Natural Analogs to Ocean Alkalinity Enhancement

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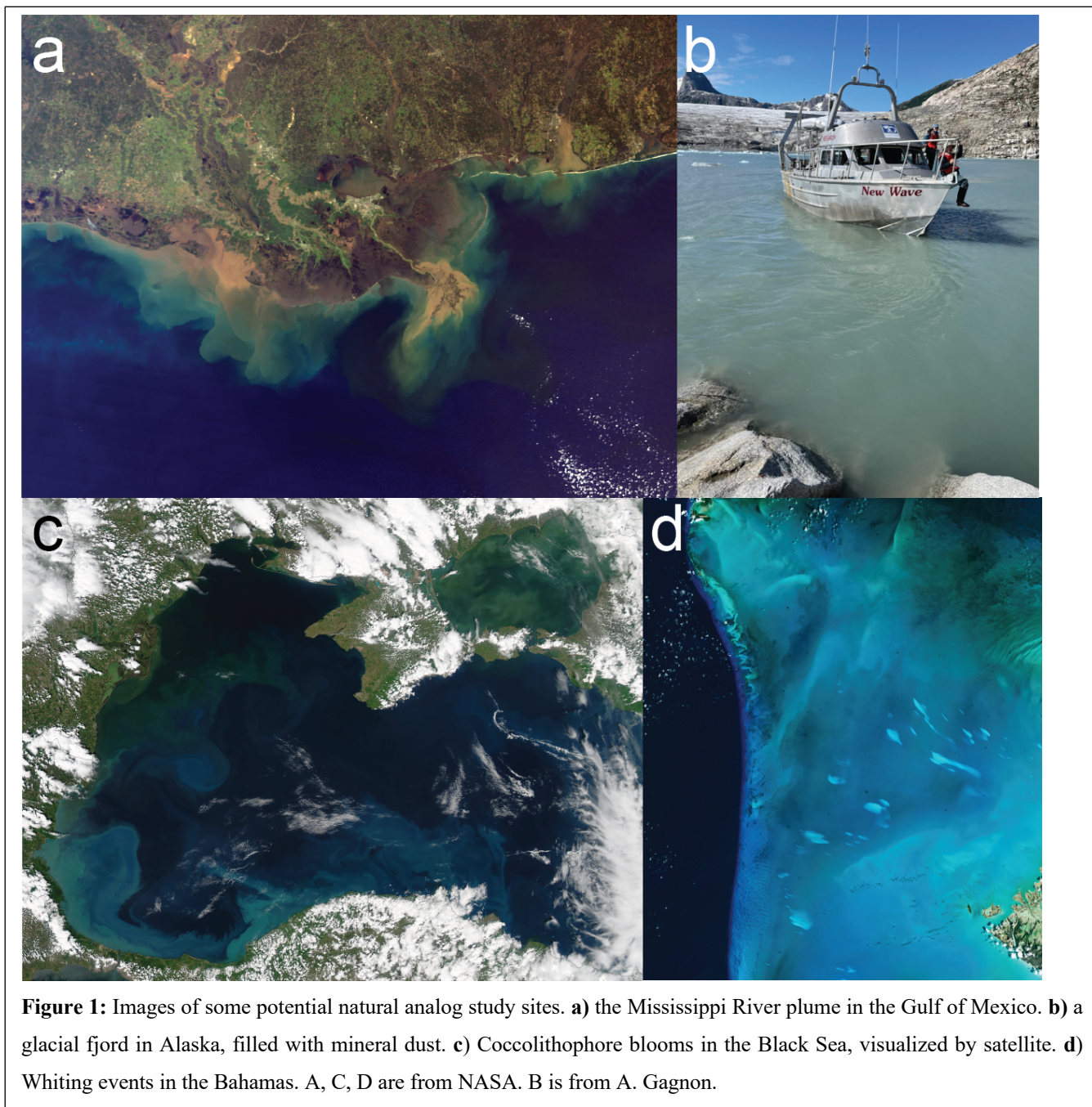
Abstract. Ocean alkalinity enhancement (OAE) research can be supplemented by studying the natural alkalinity cycle. In this
10 chapter, we introduce the concept of natural analogs to ocean alkalinity enhancement. We describe earth system processes relevant to OAE deployment and its measurement, reporting, and verification. We then describe some suitable natural analog locations that could serve as study sites to understand how these processes may interact with OAE. Approaches to examining the geological record are also considered. Practical considerations for establishing a natural analog study are discussed, including geochemical mass balance; choosing a site; establishing a control; choosing a measurement suite and platform; and
15 coordinating with ocean models. We identify rivers and their plumes, glacial fjords, whiting events, and basinal seas with elevated alkalinity, as promising candidates for initial natural analog studies. This chapter is not meant to be prescriptive, but instead is written to inspire researchers to creatively explore the power of natural analogs to advance our understanding of OAE.

1.1 A definition of natural analogs

20 Despite its residence time of about 100,000 years, there is a vigorous and dynamic alkalinity cycle in the ocean. The spatial and temporal patterns of alkalinity concentrations and fluxes are intimately linked with the cycling of dissolved and gaseous carbon dioxide (CO_2), as well as the production and dissolution of calcium carbonate ($CaCO_3$). There may be a number of other locally relevant processes, such as anaerobic remineralization, that also consume and produce alkalinity. Many OAE approaches are based on established geochemical weathering and acid-base reactions, and deploying these approaches will
25 benefit from an understanding of earth's natural processing of alkalinity. These processes operate all around us, right now, at scale. For instance, the chemical and physical weathering of terrestrial rocks produces roughly 60 Tmol alk yr^{-1} that is delivered to the oceans via rivers. This input is balanced by global $CaCO_3$ burial in ocean sediments (Middleburg et al., 2022). The calcium carbonate cycle buries roughly 36 Tmol alk yr^{-1} on shelves and along the coasts, and roughly 23 Tmol alk yr^{-1} in the open ocean (Middelburg et al., 2020). However, open-ocean $CaCO_3$ production of >100 Tmol yr^{-1} greatly exceeds deep ocean
30 burial, resulting in the recycling of ~77 Tmol alk yr^{-1} via $CaCO_3$ dissolution to keep the system at steady state (Milliman et al., 1999, Berelson et al., 2007, Sulpis et al., 2021). Other mineral reactions, such as silicate weathering and reverse weathering, also produce and consume alkalinity within the ocean system. These alkalinity inputs, outputs, and internal cycles can serve

Figure 1: Images of some potential natural analog study sites. **a)** the Mississippi River plume in the Gulf of Mexico. **b)** a glacial fjord in Alaska, filled with mineral dust. **c)** Coccolithophore blooms in the Black Sea, visualized by satellite. **d)** Whiting events in the Bahamas. A, C, D are from NASA. B is from A. Gagnon.

as natural analogs to processes that may respond to OAE, providing insight into what OAE deployment might look like at scale.

Here, we define "Natural analogs" as earth system processes that 1) resemble OAE deployments, or 2) can answer open questions about the feasibility, efficacy, and impacts of these deployments at scale. Natural analogs may offer test beds

for sensor development across alkalinity and carbon gradients, could serve as real-world frameworks for interpreting laboratory and mesocosm experiment results, and could serve as validation tools for modelers to study relevant OAE processes. In many cases natural carbonate chemistry parameters covary with other environmental variables such as temperature, salinity, nutrients, etc. Identifying alkalinity as the driver of a specific response in these systems can be challenging and must be carefully assessed. This drawback to natural analogs can also be a strength. Demonstrating the effect of alkalinity, in combination with a suite of other stressors or drivers, can be a powerful way to evaluate the real-world effect of OAE deployments at scale, without the need for expensive and time-consuming field trials. In addition, natural analogs, including periods of enhanced ocean alkalinity in the geological past, have the potential to elucidate longer-term, acclimated responses to OAE-relevant conditions.

1.2 The benefits and drawbacks of natural analogs

Natural analogs offer all of the benefits and drawbacks that come with the complexity of earth systems. They should be viewed as one of many approaches available to OAE researchers. Laboratory experiments (Iglesias-Rodriguez et al., 2023, this volume) offer ultimate control over conditions and variables, but their results can be challenging to apply to the real world. Mesocosms (Riebesell et al., 2023, this volume) are one step up in complexity, and benefit from not requiring permits to operate, but are costly and limited in their spatial and temporal applications. Field experiments (Albright et al., 2023, this volume) are valuable, and ultimately will most closely resemble real-world deployments. However, they require permits and resources that, currently, make them difficult and sometimes prohibitive to execute. Natural analogs can supplement these approaches in terms of complexity, scope, and scale. They will not necessarily give "clean" results for alkalinity effects alone; rather they offer a rich perspective on how OAE may look at scale, without requiring field experiments.

Examples of recent studies of natural analogs in the context of OAE are still limited, however, previous research on ocean acidification (OA) highlights some of the difficulties and complexity associated with natural sites (e.g., Hall-Spencer et al., 2008, Tyrrell et al., 2008; Kroeker et al., 2013; Manzello et al., 2014; reviewed in Rastrick et al., 2018). Relevant examples for OAE may include large river plumes and estuarine systems where runoff into coastal systems - depending on catchment and underlying bedrock - may create interacting gradients in environmental parameters such as alkalinity, particulate matter, dissolved inorganic carbon (DIC), salinity and/or macronutrients (Raymond & Cole, 2003; McGrath et al., 2016; Gomez et al., 2021), with each of these factors potentially triggering specific species-level or ecosystem responses.

Effects of covarying factors may be large and can wrongfully be attributed to the main variable or process of interest (in this case, alkalinity enhancement). To some degree, targeted site selection can minimize the number of confounding factors. Ideal locations for specific process studies would be sites with distinct spatial and/or temporal gradients in alkalinity and limited fluctuations in other environmental variables (e.g., temperature and salinity, particulate matter, nutrients).

2 Some defining qualities of natural analogs

2.1 Earth system processes and their relationship to OAE

The delivery of alkalinity to the oceans via OAE will interact with the natural alkalinity cycle in various ways depending

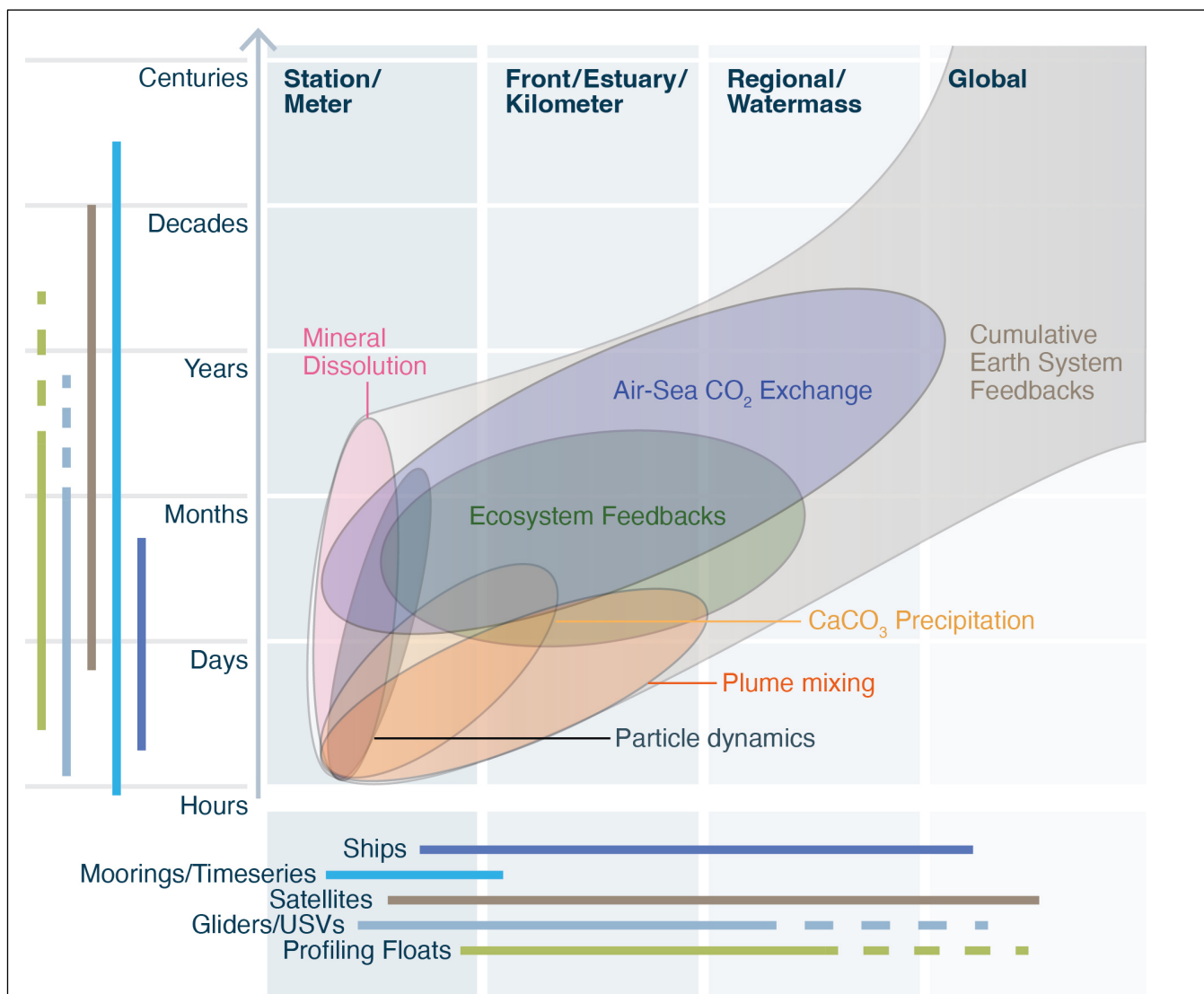



Figure 2: Processes relevant to natural analogs for OAE over a range of length and timescales. Various measurement platforms are shown in the margins, with their associated operating time and lengthscales. Studies investigating OAE should match measurement strategies to the appropriate processes being investigated. Figure concept adapted from Chai et al. (2020) and Bushinsky et al. (2019).

on the approach, scale, and location of deployment. Accordingly, the relationship between OAE and earth system processes will be expressed on a variety of spatial and temporal scales. We depict relevant earth system processes as an oval, with its

75 size and orientation determined by the temporal and spatial scale needed to characterize its influence in the earth system (Figure

2). Mineral dissolution, for example, is typically studied at the micron-to-millimeter scale of the mineral-seawater interface. But, depending on the mineral in question, dissolution rates can occur on the timescale of years. Similarly, calcium carbonate precipitation occurs rapidly at small scales, but at the platform or reef scale, observations must be made over days, weeks, or months to fully understand calcification budgets. Its oval is thus oriented at shorter timescales, but a much broader spatial scale than mineral dissolution.

Earth system processes do not always operate in isolation, but instead overlap and interact with each other, creating higher-order effects that may generate unexpected and nonlinear responses at a range of spatial and temporal scales (depicted schematically as overlapping ovals, culminating in the gray envelope in Fig. 2). Reactions with minerals could ultimately engage with the carbon cycle and ocean-atmosphere CO_2 fluxes. Particle dynamics could feed back on mineral reaction rates, or begin to affect the biological pump, or both. Whether intentional field experiments engage these higher-order effects will depend on their scale in both space and time. The benefit of natural analogs is that these effects are likely already fully coupled with each other. Studying natural analogs can thus test both (quasi) steady-state and transient effects associated with the interactions of these numerous earth system processes. The large and at times undefined scale in both time and space presents a fundamental scale challenge for studying earth system processes, and is a lesson that should be taken to heart by the OAE community. Below we discuss some of these earth system processes that have direct relevance to OAE.

Mineral dissolution. Silicate weathering is the most significant net carbon sink on geological timescales, and relevant dissolution reactions should be occurring in many environments around the globe, including marine settings. These reactions are often slow, taking place on the timescale of months to years, or even longer. In the context of OAE, mineral dissolution reactions will be limited to the treatment location where alkalinity production can be monitored. Because dissolution matrices are often complex (e.g. soils, sediments, and seawater), *in situ* dissolution rates are often hard to model and interpet. Interrogating real-world dissolution rates of these materials, either suspended in seawater or in sedimentary systems, would place useful constraints on dissolution rates and alkalinity production. Understanding real-world controls on secondary precipitation and subsequent alkalinity consumption will also be critical.

CaCO₃ precipitation. Carbonate minerals are considered some of the most reactive on the earth's surface, and their precipitation and dissolution occurs on faster timescales than most silicate mineral reaction rates. There is a major gap in our understanding of how OAE will interact with the ocean's $CaCO_3$ cycle. In the environment, biological and inorganic precipitation are related to a number of complex, interrelated natural factors. Surface seawater is already supersaturated with respect to most $CaCO_3$ minerals, and $CaCO_3$ precipitation is thought to be kinetically limited (Sun et al., 2015). Temperature, Mg^{2+} and other ionic constituents, dissolved/particulate organic matter, and the *in situ* biological community, all may influence the rate and spatial extent of $CaCO_3$ precipitation. These factors will change both in space and time, meaning that the spatial scale of precipitation is often large and poorly defined.

Particle dynamics. Several OAE approaches involve adding fine-grained material to the ocean surface, and letting it dissolve to produce alkalinity. Currently, we have limited understanding of how the sustained, large-scale addition of particles would influence seawater turbidity, flocculation, particle settling velocities, and the marine ecosystem on multiple levels. There may be feedbacks associated with mineral dissolution and precipitation reactions within the particle field. These particle dynamics occur on short spatial scales, but small particles could persist for long periods of time in the water column, leading to relatively long exchange timescales for some particle types and chemistries (Bacon and Anderson, 1982).

Plume mixing and spreading. The enhanced-alkalinity seawater plume resulting from an OAE deployment will be subject to a variety of physical forcings, and will spread out both horizontally and vertically over time. Plume dispersal will be influenced by currents, eddies, seabed topography, and other physical characteristics. Plumes of solid material will behave differently than plumes of dissolved alkalinity. The plume's dispersal will dilute its alkalinity, but will increase its surface area, creating tradeoffs for CO_2 uptake efficiency (He and Tyka, 2023, Wang et al., 2023). Alkalinity will also be lost below the mixed layer due to vertical mixing processes and circulation patterns.

Ecosystem responses. The ecosystem response to OAE is currently unknown (Bach et al., 2019). Responses may be quite variable, and will involve both immediate "shock" responses, and longer-term acclimated responses. Imagine exposing a marine ecosystem to a dispersing plume of alkalinity. Some parts of that ecosystem may sit directly in the outfall and experience sustained impacts, while others may experience periodic "whiffs" as the periphery of the plume disperses and shifts with water circulation. In the pelagic environment, the ecosystem may move along with the plume.

One ecosystem impact on OAE efficiency is whether it will stimulate biological calcification, either in open-ocean calcifiers such as coccolithophores, or in coastal ecosystems such as coral reefs or shellfish habitats. In many cases, OAE will decrease the pCO_2 of seawater, potentially limiting the availability of CO_2 for photosynthesis for some organisms. In the case of solid additions, impurities and other constituents could dissolve along with alkalinity and could begin to interfere with the structure and function of marine ecosystems. How these effects are translated to higher trophic levels, and if there are any direct impacts on higher trophic level organisms, are poorly understood.

Air-sea CO_2 exchange. The OAE approach to carbon dioxide removal (CDR) relies on the equilibration of an alkaline seawater parcel with the atmosphere. Air-sea gas exchange is thus a fundamental component of OAE and may play an important role in limiting the timescale of CDR. Carbon dioxide dynamics and equilibration timescales are generally understood, and occur on timescales of several weeks to up to a year (Jones et al., 2014). The spatial scales of this equilibration depends on the surface expression of a water mass and its physical and chemical characteristics. How air-sea CO_2 dynamics specifically change with alkalinity enhancement and the overall carbonate system in seawater is not well characterized.

Cumulative earth system feedbacks. Eventually, and especially when considering OAE at gigaton scales, the processes listed above will blend with each other, leading to large-scale feedbacks of the biogeochemical ocean system. These feedbacks will become increasingly large and diffuse, essentially becoming part of the earth's biogeochemical cycling of alkalinity and carbon. If OAE stimulates $CaCO_3$ precipitation, alkalinity outputs could fundamentally change at the platform, basin, or global ocean scale. Ecosystem feedbacks, if sustained, could lead to significant reorganization of the biological pump with implications for the organic carbon cycle and the balance of CO_2 fluxes at the ocean surface.

2.2 A non-exhaustive list of OAE natural analogs

The processes and systems discussed in this chapter are not meant to be prescriptive or limiting. We encourage researchers to think creatively about the problems associated with OAE deployment – whether they be technical or scientific – and find suitable natural systems to study solutions to these problems. Many of the current open questions may get solved or become moot in subsequent years. The natural analog concept can, and should, continue to be applied even as our knowledge base for OAE grows and evolves over time.

Ideal natural analogs for all of the above processes, and how they will interact with OAE, will typically exist at system boundaries and across defined gradients in carbonate chemistry. For relevance to OAE, it will be important to constrain the interactions between alkalinity and the system in question, and ultimately the associated implications for the efficiency, safety, and scalability of OAE.

Rivers and their plumes and deltas (Fig. 1a). There may be opportunities to study natural river chemistries and their associated plume and sediment dynamics in regions with defined, sustained inputs to the marine system. Rivers deliver most of the alkalinity to the ocean, and dedicated surveys of these plumes across a variety of river compositions and plume geometries will provide critical information for large-scale alkalinity enhancement deployments. Deltaic environments may be useful to study the impact of particle loading and sediment-water interactions.

Glacial fjords and runoff into the marine system (Fig. 1b). The delivery, settling, and reaction of glacial flour in semi-enclosed or restricted basins could be useful for mineral dissolution/precipitation, particle dynamics, and plume evolution.

Basin-scale systems with unique geochemistries and ecologies (Fig. 1c). The larger the spatial and temporal scale, the larger the natural analog system boundary must become. The advantage of natural analogs is that these large-scale feedbacks can be assessed immediately. As proposed by Bach et al. (2021), alkalinity in the Black Sea is much higher than that of 'normal' seawater, and could serve as a basin-scale analog to investigate long-term effects of OAE.

The Bahamas carbonate platform and slope (Fig. 1d): "Whiting" events– large plumes of suspended $CaCO_3$ that appear in the Bahamas – are poorly understood, and might be an ideal natural analog to study how temperature and other seawater

properties, will interact with OAE to promote the homogenous formation of $CaCO_3$ minerals from seawater. Whitings may also elucidate the role that suspended sediments play in stimulating $CaCO_3$ precipitation (Geyman et al., 2022).

180   ***Seafloor weathering of basalts.*** Low-temperature seawater-basalt interactions could be critical for alkalinity production, mineral dissolution, carbonate precipitation, and trace metal impacts.

Beach locations with unique mineral sand compositions. Black sand or olivine beaches present unique opportunities to study integrated, long-term effects of mineral addition. There may also be opportunities to study ongoing beach
185   nourishment projects that, while not strictly natural analogs, could provide systems for study without the need for additional permitting.

Wastewater and other anthropogenic outfalls. Although typically wastewater outfalls are acidic rather than basic, they represent opportunities to study the impacts of altered chemistries on the marine system. Again, these are not strictly
190   "natural" analogs, but could provide useful information for the OAE research community.

2.3 Extending OAE to geological timescales

The concept of ocean alkalinity enhancement as a means of carbon sequestration into the ocean is inspired by the conceptual mechanics of the long-term carbon cycle of the Earth System. Any additional output of acidic CO_2 to the ocean-
195   atmosphere system, derived from e.g. volcanic outgassing, is thought to be buffered naturally, and therefore stored in the ocean, on an expanding range of timescales by different components of Earth system alkalinity (Figure 3):

1.   Dissolved carbonate alkalinity (titration of CO_2 with CO_3^{2-} to yield HCO_3^- redistributes additional carbon between the different carbonate species in solution (days-years)
200   2.   Deep ocean calcium carbonate sediment (titration of CO_2 with seawater decreases the CO_3^{2-} ion yielding lower carbonate saturation which drives deep ocean dissolution and release of alkalinity from carbonate sediments through vertical migration of the saturation horizon (7-10 kyrs)
3.   Alkalinity released from increased weathering of silicate rocks as a result of elevated temperatures from additional CO_2 in the ocean-atmosphere system (Myrs).

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Geological measures of ocean alkalinity. Any period in geological history when the pH (traced with Boron (B) isotopes in foraminifera e.g. Foster et al., 2008) and/or carbonate saturation state of the deep ocean increased is reflective of an increasing ratio of total alkalinity to dissolved inorganic carbon (TA/DIC) and can point to a time of elevated ocean alkalinity relative to carbon. These periods are often defined relative to geological events, such as the Paleocene-Eocene Thermal Maximum
210   (PETM), which corresponds to a very large injection of carbon into the earth system.

Figure 3: Evolution of (top) atmospheric pCO_2 and (bottom) weathering alkalinity flux to the ocean over 1 Myr for a 5000 Gt C emission pulse with terrestrial carbonate (blue) and silicate (tan) weathering feedbacks activated, using the GENIE earth system model with a representation of terrestrial rock weathering. Note the changing timescale (adapted from Colbourn et al., 2015).

Vertical migrations of the carbonate saturation horizon, at least since the advent of pelagic calcifiers ~220 Ma, moderate the deep ocean alkalinity burial to keep it in balance with the supply of alkalinity to the ocean from the release of cations through continental weathering. Consequently, the carbonate compensation depth (CCD), defined as the depth beneath which there is no preserved carbonate in sediments, and which moves vertically largely in parallel with the saturation horizon, provides one of the best proxies for ocean alkalinity. Any deepening reflects increased ocean alkalinity and vice versa but not necessarily an increase in weathering inputs to the ocean.

A process of "biological carbonate compensation" can decouple the CCD from weathering due to environmental triggers which increase the shelf or pelagic carbonate production and burial above the CCD, and drive a shallowing or vice versa (Rickaby et al., 2010; Boudreau et al., 2019). Carbonate Ba/Ca and P/Ca have also been proposed as additional indirect measures of ocean alkalinity (Ingalls et al., 2020; Lea and Boyle, 1989).

Geological targets to study ocean alkalinity enhancement. The geological periods of enhanced ocean alkalinity are characterised by either an increase in the source of alkalinity to the ocean, or a decrease in the sink. The major levers on the global alkalinity budget are those of weathering inputs and calcium carbonate burial but smaller contributors include reverse and submarine weathering and anaerobic processes.

Robust identification of enhanced weathering rates associated with e.g. elevated temperatures in the geological record could indicate a period of elevated ocean alkalinity due to enhanced alkalinity supply to the ocean. Disentangling weathering intensity from isotopic proxies such as Sr, Os and Li isotopes is non trivial, but Earth's weathering thermostat does seem to be triggered to aid recovery after abrupt carbon perturbations e.g. of the Mesozoic (Pogge von Strandman et al., 2013) and cap carbonates are taken as evidence of an abrupt increase of global weathering rates in the elevated CO_2-induced warmth after Snowball Earth events during the Precambrian. Coupled deepening of the CCD with isotopic signals of weathering likely provide the best measure of events of ocean alkalinity enhancement.

Due to the partitioning of carbonate sediments and alkalinity burial between the shelf and the deep ocean, any periods of lowered eustatic sealevel (such as sealevel regression, glacial maxima or ice house periods) which restrict the shelf area for carbonate burial, equate to elevated whole ocean alkalinity and a deeper saturation horizon and CCD. The aftermath of major extinctions involving biomineralisers such as the Permo-Triassic, may be subject to enhanced ocean alkalinity as a result of the loss of a major biotic alkalinity sink; indeed immediately prior to the Cambrian explosion of skeletal organisms, both saturation state and alkalinity are inferred to be highly elevated, from evidence of abiotic seafloor precipitation, due to the lack of a major biotic sink of carbonate.

Events of burial of organic carbon also perturb the TA:DIC budget by removal of DIC from the ocean-atmosphere system. Any reduction in DIC elevates the relative ocean alkalinity and can trigger deepening of the carbonate saturation horizon as seen during e.g. the regrowth of the terrestrial biosphere at the end of the last glacial maximum (Berger, 1977).

3   Practical considerations for natural analog studies

The study of natural analogs is related to, but distinct from, basic research into the cycling of alkalinity and carbon through the earth system. Because many different types of researchers may be approaching OAE and its interactions with the earth system for the first time, we outline here some practical considerations for field observations and the study of natural systems. There are both theoretical and practical constraints to conducting natural analog studies that should be taken into account when determining the scope and scale of a campaign. Many of these concepts are either established in earth science, or in some cases, are still being actively developed as observational networks evolve and mature.

3.1 A primer on geochemical mass balance

The survey and sampling timescale is important here when considering the spatial/temporal scale of your natural analog (Fig. 2), the duration of the study, and the types of measurements and platforms used. When constructing a geochemical model of a

natural system, we typically make the assumption of steady state, or in other words that concentrations are not changing with time due to a balance between the inputs and the outputs on the timescale of interest:

$$\frac{dC}{dt} = 0 \text{ (eq. 1).}$$

260

This assumption allows researchers to assume that spatial gradients represent a balance of rates or fluxes – in other words, rates are now expressed as a function of space rather than time. As an example, consider a natural analog study that is investigating the removal of alkalinity as river water mixes with ocean water (Fig. 1a, Fig. 4). A survey is conducted, sampling down the river, through the plume, and into the ocean. The river flow is unidirectional, and sets up a steady-state gradient

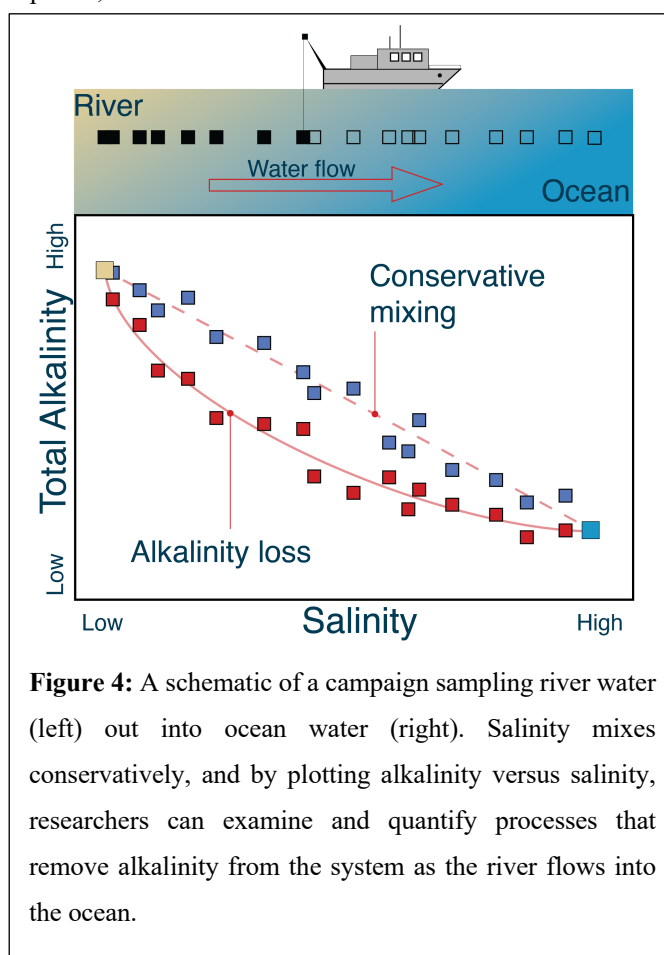



Figure 4: A schematic of a campaign sampling river water (left) out into ocean water (right). Salinity mixes conservatively, and by plotting alkalinity versus salinity, researchers can examine and quantify processes that remove alkalinity from the system as the river flows into the ocean.

265   between solutes in the river and solutes in the ocean. The total salt content, measured as salinity (S_{mix}), is a proxy for the fractions of river and ocean water in each sample, and an array can be constructed based on these measurements and the known salinity of the river (S_{river}) and ocean (S_{ocean}) end members (Boyle et al., 1974):

$$f_{river} = \frac{S_{mix} - S_{ocean}}{S_{river} - S_{ocean}}, \text{(eq. 2a)}$$

270

and mass balance is assumed between these two endmembers::

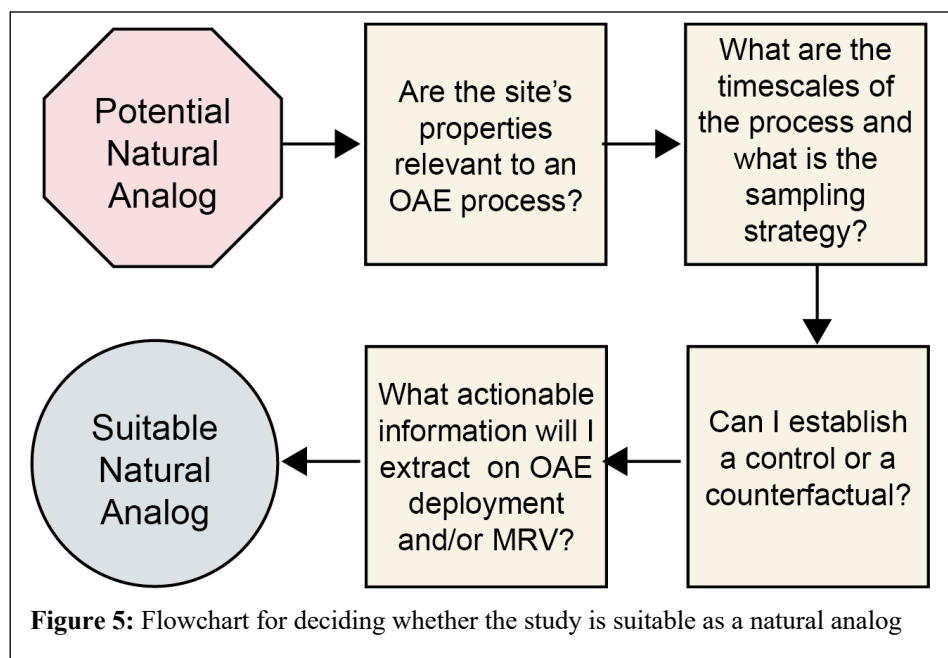
$$f_{river} + f_{ocean} = 1 \text{ (eq. 2b)}.$$

275 If alkalinity also mixes conservatively, then the samples will fall on a conservative mixing array, i.e.:

$$TA_{mix} = TA_{river} f_{river} + TA_{ocean} f_{ocean}, \text{(eq. 2c)}$$

where the measured "mixture" value is a linear combination of the river and ocean endmembers. This relationship indicates
280 no addition or removal of alkalinity during the mixing process, and can be confirmed visually by plotting alkalinity versus
salinity: If the data falls on a straight line between the endmember values for salinity and alkalinity, then alkalinity is not being
produced or consumed in the system (Fig 4). However, if the alkalinity data falls below this conservative mixing line, then
alkalinity is being removed during the mixing process. Critically, the signal of interest must be larger than the scatter in the
data to quantitatively establish a reaction process, as illustrated by the scatter of data points in Fig. 4. At steady state, the
285 alkalinity loss can be quantified by multiplying the river flux by the difference between these two curves.

The concepts of steady state and (non)conservative mixing are useful frameworks for setting up a study, interpreting
the results, and quantifying biogeochemical processes over space and time, and can be applied to any water property that mixes

Figure 5: Flowchart for deciding whether the study is suitable as a natural analog

linearly. In this river example, DIC-salinity relationships could be used for quantifying carbon uptake and loss due to gas exchange, photosynthesis, and calcium carbonate precipitation. For pCO_2 and pH, the relationships become more complicated

290 because they are nonlinear functions of TA and DIC (Schulz et al., 2023, this volume). In addition, if there are more than two endmembers interacting in the study area, then this binary mixing model is not appropriate. We discuss other methods of analyzing field data in Section 3.5.

3.2 Determining a suitable natural analog location

295 Determining whether a site is a suitable natural analog can be accomplished by asking a series of questions about its relevance to OAE deployment and/or its MRV (Figure 4). When considering a candidate site, researchers should ask themselves: What qualities make the site relevant to OAE? Relevance can be clearly established through the presence of either enhanced alkalinity and/or solid materials that are producing alkalinity through interaction with seawater. However, other processes such as particle loading and plume mixing may be appropriate even in the absence of large alkalinity gradients

300 (Figure 1).

The next consideration is timescale. How fast does the system change, and can alkalinity effects be assessed with an effective sampling strategy? Matching the measurement scheme to the process timescale (Figure 2, 3) is critical at this stage, and should guide the choice of measurement platform(s) (Section 3.3), and the associated measurement suite (Section 3.4). Alkalinity effects can only be assessed through to the counterfactual case, in a similar manner to how MRV will be conducted

305 (Ho et al., 2023, this volume). A control or counterfactual, either in space or in time, should be established and should be quantifiable from the "OAE" condition (Section 3.5). The platform, measurements, and counterfactual conditions will all determine the approach for extracting alkalinity effects from the study location (Section 3.5). In some cases, it may be useful to pair field observations with models to contextualize your results (Section 3.6).

In sum, given all of these considerations, it is critical to think through how the results of the study will be synthesized

310 into actionable information about OAE deployment and its MRV. For example, if a feedback on alkalinity is established, can you relate that feedback to alkalinity loading to provide thresholds for OAE deployments, or minimum detection limits for MRV? Quantifying efficiencies on CO_2 uptake as a function of alkalinity loading are another example of a useful outcome from a natural analog. If these questions can be answered, then you have found yourself a natural analog. As shown in Fig. 1, rivers and their plumes, glacial fjords, the Black Sea, and whiting events in the Bahamas, immediately stand out as targets for

315 natural analog studies.

3.3 Choice of platform

Once a potential process or site is chosen, it is important to consider what measurements are best suited for the study. Measurements can be conducted either in the lab or in the field, on vessels or remotely using autonomous assets (depicted in

320 the margins of Fig. 2). Choosing an appropriate platform and measurement suite will depend on the timescale of the process;

access to equipment and instrumentation; and the practicality of the planned operations. Each platform operates within a specific window in both space and time, and these ranges should be considered when planning the field campaign.

325 *Research vessels* have been part of the oceanographic toolkit for decades, from small boats all the way to 300+-foot global-class ships. These vessels offer flexibility, a range of built-in scientific instrumentation and equipment, research labs, and well-trained crew. Many research stations around the world operate their own smaller vessels that can be chartered for surveys. They can sample across entire ocean basins, but are limited in their temporal coverage to at most two months of continuous operation.

330 *Moorings and timeseries* can be invaluable for studying a specific location over extended periods of time. Timeseries stations are critical for establishing the ranges of natural variability, and can be outfitted with a number of sensors and instruments. However, their applicability to a broader spatial scale is often limited, without other regional data or a model for context.

335 *Satellites* can be tasked to investigate ocean-surface processes, and essentially cover the entire planet. Their timescales are often limited by their orbits, and thus cannot provide very high temporal resolution. Smaller constellations of cube-satellites can sometimes be tasked to give very high (sub-meter) resolution, and sometimes multiple transits in a single day, but their spatial scales are limited to coastal areas, and many are never tasked for open-ocean work.

340 *Gliders and Uncrewed Surface Vehicles (USVs)* are becoming an important part of observational networks. Gliders can provide high spatial resolution, but their operating speeds are often slower than crewed vessels. Depending on the operation, this limitation can be overcome by deploying glider fleets with a suite of intercalibrated sensors. Their operations are also limited by power, either batteries or access to solar or wind energy. Currently, gliders cannot sample the deep ocean, and can also not operate in very shallow or tightly constrained locations due to navigation 345 constraints. Some vehicles can be piloted and reprogrammed on the fly, but many gliders have fixed trajectories that are set upon deployment.

Profiling floats such as those used for the ARGO and Bio-ARGO program have been immensely helpful for establishing state estimates of the global ocean. Integration of biogeochemical sensors is ongoing. However, many 350 profiling floats are limited to the open ocean, and cannot operate in coastal or shelf areas with shallow seabeds.

Existing geological archives such as sediment cores from drilling programs can be investigated for time periods and geological events that are relevant for OAE.

3.4 Choice of measurement suite

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Oceanographic platforms host a unique set of measurements and capabilities, and come with tradeoffs between coverage, what you can measure, and how well you can measure it (Table 1, Bushinsky et al., 2019, Chai et al., 2020). Although bottle samples in the lab provide the highest precision and accuracy, they are limited in terms of sample throughput, preservation and shipping, and the need for expensive instrumentation. Underway or pumped systems can provide high-

360 frequency surface data, but can clog/foul and need a source water to be pumped through them. They are best suited for research vessels or moorings. *In situ* sensors can provide very high frequency data and be deployed on a range of platforms including gliders and profiling float. However, they must be calibrated, they can drift, and they are currently limited in what parameters they can measure. Remote sensing from satellites has by far the greatest spatial coverage, but is limited to the surface layer and by weather. Data are limited to optical measurements and imagery.

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The natural variability of the site will be important to balance against your analytical capabilities. For instance, if an estuary experiences tidal changes of >100 µmol kg^{-1} alkalinity, it may not be informative to take daily samples. *In situ* sensors with lower precision may not be able to detect small alkalinity enhancements above large natural variations. In addition, it is important to consider which carbonate chemistry variables are ideally suited for the sampling scheme. Alkalinity and DIC are both conservative and can be easily unmixed, but in many cases pH may be more effective as a diagnostic tracer of multiple

370 processes (e.g. alkalinity enhancement and subsequent CO_2 uptake). Combined with its relatively high measurement precision, frequency of measurement, and sensor availability, pH may be an attractive parameter for many early studies especially if it can be ground-truthed against alkalinity and DIC bottle data.

Table 1: Tradeoffs associated with various measurement approaches.

	Bottle Samples	Underway Systems	In situ Sensors	Remote Sensing
Pros	• Very high precision + accuracy • Well standardized • All carbonate system parameters	• High frequency • Immediate data • Well standardized	• Very high frequency • Can profile the water column • Integration on a range of platforms • Optical measurements possible	• Wide spatial coverage • High spatial resolution
Cons	• Need for poisoning • Requires laboratory • Transport/shipping costs • Lower temporal resolution	• Surface only • Need vessel and pumped water flow • Can foul/clog	• Limited carbonate chemistry parameter set • Lower precision+accuracy • Drift must be calibrated • Integration is a challenge	• Limited temporal resolution (clouds, orbit) • Must be ground-truthed • Surrface only • No carbonate chemistry, only optical measurements

3.5 Establishing a control

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In natural systems, there may not be a "perfect" control condition; instead, establishing relative changes between conditions (spatial, temporal, etc.) may be all you can do. However, these relative changes should be clear and measurable given the sampling approach you have outlined. Controls can be established both in space and in time. For instance, different

beaches, bays, or fjords can exhibit unique water chemistries and rock/sediment types. Setting up a similar survey or measurement scheme in two or more of these locations will yield a dataset that can be easily compared and contrasted.

380   Systems also change over time. For instance, the water chemistry, or river state, can be used to compare geochemical processes when one endmember changes significantly from season to season. As an example, many rivers exhibit different solute concentrations and total water fluxes between the dry and rainy seasons. One season's survey can serve as a control for the second survey, provided that the conditions – and the expected geochemical signatures that result – change significantly on a seasonal basis. These conditions must be established in the context of the spatial and temporal timescales of the process

385 of interest. In addition, similar assumptions for the steady state nature of the surveys should be verified, to ensure that the results can be effectively compared.

3.6 Isolating alkalinity effects in your data

      One of the main challenges when studying natural analogs in the context of OAE arises from potential concurrent

390 effects of various confounding factors (e.g., temperature, salinity, nutrients, light, other carbonate system parameters) varying in space and/or time along a gradient in TA. Unequivocally attributing specific biogeochemical or ecosystem responses (e.g., precipitation of calcium carbonate, species performance and distribution) to a single environmental variable (e.g., TA) remains challenging. Targeted monitoring combined with statistical tools can help to assess the impact of confounding factors and identify relationships between various covarying factors and specific response variables. The choice of the statistical analysis

395 depends on the particular question of interest and the complexity of the system to be studied.

      Multivariate analyses. Multivariate analyses, such as principal component analysis (PCA), may be useful tools in cases where multiple environmental variables are present, with the objective being to determine underlying patterns and variability of a particular system without necessary predicting the relationship between a specific dependent (i.e., response)

400 and independent (i.e., predictor) variable(s). PCA has been successfully employed to evaluate impacts of hydrography and carbonate chemistry on species performance along the California Current (Kroeker et al., 2016), to identify empirical relationships between physical and biological variables and pCO_2 variation across the Mississippi River delta (Lohrenz and Cai, 2006), and to determine the main drivers of 'whiting' events on the Bahama Banks (Yao et al., 2023).

405   ***Simple and multiple linear regression models***. Often, the objective of *in situ* observational studies is to assess the link between a particular response variable and the variability in one or more predictor variables. A simple linear regression analysis specifically assesses the relationship between one continuous predictor variable and one continuous response variable. While simple linear regressions may particularly be useful under set laboratory conditions where individual parameters are manipulated, *in situ* or natural experiments are generally more complex and often include multiple environmental factors to

410 be investigated simultaneously. Thus, a multiple linear regression (MLR) model can be a useful tool in cases where a response variable is expected to vary based on two or more predictor variables. Single or multiple linear regression models are

commonly used to study links between changes in carbonate chemistry (e.g., TA, pCO_2, $\Omega_{Calcite}$) and biogeochemical or ecosystem responses (e.g., phytoplankton growth, calcification; Krumhardt et al., 2016; Silbiger et al., 2017). Endmember mixing models are common tools along estuarine and coastal systems where large gradients in physico-biochemical parameters

415 persist to extract potential sink and source processes of, for instance, alkalinity or DIC from conservative mixing influences (Figure 4; Guo et al., 2012).

While general regression models come with clear benefits due to their simplicity, they have some major disadvantages. Linear regression models can be restricting in their application given the assumption of linearity between dependent and independent variable(s). For example, DIC and TA mix linearly, but pH and pCO_2 do not. The model thus may

420 perform poorly at capturing the complexity within certain data. In addition, regression models are highly sensitive to missing values and outliers, particularly in studies with a small sample size. To avoid some of the pitfalls associated with linear regression models, it is advised to visually inspect the data and verify that the basic assumptions of the model are met before implementing a regression model. For example, graphical tools such as a scatterplot matrix help to verify that the relationships between dependent and independent variables are linear. When including multiple predictor variables in MLR models it is

425 further advised to evaluate the independent variables for multicollinearity (e.g., independent variables should not be highly correlated among each other). A simple Pearson's bivariate correlation matrix allows the identification of highly correlated independent variables. Once a model has been implemented, additional useful validation tools to test whether basic assumptions are met may include histograms and Normal Q-Q plots to assess normality or scatterplots to check for homoscedasticity.

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Extensions to simple linear models. In cases where particular assumptions are violated (e.g., non-linearity, non-normal distribution, heteroscedasticity), extensions to simple linear models may be applied. For example, in cases where data do not follow a Gaussian distribution, data transformation may be applied, or a generalized linear model (GLM) for non-normal distributions may be implemented. To address non-linearity, possible modifications to the simple linear regression model

435 include (1) data transformation, which requires some prior knowledge of the input transformation being performed or (2) implementing a generalized additive model (GAM). GAMs are extensions of GLMs, yet are more flexible in their application as they allow for non-linear relationships between the response variable and predictor variable(s), thus are more suitable for describing more complex data sets. Given this higher flexibility, one of the drawbacks of GAMs includes the higher complexity and potential associated effects on model interpretability (e.g., non-linear features potentially less intuitive and more

440 complicated to interpret). The quantitative comparison of model performance and model selection can be guided using an analysis of variance (ANOVA) and/or comparative indices such as the Akaike information criterion (AIC), a generalized cross validation (GCV) score and/or adjusted R-squared.

3.7 Regional modeling for field data validation

445   Studying natural analogs in the context of OAE has some clear limitations, largely due to the high complexity of the natural system and the difficulty in isolating the effects of TA from other environmental variables. Regional ocean models provide complementary tools that can help to disentangle the effects of confounding factors and determine underlying mechanisms driving observed patterns in the field. For example, Gomez et al. (2021) implemented a regional model for the Gulf of Mexico and decomposed the carbonate system into individual components (e.g., pCO_2, pH, TA, Ω_{Ar}) to determine

450   their relative importance on overall OA progression and assess specific impacts of increased riverine alkalinity from the Mississippi River.

        Regional models provide a verification framework for underlying physical and biogeochemical processes occurring in a system and, as such, can be a valuable tool to test our conceptual understanding of specific processes. Coupled physical-biogeochemical models to evaluate artificial ocean alkalinization on a regional scale are emerging (e.g., Butenschön et al.,

455   2021, Mongin et al., 2021; Wang et al., 2023; see Fennel et al., 2023, this volume, for details), yet similar modeling exercises applied to validate physical and biogeochemical processes along natural gradients are currently limited. Implementing a regional model, for example, in areas where natural 'whiting' events occur (e.g., Bahama Banks) could be useful to test some of the various proposed mechanisms (e.g., abiotic/biotic calcification, sediment resuspension) leading to the observed accumulation of suspended calcium-rich particles in the water column (e.g., Larson & Mylroie, 2014; Yao et al., 2023). Recent

460   model simulation implemented a point-source OAE approach in the Bering Sea to evaluate the efficiency in CO_2 removal associated with a TA addition (Wang et al., 2023). Similar approaches could give valuable insights when applied to natural analogs, for example to study the dispersal of an alkaline river plume and associated impacts on pCO_2 and carbonate chemistry, porewater alkalinity fluxes, or the interaction of mineral dissolution and circulation in enclosed basins.

        In addition to hypothesis testing, models provide a means to increase the spatio-temporal resolution of *in situ*

465   observations. The coverage of *in situ* observational data is often spatially and temporally limited due to logistical constraints (e.g., financial constraints, rare or remote location of natural analog) and/or natural variability of the system (e.g., seasonality, episodic occurrence), which can make replication challenging. Using ocean models in conjunction with natural (and field) studies allows to extrapolate spatially and temporally and fill in gaps in field observations.

        In turn, models are evaluated in regard to how well observed patterns are reproduced, giving insights into underlying

470   processes and how well these are represented in model parameterization. As such, model simulations rely on underlying assumptions that may not fully reproduce the high complexity and observational pattern of the natural system, in particular in regard to complex biological interactions (e.g., TA loss through carbonate mineral precipitation, trophic interactions, acclimation). For steady state systems (e.g., Black Sea), models are currently unable to capture the adaptive response of the phytoplankton community to chronic high-TA exposure. Natural analogs provide an opportunity to study long-term responses,

475   and to continue developing modeling tools that are capable of resolving critically important biogeochemical processes.

4 Conclusions and considerations for future natural analogs

Studying natural analogs in the context of OAE is currently to some degree hindered by the availability and quality of oceanographic data. The ongoing expansion of the observational infrastructure, including the deployment of autonomous
480 vehicles such as gliders and BGC-Argo floats, continuously increases data coverage, quality and availability, making it progressively easier and cheaper to study natural analogs. *In situ* profiling platforms such as Argo floats are particularly useful for off-shelf regional and basin-scale studies. Autonomous platforms allow the expansion from remotely-sensed surface observations (e.g., satellite observations) to high resolution depth profiles, enabling the study of depth-resolved physical and biogeochemical processes. Recent examples relevant for OAE include the depth-resolved detection of coccolithophores using
485 BGC-Argo floats (Terrats et al., 2020), increasing the spatial and temporal resolution of ship-based observations and expanding previous satellite-derived estimates to well below the surface layer.

The list of natural analogs and targets in the geological record highlighted in this chapter is by no means exclusive and additional suitable natural sites are likely to be identified as additional questions in the context of OAE arise. Natural analogs with potentially different natural gradients, spatio-temporal resolutions and/or processes that are not accounted for yet
490 in current surveys may be studied as sensor development and the ability to measure additional parameters evolve. Identifying key biogeochemical processes and ecosystem responses that can be measured and empirically linked to impacts of enhanced alkalinity is crucial in advancing our understanding of potential OAE impacts. Combining natural observational studies with controlled small-scale field manipulation or laboratory experiments will be key for addressing knowledge gaps and questions in regard to specific biogeochemical reactions, spatial/temporal patterns and species interactions currently emerging from
495 ongoing observational surveys. Importantly, no single approach will be able to resolve the full spatial and temporal extent and complexity of the system, and a combination of approaches (field studies, laboratory experiments, modeling exercises) will be required to address different physical and biogeochemical processes and levels of complexity.

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500 AVS, NL, and REMR conceived, wrote, and edited the paper.

Competing interests

The authors declare no competing interests.

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