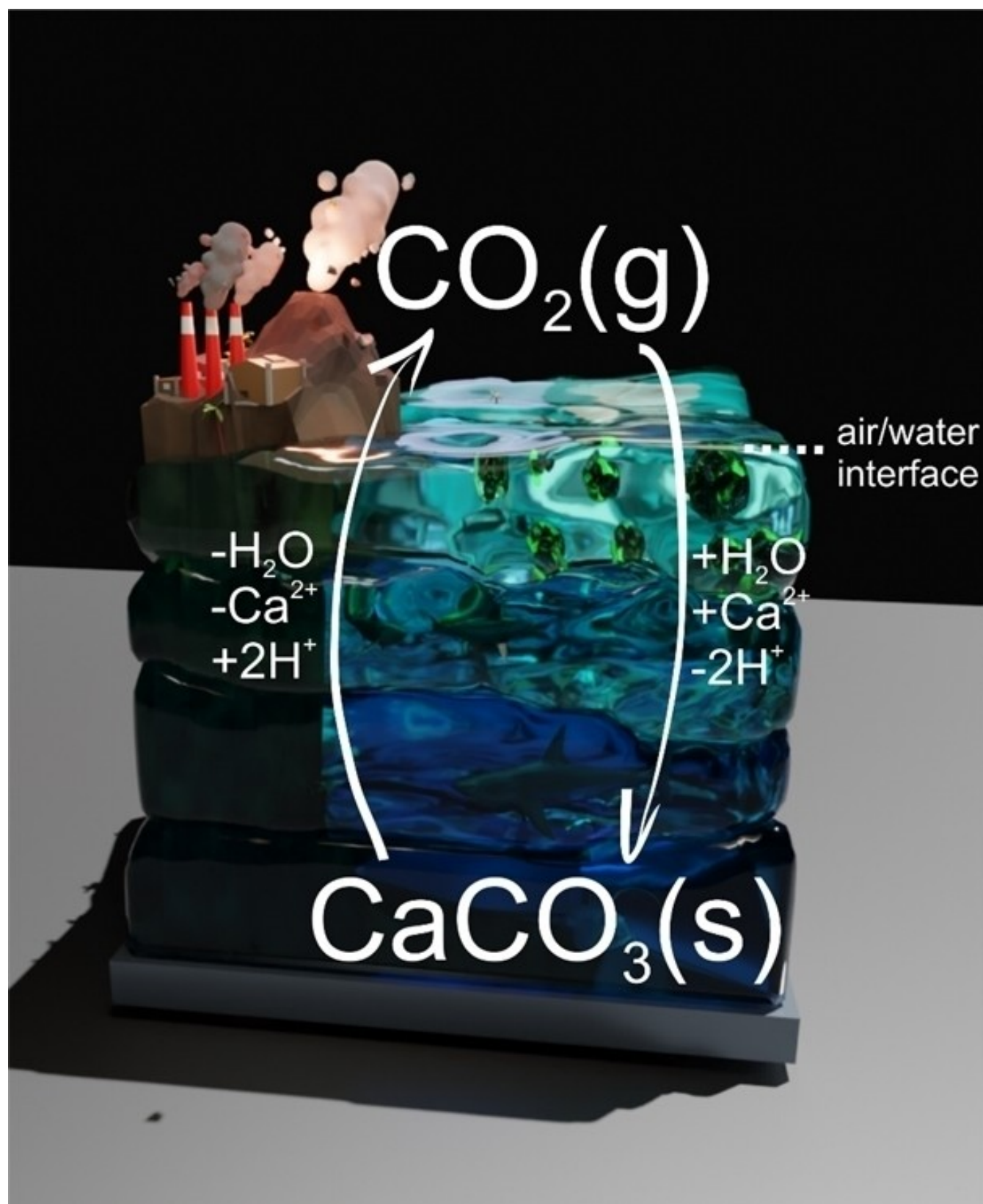# Calcium Carbonate Dissolution from the Laboratory to the Ocean: Kinetics and Mechanism

Abstract: The ultimate fate, over the course of millennia, of nearly all of the carbon dioxide formed by humankind is for it to react with calcium carbonate in the world's oceans. Although, this reaction is of global relevance, aspects of the calcite dissolution reaction remain poorly described with apparent contradictions present throughout the expansive literature. In this perspective we aim to evidence how a lack of appreciation of the role of mass-transport may have hampered developments in this area. These insights have important implications for both idealised experiments performed under laboratory conditions and for the measurement and modelling of oceanic calcite sediment dissolution.

Introduction

An aqueous 1 mM solution of sodium hydroxide has a pH of ~11. However, if left open to the atmosphere, then due to the carbon dioxide in the air transferring to the solution and in hydrated form acting as a weak acid, then the pH of the solution will drop to ~8.3 after equilibration. The hydroxide reacts with the carbon dioxide leading to the formation of bicarbonate. This acid/base titration reaction is essentially what has happened in the world's marine surface waters; alkaline moieties released from weathered rocks have reacted with atmospheric CO_2 resulting in a carbonate rich solution.[1] Seawater has a pH of ~8.1 and contains a total of approximately 2.1 mM inorganic carbon present predominantly as bicarbonate but with carbonate, and dissolved carbon dioxide also present.[2] Seawater also contains other salts including around about 10 mM of calcium ions. Due to the presence of these calcium ions the surface of the oceans are oversaturated with respect to calcium carbonate minerals. Importantly, at low to moderate oversaturation levels, and in the presence of precipitation inhibitors such as Mg^{2+}, SO_4^{2-} and organic acids, calcite precipitation is extremely slow.[3] Any "inorganic precipitation" that does occur is generally of aragonite[4–5]. Hence, although the surface waters are oversaturated with respect to calcite, this is a kinetically metastable situation; the world's oceans have been oversaturated with respect to calcite likely for the entirety of the presence of the ocean on Earth (>3 billion years). As a consequence, this metastable oversaturation has been biologically harnessed by a range of marine calcifiers that use biogenically precipitated calcium carbonate to form protective shells and exoskeletons. Furthermore, the degree of oversaturation has declined as different biomineralisers have evolved and advanced.[6]

The emergence of pelagic calcifying organisms, the coccolithophores ~220 Ma,[7] transported calcite to the deep sea for the first time. Not only did this "ballast" enhance export of organic matter to the deep ocean, potentially leading to the deepening of the oxygen minimum zones,[8] but it also provided a sedimentary layer of calcium carbonate that was able to interact, via dissolution, with a dynamic calcite saturation horizon. Such a mechanism of "carbonate compensation" is thought to buffer seawater pH against significant change since any disruption to the alkalinity (or acidity in the form of CO_2) supply to the ocean can be kept in balance with the alkalinity burial into sediments via vertical movement of the saturation horizon.[9–10]

Calcite precipitation and dissolution plays a key role, as schematically outlined in Figure 1, in the oceanic carbon cycle. Once biogenically formed the calcite descends the water column. Particles of calcite start to dissolve in environments where the ambient seawater carbonate ion concentration falls beneath the equilibrium carbonate ion concentration (which is elevated towards the deeper ocean because of the effects of cooling T and increasing pressure). Such dissolution can occur in microenvironments of organic rich particles as a result of respiration dissolution, even above the saturation horizon, or where the accumulation of respired carbon dioxide at depth is sufficient to lower the deep water mass carbonate ion concentration beyond the equilibrium concentration under those physical conditions.[11–12] The saturation horizon can lie 100s of metres above the calcite compensation depth (CCD), the depth where the settling rate equals the dissolution rate and carbonate contents are <5% of the sediment. The depth range between the saturation horizon and the calcite compensation depth is termed the lysocline. The kinetics of calcite dissolution are therefore key to how any mechanism of seawater buffering with deep sea calcite works, and its reaction timescale, which is not well constrained.[13] Yet knowledge of dissolution rates is ever more urgent to understand whether significant buffering could occur quickly via naturally or intended anthropogenic accumulations of atmospheric CO_2 in the ocean.[14]

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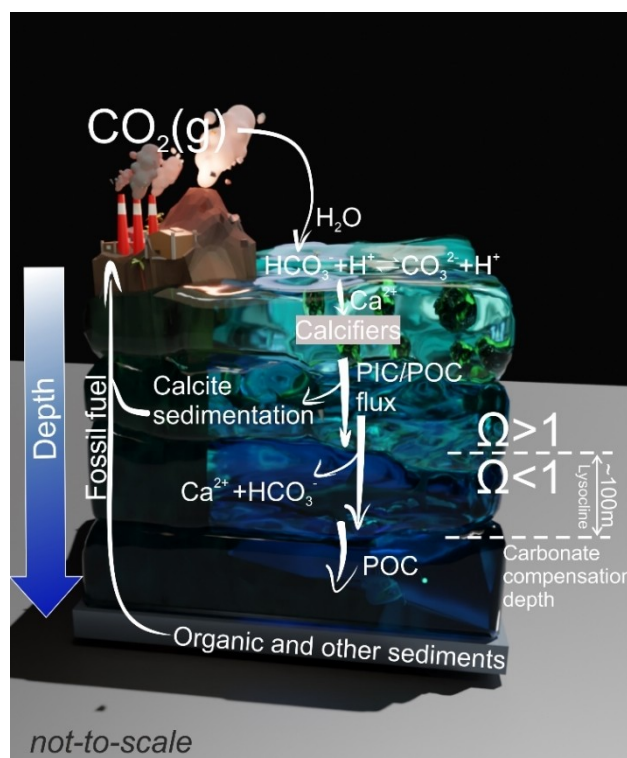
Figure 1. Schematic of the oceanic carbon cycle emphasising the role of calcite and its dissolution in the system.

Extensive work from over a century of research has yielded exquisite detail and knowledge regarding the thermodynamics of the associated carbonate chemical equilibria.[2] However, aspects of the kinetics of the calcite dissolution process even in laboratory conditions remain obscure and poorly described. From a physical chemistry perspective calcite dissolution is a heterogeneous process and importantly calcite is only sparingly soluble. At low ionic strength the stoichiometric solubility product[2] (K_{sp}, as defined on a concentration basis) is $3.3 \times 10^{-9} M^2$. Hence at equilibrium the solution phase carbonate concentration is of the order of a few 10s of micromolar. A complicating factor here is that carbonate is a base and so its speciation plays an important role in controlling the total calcite solubility and its dependence on the pH and buffering of the aqueous system. However, as summarised in Figure 2, in the absence of other acids and bases there are four fundamental processes that can drive the calcite dissolution reaction (see SI section 1 for more details). These reactions are all heterogeneous processes and the rate of the reaction has units of amount per area per time ($mol\,m^{-2}\,s^{-1}$). As also schematically summarised in Figure 2, and as with any heterogeneous reaction, the overall reaction rate is an interplay between the transport of material to/from the interface and the rate of reaction at the surface. Importantly, which process is rate determining, the interfacial reaction kinetics or the mass-transport of material to/from the interface, can change depending on the prevailing conditions and the size of particle being dissolved. How the reaction rate can switch between different
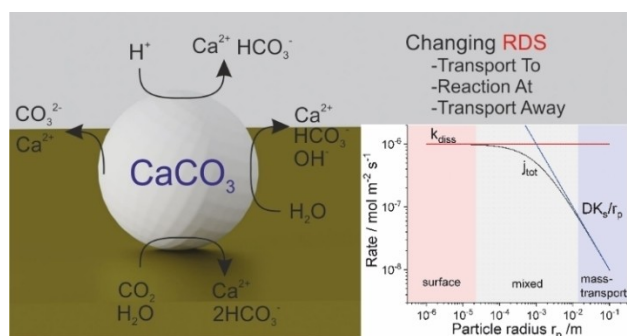
Figure 2. Schematic of calcite dissolution showing the four thermodynamic pathways by which the mineral can dissolve in DI water. Also depicted is a theoretical plot showing how an interfacial reaction rate can change from being surface to mass-transport controlled as a function of the particle size. Further discussion and derivation of this idealised model is provided in the Supporting Information section 2. For any interfacial process the reaction rate can be controlled by the transport of material to the interface, reaction at the interface or the transport of material away from the interface.

limits as a function of particle size is exemplified further in the Supporting Information Section 2 and is integral to the discussion of the literature.

Due to the breadth of the subject, it is far from possible to provide an exhaustive review of the literature and this article only focuses on some of the key papers from the last half century. Further, building from a fundamental physical chemistry perspective, in this short review we first summarise the important calcite dissolution results obtained under laboratory conditions, highlighting potential errors and pitfalls. We next consider if these results can or cannot help in understanding calcite dissolution in marine waters. Finally, we explore how we may bridge between experiments and observations that are made under very different conditions.

Laboratory Measurements Under Idealised Conditions

In 1978 Plummer, Wigley and Parkhurst (PWP)[15] reported the dissolution of sub millimetre (ca. 300–600 μm) sized calcite particles in a pure water system (i.e. at low ionic strength). They quantified the overall dissolution reaction rate using the following semi-empirical expression:

$$Rate \text{ (mol m}^{-2}\text{s}^{-1}) = k_1[H^+]_0 + k_2[H_2CO_3{}^*]_0 + k_3 \quad (1)$$

where the concentrations are those at the calcite surface and $[H_2CO_3{}^*]$ is the sum concentration of both solution phase H_2CO_3 and CO_2. Note in the original paper by Plummer et al. it was assumed that, under constant stirring, the surface concentrations were equal to that in the bulk solution. At low pH (pH < 4) the k_1 term dominates the rate of reaction where a value of 4.3×10^{-4} m s^{-1} has been reported.[16] k_2 has a reported value of 3.4×10^{-7} m s^{-1} and k_3, 1.2×10^{-6} mol m^{-2}s^{-1} (at 25 °C)[17]; consequently, for a pH 8 solution in equilibrium with the air

(dissolved $[CO_2]$ ~1×10^{-2} mol m^{-3}) then k_3 is expected to be the dominant term. This work was later extended by Plummer to consider the influence of other ionic species on the dissolution kinetics.[18] However, this value for k_3 (1.2×10^{-6} mol m^{-2}s^{-1}, which is generally reported on a per square centimetre basis, 1.2×10^{-10} mol cm^{-2}s^{-1}) is still often used as the benchmark against which other measurements are referred. However, this measurement was made under poorly defined hydrodynamic conditions, with a low electrolyte concentration and was inferred from data taken as the system drifts towards equilibrium. During the 1980s, a series of important articles were published by Sjöberg and Rickard.[19–25] A number of beneficial insights were made in this work, the first primary point is that the use of particle suspensions, with the particles as the reactant, is subject to considerable errors since measured rates may differ due to varying hydrodynamic conditions arising from the experimental design.[21,25] As further discussed by the authors, it is often assumed that if an interfacial reaction rate is not sensitive to the solution stirring rate then the reaction is controlled by the rate of the interfacial reaction. This does not have to be the case, this situation can simply indicate that the hydrodynamic conditions near the particle surface are not sensitive to the bulk stirring rate. Second, using a macroscopic calcite crystal disc that could be rotated up to a rate of 10,000 rpm Sjöberg and Rickard demonstrate that in the absence of other inhibiting species at high pH (> 5.5) the dissolution kinetics are under a mixed kinetic regime.[19] Under the studied conditions the reaction is neither fully controlled by mass-transport nor controlled by the rate of the surface reaction. However, implicit in this is that in cases where such a high mass-transport conditions are *not* used then the reaction *will* be mass-transport limited. Third, they show that the dissolution rate under these neutral conditions is sensitive to the used calcite material. Having corrected for the effects of mass-transport the dissolution rates differ depending on the material; Icelandic Spar has a reported dissolution rate of 1.44×10^{-5} mol m^{-2}s^{-1} whereas for Carrera marble the rate is even greater at 4.8×10^{-5} mol m^{-2}s^{-1}.[19] These high dissolution rates were also confirmed by Compton et al. who reported a mass-transport corrected dissolution rate of 2.1×10^{-5} mol m^{-2}s^{-1} for Icelandic Spar.[26] Later work, as will be expanded upon below, also demonstrated how the heterogeneous dissolution rate is sensitive to the crystal surface preparation and morphology.[27] Notably, these mass-transport corrected rates constants (see Supporting Information section 3 for a discussion of mass-transport correction) are over an order of magnitude higher than those reported in the work of Plummer et al.[15]; however, in the work of Sjöberg and Rickard, not only is the mass-transport now well-defined and corrected for but the system is also being studied at a higher ionic strength. Key to appreciating this difference is an understanding of how, for an interfacial reaction, the interplay between the surface kinetics and the local mass-transport regime can be important in determining the overall reaction rate and how the rate determining step can switch between these two limits. As mentioned in the introduction, the Supporting Information

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section 2 presents a basic model exploring how an interfacial reaction can switch from surface to mass-transport control.

As alluded to above, the crystal surface morphology can be important in controlling the dissolution rate. Freshly cleaved Icelandic Spar crystal surfaces can be initially essentially unreactive even to millimolar solutions of protons.[27] In contrast mechanically well prepared Icelandic Spar surfaces that have not been previously subject to dissolution can exhibit mass-transport corrected dissolution rates of $\sim 10^{-6}$ mol m^{-2} s^{-1}.[27–29] However, this dissolution rate will increase during the course of the dissolution reaction as the roughness of the crystal surface increases.[27] For other surface preparations of Icelandic Spar and Carrera marble surfaces the dissolution rate can be higher in the range of 10^{-5} mol m^{-2} s^{-1}.[19,26] This sensitivity to the history of the calcite material preparation complicates the comparison of results between different research groups.

Table 1 summarises the reported heterogeneous dissolution rates under neutral conditions, using *macroscopic single crystals* and where the effects of mass-transport have been fully accounted for. Given the sensitivity of the reported data to the crystal surface preparation method, it is not unreasonable that small particulate calcite and powders may be expected to exhibit even higher dissolution rates. Interestingly, work by Hassenkam et al. studied the dissolution of individual calcite particle attached to an AFM tip. They did not correct their data for the effects of mass-transport but found the raw experimental dissolution rates to be of the order of 1×10^{-5} mol m^{-2} s^{-1}.[30] In fact their time transient data for the dissolution of calcite under deionized water conditions has been shown to be fully consistent with being at the mass-transport limit. Further, though the development of a new optical microscopy methodology Fan et al.[31] have been able to demonstrate that for micron sized precipitated calcite the interfacial dissolution rate is at least 1×10^{-5} mol m^{-2} s^{-1}. These rates are markedly higher than much of the data reported in the literature. However, as will be outlined below, a major complicating factor in assessing the historical literature is that in many cases the reported heterogeneous reaction rates have not been corrected to account for the prevailing mass-transport and have assumed that the measured rates directly reflect the kinetics of the

interfacial dissolution reaction, this limits the wider use and applicability of these studies.

The results by Rickard and Sjöberg, evidencing that the dissolution kinetics at pH > 5.5 are often under a mixed kinetic regime, have certainly not been ignored in the literature,[3,32] although its perhaps fair to say the implications of the work have not, in some cases, been fully appreciated. For example, Schott et al.[33] only a few years after Sjöberg and Rickard, used a rotating cylinder of calcite to investigate the effects of crystal strain on the dissolution rate at higher pH. The cylinder was rotated at a rate of 220 rpm with dissolution rates in the range of $1–2 \times 10^{-6}$ mol m^{-2} s^{-1} for the raw experimental dissolution rates without mass-transport correction. In this case inferring physically meaningful information about the effect of strain on the sample without accounting for the influence of mass-transport is problematic. Similar errors arise with later work of MacInnis and Brantley[34] where they used a disc rotating at 1160 rpm so as "[…] to lie within a regime of minimized transport control." In this work they are certainly aware of the work of Sjöberg and Rickard referencing and discussing it; however, again their reported dissolution rate (3.1×10^{-6} mol m^{-2} s^{-1}) was not corrected for mass-transport effects. Quantitatively comparing their results to other experimental setups with different hydrodynamic conditions will be fraught with difficulty and further *directly* correlating any changes in dissolution rate they may observe to anything physical meaningful should be approached with caution. These are just two examples of papers in the literature that either do not use a well-defined mass-transport regime and/or do not demonstrate that their measured interfacial kinetics are not approaching the mass-transport limit. Further, it is on the basis of articles like these[15,33–34] that new or more complex techniques[35] are sometimes 'validated'. Often confirmation that the calcite surface dissolution kinetics are under surface reaction control is achieved by first demonstrating that the dissolution rate is apparently insensitive to changes in the hydrodynamic conditions in a given limit and second showing that the measured kinetic results are consistent with prior published work (i.e., that the rate is $\sim 1 \times 10^{-6}$ mol m^{-2} s^{-1}). Due to the fact that in these articles the mass-transport properties of the system are not directly considered, then the use of literature results to validate a measurement leads to the potential for confirmation bias to propagate a false narrative.

Ideally the mass-transport in an experimental system should be quantifiable, so as to provide independent and direct evidence that the measured rates reflect the interfacial kinetics of the reaction and not the movement of material in the solution phase. In the following section we provide estimates and insight into what the rate of mass-transport is likely to be in a number of different experimental setups. Further evidencing that the experimental rates reported in the literature for the calcite dissolution reaction are often at least comparable to that expected for a process that is under mass-transport control. Hence, some of these literature reported rates may give little to no insight into the true underlying interfacial kinetics of the calcite dissolution reaction.

Table 1. summary of the reported literature data for the calcite heterogeneous dissolution rate of macroscopic calcite crystals where the effects of mass-transport have been fully accounted for.

Material	Preparation	Rate/ mol m^{-2} s^{-1}	Method	Reference
Icelandic Spar	Polish (600 mesh)	1.44×10^{-5}	Rotating Disc	[22,25]
Carrera Marble	Polish (600 mesh)	4.8×10^{-5}	Rotating Disc	[22,24–25]
Icelandic Spar	Polish	2.1×10^{-5}	Rotating Disc	[26]
Icelandic Spar	Fine Polish or Cleaved	1.41×10^{-6}	Rotating Disc	[27]
Icelandic Spar	Fine Polish	9.5×10^{-7}	Channel Flow	[29]
Icelandic Spar	Fine Polish	$6.2 \pm 3.6 \times 10^{-7}$	Channel Flow	[28]

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Assessing Mass-Transport Effects in Laboratory Experiments

To date the main two experimental setups that facilitate calcite dissolution kinetics to be studied under well-defined hydrodynamic conditions are the rotating disc[19,26] and channel flow cell[29] systems. However, these experimental techniques find limited use in the literature. Likely due to experimental ease, dissolution kinetics are more often studied using either using a particle suspension[36] or a macroscopic crystal.[35] However, fully and quantitively defining the mass-transport regime in these two cases is at best challenging, but useful initial estimates can be readily made. Here we will consider both the mass-transport flux to a suspension of micron sized particles in the solution phase and further the situation in which we have a large planar calcite crystal. If we ignore the influence of ion-pairing then at equilibrium a deionised aqueous sample in contact with an excess of solid calcite but closed to the atmosphere will be pH 9.78 and have a calcium ion concentration of 0.123 mM (at 25 °C). If this system is left open and allowed to equilibrate with the atmosphere then the pH of the solution will drop to 8.26 with an associated increase in the calcite solubility with a calcium ion concentration of 0.447 mM. The addition of supporting electrolyte to the system increases the calcite solubility. In the presence of 0.7 M KCl the calcite solubility product is raised from $3.3 \times 10^{-9}\,M^2$ to $4.0 \times 10^{-7}\,M^2$, where the solubility products have been defined in terms of the concentrations as opposed to the activities of the species.[2] Consequently, in 0.7 M KCl the calcite solubility is increased to 0.73 mM (closed) and 1.35 mM (open). In many experimental cases it is reasonable to assume that the calcite crystal surface is not in equilibrium with the atmosphere and that the dissolution system is essentially closed. This does not always need to be the case and there are potential situations in which carbon dioxide mass-transport and/or the hydration kinetics[37] may be the rate determining process for the calcite dissolution reaction. Certainly, for the case in which calcite dissolution is driven to occur in a carbonate solution at about pH 6 then under these conditions the primary proton source in the system will be dissolved carbon dioxide and the system should be sensitive to the carbon dioxide hydration kinetics.[36]

From these equilibrium concentrations it is possible to estimate the mass-transport limited flux (j/mol m^{-2} s^{-1}) to the particle surface as given by:[38]

$$j = \frac{D_{average}\left(C_{eq} - C_{bulk}\right)}{R_f \delta} \tag{2}$$

where C_{eq} is the calcite solubility at equilibrium under a given set of conditions, C_{bulk} is the concentration of calcite already dissolved in the bulk solution. $D_{average}$ is the average diffusion coefficient of the aqueous species; initially as a first approximation it is sufficient to assume that this average diffusion coefficient is simply equal to the geometric mean of the calcium and carbonate diffusion coefficients. Herein we use a value of $8.7 \times 10^{-10}\,m^2\,s^{-1}$.[39] In equation (1) the rate of reaction is given

relative to the true or real surface area[40] of the particle. This expression for the diffusion limited flux is essentially the same as given by Berner[41] apart from here we additionally include a roughness factor term (R_f) so as to account for the roughness of the particle. The use of a roughness factor provides a link between the rates that are expected due to the mass-transport of material and those measured for a sample with a known surface area as determined, for example, from a BET measurement. Here we are assuming that the particle is quasi-spherical. Hence, R_f is a measure of the real surface area of the material compared to the geometric area of an equivalent sized sphere, if the surface of the particle is atomically smooth and is a perfect sphere then R_f will have a value of 1. As the particle is roughened the R_f increases, where in many cases a non-porous particle might be expected to have a R_f value of ~2. However, for simplicity, in the following we will assume a value of 1. Finally, in equation (1) δ is the diffusion layer thickness. Importantly in using equation 2 we are implicitly assuming that the mass-transport near the calcite surface is well described as a diffusion only process.[42] First, by referring to the a system's mass-transport as well-defined we are essentially stating that the value of δ is known with a reasonable degree of accuracy (ideally within 10% of the true value). Second, for a micron sized quasi-spherical calcite particle isolated in the solution phase then the diffusion layer thickness is approximately equal to the particle's radius.[43] Consequently, assuming the particle concentration is sufficiently low, so as to ensure that the inter-particle distance is large relative to the radius of the crystal then we can use equation 2 to estimate the diffusion limited flux. If we have a monodisperse suspension of calcite particles with a radius of 10 μm then the estimated diffusion limited calcite dissolution rate in a deionised water sample is 1.1×10^{-5} mol m^{-2} s^{-1} for a system closed to the atmosphere. In the presence of 0.7 M KCl these rates will increase to 6.4×10^{-5} mol m^{-2} s^{-1}. Both of these sets of rates are essentially comparable to the rates reported for the dissolution of Carrera marble (4.8×10^{-5} mol m^{-2} s^{-1}) and Icelandic Spar (1.4×10^{-5} mol m^{-2} s^{-1}). Further we might anticipate that small calcite crystallites have more defects such that the surface limited reaction rate might reasonably be greater than that measured for these more ideal materials. Hence, even if we have a suspension of small calcite particles in a solution of deionised water or 0.7 M KCl, we expect the rate to be likely at least partially controlled by the physical transport of the dissolved material away from the mineral interface. It is worth commenting that this situation where calcite particles are in a suspension is somewhat complicated by the possibility of the calcite particles agglomerating in the solution phase, certainly in higher ionic strength media then even with stirring the agglomeration of the inorganic particles is very likely.[44] In this case equation 2 can be modified to give an approximate expression accounting for the particle agglomeration:

$$j = \frac{r_p}{0.65 R_f r_{agg}} \frac{D_{average}\left(C_{eq} - C_{bulk}\right)}{r_{agg}} \tag{3}$$

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where r_{agg} is the effective radius of the aggregate and r_p is the radius of the constituent particles (as indicated on Figure 3) and the value of 0.65 is used to account for the fact that the packing of the particles in the agglomerate will not be closed-packed but more random in structure (this value is only approximate and will depend on the actual structure and packing density of an agglomerate). Here R_f again refers to the roughness of the constituent particle of the agglomerate compared to its geometric surface area and we assume that the concentration of solution phase species is uniform throughout the agglomerate. The first term in equation (3) accounts for the fact that the total surface area of an agglomerate particle is significantly larger than that of a solid sphere. Consequently, if we have constituent particles with a radius of 10 µm and the resulting agglomerate has an effective radius of 100 µm then on the basis of comparison of equations 2 and 3 we predict the mass-transport limited flux to (or from) the material to be almost two orders of magnitude less! In these particle suspension experiments agglomeration of the material can have a big effect on the measured rate. A further complication for these experiments is the assumption that the flux to the particle is a diffusion only process, which is questionable when the solution is stirred. To what extent the diffusion layer thickness δ is decreased with stirring is not easily answerable, certainly the larger the particle or agglomerate the more stirring will influence the mass-transport rate but making any semi-quantitative predictions is difficult. It is these latter two problems that ultimately means that quantitative analysis of the mass-transport in particle suspensions is not well-defined i.e., there are significant uncertainties in the value of δ and the experimental interpretation can in some situations be ambiguous. As highlighted by Sjöberg[25], rates determined using particle suspensions are highly dependent on experimental design.[21] They can therefore only be used qualitatively in anticipating dissolution rates in hydrodynamically different systems such as the oceans.

Apart from the dissolution of a suspension of calcite particles, another common laboratory experimental setup is the
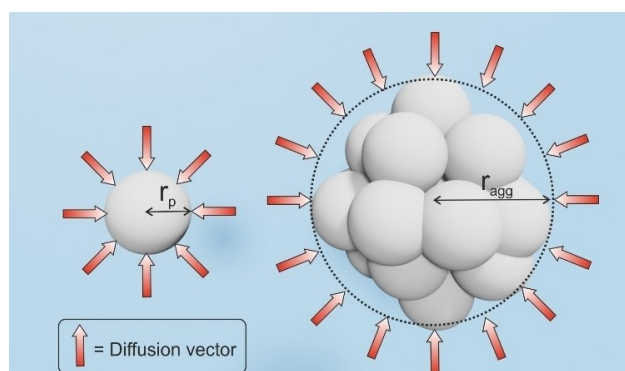

Figure 3. Schematic showing the simple diffusional model considered for the flux to an agglomerate. The diffusion limited flux to an agglomerate is significantly less than to that of an isolated sphere. This occurs due to the increase in the particle's effective radius (r_p vs. r_{agg}) and the increase in the particle's effective surface area.

situation in which a large (>millimetre) sized planar calcite surface is dissolving when in contact with a solution that is not being actively stirred. Such a situation may arise for example when studying calcite dissolution using an atomic force microscope (AFM). Hydrodynamic AFM techniques have been developed[35,45] and used but what is far less regularly undertaken is the full and direct assessment of the mass-transport properties of the system.[46] In the absence of a fuller mathematical analysis of the mass-transport properties of an experimental design, validation that the dissolution reaction is not influenced by mass-transport is reliant on inferences to be made from the experimental data. Further without knowledge of the mass-transport properties deconvolution of the surface kinetics from mass-transport cannot be undertaken (see Supporting Information section 3 for further detail). In the case of a macroscopic crystal in contact with a quiescent solution, what is the diffusion layer thickness in this case? If there was no stirring in the solution and the rate was controlled by the diffusion of the species away from the surface of the calcite crystal then the diffusion layer thickness would be expected to increase with the square-root of time. Consequently, as the diffusion layer increases the flux decreases in accordance with equation (2) and will tend to zero at long times. This ideal result is essentially that predicted by the Cottrell equation in 1D.[47] The Cottrell equation is used in electrochemistry to describe the diffusion limited flux to a planar macroelectrode as a function of time under semi-infinite diffusion conditions. Usually, the flux is expressed as a current but can equally be defined in terms of the amount of material reacting per area per time, that is, a flux which is proportional to current. Importantly for a macroscopic surface the diffusion layer thickness increases as a function of the square-root of time. The problem with the expanding diffusion layer is that natural convection almost always occurs in such systems; imperfect thermostating leads to temperature gradients that are able to drive convective fluxes in the bulk solution phase.[48] Importantly, in the electrochemical field the influence of this natural convection on the diffusional flux to/from a planar surface has received attention. Work by Amatore et al. demonstrated that at longer times (for a millimetre sized interface >10 s) then the diffusion layer thickness will be controlled by this convective flux in the bulk solution.[49–50] δ_{conv} has been measured for a range of interface sizes and found to generally be in the range of 200–250 µm.[49] As an aside the physical explanation for this convective motion of the solution, has been questioned and revised[48]; however, the empirical observation and quantification of the effects of the convective motion remain valid and important. Consequently, if the dissolution of a planar macroscopic calcite crystal is studied in a solution without forced convection, then on the basis of equation (2) in a deionised solution a mass-transport dissolution rate of 5×10^{-7} mol m^{-2} s^{-1} is expected, similarly for a higher ionic strength solution then rates in the range of 3×10^{-6} mol m^{-2} s^{-1} are predicted. The exact value will depend on the precise details of the experiment i.e., the system's ionic strength, the quality of the system's thermostating, the levels of evaporation from the system, if the solution is in equilibrium with the atmosphere, how well vibrationally isolated the

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solution is and clearly what, if any, forced convection/flow rate is imposed. Generally, the mass-trasnport limited flux for AFM type experiments is expected to be comparatively low and notably there have been issues, reported in the literature, in reconciling data measured using AFM with other data sources.[3,45]

In summary for these two common experimental geometries, that of a suspension of dissolving particle and that a dissolving planar macroscopic surface, the mass-transport limited flux is predicted in some cases to be comparable to the reported interfacial dissolution rates. As a minimum it seems reasonable to conclude that in a number of literature examples the reported dissolution rates at least in part reflect the local hydrodynamics of the system and that the reported heterogeneous dissolution rates could be beneficially corrected to account for the limiting effects of the mass-transport of material in the solution phase.

From the Laboratory to the Ocean

What is the wider relevance of the above experiments? The dissolution rate of the order of 1×10^{-6} mol m^{-2} s^{-1} under near neutral conditions is viewed as being representative of calcite dissolution rates in highly undersaturated conditions and as relevant in understanding the calcite dissolution in both fresh[51] and seawater[52–53] samples. Further this measured rate is reported in compiled lists of data for use in geochemical modelling.[54] However, in seawater the presence of other ionic species such as magnesium,[55] phosphate,[56] calcium[24] and carbonate in the bulk solution clearly have a significant effect on the overall dissolution kinetics making interpretation of the data more complex. But the experimental challenges in determining the calcite dissolution rate, as highlighted in the above discussion, also have implications for work in the literature that tries to tackle the bigger problem of dissolution in real or artificial seawater. In an article in 1974 Berner and Morse[56] presented a theoretical analysis of the expected mass-transport dissolution rate of small calcite particles in suspension. They concluded that in pseudo seawater (a NaCl-CaCl$_2$ solution) at high undersaturation and low carbon dioxide concentrations the dissolution rate was of the order of 4×10^{-6} mol m^{-2} s^{-1} and that this rate was orders of magnitude below that expected for a mass-transport limited rate. This result seems to be in stark contrast to the data present later by Sjöberg and Rickard[24] who demonstrated that at higher ionic strength the addition of calcium (albeit at concentrations below millimolar) shifts the dissolution reaction away from being under mixed kinetic control towards being fully under a mass-transport control limit. How can these two results be reconciled; one potential explanation lies in the fact that the analysis presented by Berner and Morse assumes that the particles do not agglomerate in solution. As quantified in equation (3) in the above section, agglomeration can have a major effect on the mass-transport limited flux and it would seem unlikely that a suspension of small (ca. micron) *inorganic* calcite particle would be stable in an ionic strength of ∼0.7 M. The work of Berner

and Morse[56] does however evidence that at low undersaturation levels and in genuine seawater the calcite dissolution rate is markedly lower than that measured in a NaCl–CaCl$_2$ solution. However, generally, for any given experiment performed at high calcite undersaturation, how far below the mass-transport limit the measured kinetics are, will depend on the experimental design and reaction conditions. Experimental work by both Subhas[36] and Cubillas[51] on seawater and fresh water samples are, at high undersaturation, consistent with being close to or at the mass-transport limit (see the Supporting Information section 4 for further details).

More broadly however, a regular implicit assumption in the oceanic science community is that the calcite dissolution rate is surface controlled, this probably stems directly from the work of Berner and Morse.[56] In part as a consequence of this assumption, in a significant amount of the geological literature the calcite dissolution rate is described using the following equation[57]:

$$\frac{d[CaCO_3]}{dt} = -k_c[CaCO_3](1 - \Omega)^n \tag{4}$$

where [CaCO$_3$] is the calcite concentration (mol m^{-3}), Ω is the solution saturation state ([Ca^{2+}][CO$_3^{2-}$]/K_{sp}), n is a fitting parameter and k_c is the calcite dissolution rate constant (s^{-1}). One irksome quirk of the literature is that the rate constant, k_c, is often presented with units of percent per day (% d^{-1}); however, for consistency we will remain using SI units but also report in parenthesis the values with these literature units. The major conceptual problem here is that the calcite dissolution reaction is a heterogeneous process; the use of equation 4 implies that it can be treated and modelled as a homogeneous reaction! In the literature a wide range of values for both k_c and n have been reported. Depending on the experimental conditions n has been reported to be in the range of 1–4.5; furthermore, values of k_c range over multiple orders of magnitude and the value reported largely depends on the value of n used in the fitting process.[58–60] This apparent ambiguity in the calcite dissolution kinetics has led to the system being described as 'virtually unconstrained'.[57] Broadly however, assuming an n value of 1, higher rates of $k_c > 4.3 \times 10^{-6}$ s^{-1} (> 38% d^{-1})[58] have been reported for laboratory experiments using particle suspensions than field measurements on sediment samples which generally yield significantly lower rates 1.1×10^{-9} s^{-1} (0.01% d^{-1}). Further, although there is significant empirical evidence that for a suspension of particles the dissolution rate has an n value of ∼4.5,[61] in contrast for sediment samples a value closer to one is reported to be more credible.[58]

How then can these effective first order homogeneous rate constants (k_c / s^{-1}) be related to measurements made in the laboratory? If *and only if* the calcite dissolution reaction is a surface limited process then for a solid spherical particle:

$$k_{c,surf}(s^{-1}) = \frac{3R_f M_w k_{het}}{r_p \rho} \tag{5}$$

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where k_{het} is the heterogeneous rate constant ($mol\,m^{-2}\,s^{-1}$), M_w is the molecular weight of calcite ($100.1\,g\,mol^{-1}$), ρ is the density of calcite ($2.71 \times 10^6\,g\,m^{-3}$) and all other terms are the same as used earlier. For a fuller derivation of equation 5 and exploration of the relationship between the homogeneous and heterogeneous reaction rates the reader is referred to section 5 of the Supporting Information. From equation 5 and using a heterogeneous rate constant of $1 \times 10^{-6}\,mol\,m^{-2}\,s^{-1}$, and a particle size of 100 μm then k_c has an expected value of $1.1 \times 10^{-6}\,s^{-1}$ ($9.5\%\,d^{-1}$). As long as the reaction remains under surface control then the above expression will be correct whether the particles are in suspension or in a sediment. However, this is not the case if the reaction is under mass-transport control. It's useful to consider two cases, first, that of a suspension of particles and, second, a thin idealised sediment layer. If the particles are isolated in solution such that their diffusion layers do not overlap then using equation 2 and setting delta equal to the particle radius then:

$$k_{c,MT\ suspension} = \frac{3M_w D_{average}\left(C_{eq} - C_{bulk}\right)}{r_p^2 \rho} \tag{6}$$

If, for example, we take a particle radius of 100 μm and a concentration difference of $0.4\,mol\,m^{-3}$ as may be reasonable for a completely undersaturated seawater solution then the predicted rate is $3.8 \times 10^{-6}\,s^{-1}$ ($33\%\,d^{-1}$). Clearly, if the particle is of the order of 10 μm then the rate will be significantly larger. But what happens if the particles are not diffusionally isolated? Imagine we have a layer of sediment with a thickness L, which on a volume basis contains only a fraction (f) of calcite, further let us assume that the particles are small and dense enough that in this sediment layer the solution is saturated with respect to calcite. Moreover, this layer is in contact with a completely unsaturated seawater solution and the rate of loss of material from this layer is controlled by the flux through a diffusion boundary. Then in this highly idealised case:

$$k_{c,MT\ sediment} = \frac{M_w D_{average}\left(C_{eq} - C_{bulk}\right)}{\delta L f \rho} \tag{7}$$

taking a diffusion layer thickness of 100 μm, and a sediment layer thickness of 1 cm and a fill factor (f) of 20% then on the basis of equation 6 the effective first order homogeneous rate constant is predicted to be $6.4 \times 10^{-8}\,s^{-1}$ ($0.56\%\,d^{-1}$). Again, derivation of this expression can be found in section 5 of the Supporting Information. This rate ($6.4 \times 10^{-8}\,s^{-1}$) is almost two orders of magnitude less than the rate to an isolated 100 μm particle ($3.8 \times 10^{-6}\,s^{-1}$); fundamentally mass-transport in and out of a sediment layer is significantly slower than that to/from a micron sized particle isolated in solution. Equation (7) assumes that the rate determining step is the transfer of material from the sediment layer to the seawater, in cases where diffusion through the sediment is important even lower rates should be anticipated.

This simple sediment layer example is not intended to be fully physically correct but serves to highlight that if the calcite dissolution reaction is under mass-transport control then the use of an effective first order homogeneous kinetic expression (as given in equation 4) will yield values that range over multiple orders of magnitude and are case specific depending on the prevailing mass-transport. The fact that the experimentally reported values for k_c vary so greatly may, in reality, provide indirect evidence for the calcite dissolution reaction in sediments being – in many cases – under mass-transport control. Challengingly, the use of a homogeneous rate equation (as in equation 4) to approximately describe the calcite dissolution kinetics has been employed in a number of sediment models.[62–64] The fact that this homogenous approximation has been used does not necessarily undermine the conclusions and results of this work. However, in light of the above, k_c should arguably be viewed as an unknown fitting parameter that in some cases reflects not the calcite heterogenous dissolution kinetics but the prevailing mass-transport conditions. This conclusion that the calcite dissolution kinetics of sediment layers are likely under mass-transport control has been previously evidenced in the literature and is supported by both laboratory[65–66] and field-based studies.[67] As early as 1971 Berner[41] reflected that dissolution is usually diffusion controlled and later that decade Morse recognized that mass-transport may limit the rate of dissolution at the seafloor.[68] More recently, Sulpis et al.[69] combined laboratory measurement with an individual particle dissolution model to show that difference in seafloor dissolution rates are caused by solute transport, the rate limiting step in overall dissolution.

The need for an extensive diagenetic model for sedimentary $CaCO_3$ to explain oceanic dissolution has been previously questioned.[70] We echo this sentiment and further highlight that due to the limitations in using equation 4, directly relating laboratory experiments to oceanic measurements can only realistically at present be achieved on a case by case basis.

Summary and Outlook

A unifying theme of this review is that calcite is a reactive mineral and that *under some conditions* at near neutral pH its dissolution is so fast that the rate becomes controlled by the mass-transport of the ions in the solution phase. This is not a new insight[20–25] but it seems beneficial for this statement to be remade.

Mass-transport control has significant implications for both laboratory and field experiments. A potential lack of recognition of this point – that a dissolution process may be under mass-transport control – may have caused apparent reproducibility or inconsistency between labs and different measurement techniques. First, in the laboratory under highly undersaturated conditions the calcite dissolution is fast and, in some cases, approaches the mass-transport limit. Not recognising that the reaction mechanism is at least partially under mass-transport control may well have led to the development of some ornate, but potentially unfounded, molecular scale mechanistic descriptions of the process. However, it needs to be clearly stated that, at the single particle level under seawater conditions and at near saturation, the calcite dissolution reaction is likely con-

trolled by the interfacial kinetics of the calcite dissolution reaction and not mass-transport. But this conclusion does not hold true for all experiments using seawater. Second, and following on from this, in terms of dissolution in the oceans although it seems likely that in the water column the dissolution of suspended particles *is controlled by the surface reaction kinetics* and influenced by the presence of inhibitors such as magnesium, phosphate and organics, this *may* not be the case for sediments. The reported calcite dissolution kinetics in sediments seem to be markedly lower than that reported for suspensions of particles. As evidenced above, one plausible interpretation is that this variability in the measured dissolution rate arises in part from the fact the heterogenous reaction is modelled and treated as a homogeneous process. This approximate homogeneous rate is unable to describe the shift in behaviour from a surface to a mass-transport limited process. Consequently, the reported values of k_c should potentially be viewed in some cases as not reflecting the kinetics of the dissolution process but as parameterising the prevailing mass-transport conditions.

Fully unifying these two experimental areas (laboratory and field) likely requires the development of sediment models that more fully account for the heterogeneous nature of the calcite dissolution reaction and a better appreciation in the analysis of laboratory data as to how and when mass-transport limitation of the calcite dissolution reaction is influential. Improvements in experimental design and recognition of the limitations of using particle suspensions to study calcite dissolution is imperative if a more holistic physical description of calcite dissolution kinetics is to be gained.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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