An apparent association of hydrocarbon source rocks with an increased volcanogenic component of marine sediments in the North Sea region has been suggested, but the causes of this relationship remain to be examined (e.g. Zimmerle, 1985). Similarly, the concentration and mineralogy of authigenic clay in sediments in the region has been interpreted to reflect alteration of large tephra inputs into these basins associated with continental breakup (Jeans, 2006). Indeed, it has been suggested that increased C_{org} burial and weathering of fresh volcanic material following the heightened explosive volcanic activity in the Late Jurassic contributed to a lowering of atmospheric CO₂ and the initiation of the Cenozoic icehouse world (McKenzie et al., 2016). Other studies suggest, however, that the association of C_{org}-rich sediments with ash layers is largely coincidental and of no general significance (Oschmann, 1988), and that the clay minerals are largely derived from detrital sources (Hesselbo et al., 2009). As noted above, however, the quantification and detection of the presence of tephra in marine sediments is frequently obscured and underestimated (Berkley and Baird, 2002; Smyth et al., 2008).

The proximity of the Middle-Late Jurassic sedimentary basins of northwest Europe to both marine and terrestrial volcanic sources suggests they likely received tephra inputs. While fertilization may have contributed to increased C_{org} production, oxidation of Fe^{II} in tephra is likely to have been more important; contributing to lowering O₂ concentrations in both the water column and sediments of the shallow, restricted circulation basins.

3.4. Geoengineering

The discussion above has indicated that tephra addition to the oceans plays a role in C_{org} preservation in the modern global ocean and that this role has been greater at various points in Earth history. Industrial anthropogenic carbon emissions are of the order of $\sim 10^{16}$ gC yr⁻¹ (Oelkers and Cole, 2008), and the consequent rising atmospheric CO₂ levels and the associated climatic effects have led to an upsurge of studies into a range of geoengineering and CO₂ sequestration strategies (Broecker, 2008). It is, therefore, of interest to consider whether purposeful addition of tephra to the oceans might contribute to greenhouse removal strategies.

The present-day rate of C_{org} burial in the oceans of ~ 0.3 Gt C yr⁻¹ is the residue after $\sim 85\%$ of the 2.3 Gt C yr⁻¹ of C_{org} reaching the ocean floor has been oxidized (Burdige, 2007). The highest burial efficiency ($\sim 30\%$) occurs in shallow (0-200 m water depth) sediments that occupy $\sim 7.5\%$ of the total seafloor area. There are, however, wide variations in burial efficiency in these shallow sediments, such that only $\sim 1\%$ of the C_{org} deposited in sandy sediments (that comprise 70% of the areal extent of sediments at water depths of 0-200 m) is preserved compared to $\sim 30\%$ burial efficiency in muddy sediments at the same water depth (Burdige, 2007). The low C_{org} burial efficiency in sandy sediments arises from the lack of protection of the C_{org} by fine-grained sediments (that contribute to reactive oxide- C_{org} complexing) and the greater penetration of dissolved O₂ into permeable sand compared to fine-grained mud. Artificially increasing the burial efficiency of sandy sediments to the same level of muddy sediments could, therefore, potentially result in the additional burial of 0.24 Gt C yr⁻¹, if carried out on a global scale.

This potential carbon removal rate is of the same order as several other proposed geoengineering strategies; including artificial ocean fertilization (0.3 – 0.8 Gt C yr⁻¹), enhanced terrestrial weathering (0.1 – 1 Gt C yr⁻¹) and direct air capture (0.1 – 1.4 Gt C yr⁻¹) (Royal Society, 2018). Clearly, as with all other proposed geoengineering strategies (Schäfer et al.,

2015), much study would be required to test the feasibility of tephra addition to seafloor sediments as a viable mechanism for carbon removal. For example, the financial cost/benefit ratio, as well as the socio-political barriers that would need to be considered (Cox et al., 2018). There are, however, a number of benefits which tephra addition may have relative to other strategies. Unlike terrestrial based carbon removal strategies, there would be no direct impact on human populations through changes to land use. In contrast to ocean fertilization, the studies of natural tephra addition to sediments indicate that a single episode of tephra loading would have an impact over ~100 yr timescales. Studies of areas of the seafloor that have experienced tephra addition also suggest that there is no long term harm caused to benthic biota (Hess et al., 2001; Kuhnt et al., 2005). Tephra is a natural, renewable resource that can be found at many locations over the globe and is not currently competitively sought after. Unlike mineral carbonation and direct air capture strategies, no major technological infrastructure is required. In contrast to enhanced terrestrial weathering strategies that largely require airborne delivery of minerals, tephra could be delivered over wider areas of the ocean floor in large quantities by relatively low carbon emitting, low technology, and readily available bulk cargo ships.

In terms of efficacy evaluation, this would include studies of the importance of grain size, composition and required loading to achieve meaningful increases in C_{org} burial. Safety considerations would primarily include the impact on marine ecology. The economic cost and technologic development of the tephra processing and delivery would have to be evaluated. Importantly, there would need to be international collaboration on any law-of-the-sea ramifications of tephra delivery to the oceans, together with a public engagement strategy.

Many of the initial studies of the efficacy of the process could be undertaken in simple laboratory experiments already undertaken to study organic carbon – mineral interaction (e.g. Ottley et al., 1997; Postma, 1990; White and Yee, 1985) and initial toxicity tests could be undertaken in marine mesocosm experiments (Vallino, 2000). Studies of natural field

experiments as a consequence of tephra fall into the oceans from volcanic eruptions could be extended and augmented by small scale field experiments. Indeed, it is likely that the greatest barriers to implementation of this, and any other geoengineering strategy, are likely to arise in the areas of social policy and engagement.

4. Conclusions

Deposition of tephra in marine sediments increases C_{org} burial directly through enhanced production and preservation, and indirectly through trapping of oxidized C_{org} in authigenic carbonate within tephra layers.

- Increased preservation is most important in areas where a high proportion of organic material arriving at the sediment-water interface is otherwise oxidized. Data from surface sediments around volcanic islands that contain tephra support the hypothesis that tephra plays a role in increased C_{org} preservation. Deposition of tephra in the modern oceans likely contributes to 5-10% of the overall C_{org} burial flux.
- There is evidence that more deeply buried tephra layers in C_{org} -rich sediments frequently contain high concentrations of authigenic carbonate. This is formed from dissolved CO_3^{2-} produced by sulfate reduction and anaerobic oxidation of methane. This process may contribute to between 10 and 40% of the modern day C_{auth} burial rates in the oceans.
- Increased tephra deposition in the geologic past is unlikely to have played a major role in the ocean-atmosphere carbon cycle through direct increases in C_{org} preservation. However, deposition of tephra in localized environments that are situated at the oxic-anoxic boundary may lead to increased C_{org} preservation and have played a role in generation of hydrocarbons.
- The presence of massive bentonite layers with high concentrations of authigenic carbonate cement at times of increased explosive volcanic activity (e.g. the Ordovician)

suggests that this process may have inhibited the return of oxidized C_{org} to the ocean-atmosphere system in the geological past.

- A more accurate assessment of the role of deposition of tephra in the oceans with respect to the ocean-atmosphere carbon cycle—past and present—will, however, require a more integrated approach from volcanologists, who generally do not analyse non-igneous material in tephra layers, and sedimentary geochemists and palaeoceanographers, who tend to avoid interpretation of non-pelagic sedimentary intervals.
- Evidence from the natural environment suggests that there is a prima facie case for study of the possible role of purposeful addition of tephra to areas of shallow marine sediment as a geoengineering method for enhancing organic carbon burial and reducing CO₂ levels in the oceans and atmosphere.

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