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# The Alkaline Dissolution Rate of Calcite

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## Abstract

Due to the widespread presence of calcium carbonate on Earth, several geochemical systems, among which the global CO<sub>2</sub> cycle, are controlled to a large extent by the dissolution and precipitation of this mineral. For this reason, the dissolution of calcite has been thoroughly investigated for decades. Despite this intense activity, a consensual value of the dissolution rate of calcite has not been found yet. We show here that the inconsistency between the reported values stems mainly from the variability of the chemical and hydrodynamic conditions of measurement. The spreading of the values, when compared in identical conditions, is much less than expected and is interpreted in terms of sample surface topography. This analysis leads us to propose benchmark values of the alkaline dissolution rate of calcite compatible with all the published values, and a method to use them in various chemical and hydrodynamic contexts.

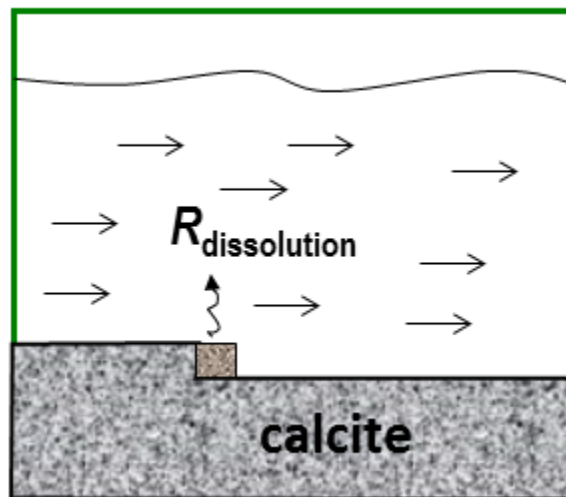


Figure 1: TOC graphic

**Keywords:** dissolution, kinetics, calcite, alkaline

The distribution of calcium carbonate on Earth surface is so wide that the dissolution and precipitation of this mineral have a leading role in the global CO<sub>2</sub> cycle. Thus the weathering of terrestrial calcium carbonate as much as the fate of marine sediments of calcite or dolomite have a major influence in the control of the pH of the ocean and the atmospheric pressure of CO<sub>2</sub>.<sup>1</sup>

Besides, the success in the long-term sequestration of anthropogenic CO<sub>2</sub> into geologic formations needs reliable kinetic informations about the dissolution of calcium carbonate minerals. Many industrial processes rely also on the knowledge of the dynamics of carbonate-containing materials, like storage of vitrified nuclear wastes, Portland cement elaboration, ...

For all these reasons, calcite is most probably the mineral the dissolution of which has been the most studied. Unfortunately, as has been often noticed, no consensus has emerged yet about the order of magnitude of the dissolution rate of calcium carbonate. Values inside a given study appear almost every time consistent, i.e., reproducible and monotonously evolving with the under-saturation, but no coherence exists among different studies. Values in very acid conditions are quite high and easy to measure, but experimental dissolution rates in alkaline condition span over several orders of magnitude, from 10<sup>-8</sup> to 10<sup>-5</sup> mol m<sup>-2</sup> s<sup>-1</sup>.<sup>2</sup> This inconsistency has not received a valid explanation yet, and it has been even claimed recently that no well-defined dissolution rate of calcite exists.<sup>3</sup>

However, experiments found in the literature have been performed in extremely diverse conditions. The measurement device, flow rate, under-saturation, ionic strength, atmosphere composition, grain size, ... are never identical from one author to the other. For this reason, it is not possible, neither to estimate properly the consistency between various studies, nor to benefit from the large amount of available measurements to gain statistical accuracy.

To evaluate the level of predictability of calcite dissolution, we propose in this article a quasi-exhaustive analysis of the published values of the dissolution rate of calcite in alkaline conditions. We have particularly construed the influence of solution chemistry, of fluid mechanics, and of surface topography on the dissolution rate. We can infer from this critical evaluation of the available corpus that the dispersion of measured values, when performed in comparable conditions, is much

less than expected and ranges on one order of magnitude. This analysis enables one to propose a benchmark value of the alkaline dissolution rate of calcite, consistent with the whole existing literature, and rules to adapt this value to the various encountered environments (nature of the solution, of the flow, of the mineral surface).

One of the only shared opinion about the dissolution of calcite is that the alkaline regime begins at  $\text{pH} \simeq 6$ . In this  $\text{pH} > 6$  range, all authors have observed the far from equilibrium dissolution rate as being constant with the  $\text{pH}$ .<sup>2,4-8</sup> As the decrease of the calcium carbonate surface charge with the increase of  $\text{pH}$  leads to expect a diminishing of the dissolution rate, the origin of this constancy is still unclear.<sup>7,9</sup> Dealing with the alkaline regime, all measurements below  $\text{pH} 6$  have been discarded.

Comparisons have often been carried out between measurements performed in different under-saturation conditions, which compromise their validity. Therefore we have represented all the dissolution rates as a function of the under-saturation, written as  $a/a_{\text{sat}}$ , with  $a$  the mean ionic activity of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$ ,  $a_{\text{sat}} = K^{1/2}$  and  $K$  the solubility product of calcite (see Experimental Methods section). We observe in Figure 2 that the values of  $R$  span over two orders of magnitude.

Beside under-saturation, the second troublesome feature of the existing comparisons is that they generally agglomerate experiments performed in different aqueous solutions, whereas the ions present in the liquid soaking the solid have a strong influence on the chemical state of the system. In the  $a/a_{\text{sat}} - R$  plane, this influence is taken into account in the left-hand term, in computing the under-saturation from the mean ionic activity, that varies with the electrolytic composition of the solution. But the ionic strength  $I$  is never taken into account in the right-hand term: the dissolution rate  $R$  is always deduced from the evolution of the concentration in the solution, not from the evolution of the activity of the present species, as if the solution was infinitely diluted. Among all the works studied here, only one treats this question in detail, and its conclusion is unambiguous. Rickard & Sjöberg have measured the dissolution rate of calcite in solutions containing 0.1 or 0.7 M of KCl.<sup>10</sup> To make these two dissolution data collapse, the  $R = f([\text{Ca}^{2+}]^{1/2}[\text{CO}_3^{2-}]^{1/2})$  curves have to be transformed into  $(\gamma_{\text{Ca}^{2+}}\gamma_{\text{CO}_3^{2-}})^{1/2}R = f((\gamma_{\text{Ca}^{2+}}[\text{Ca}^{2+}])^{1/2}(\gamma_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}])^{1/2})$  curves,

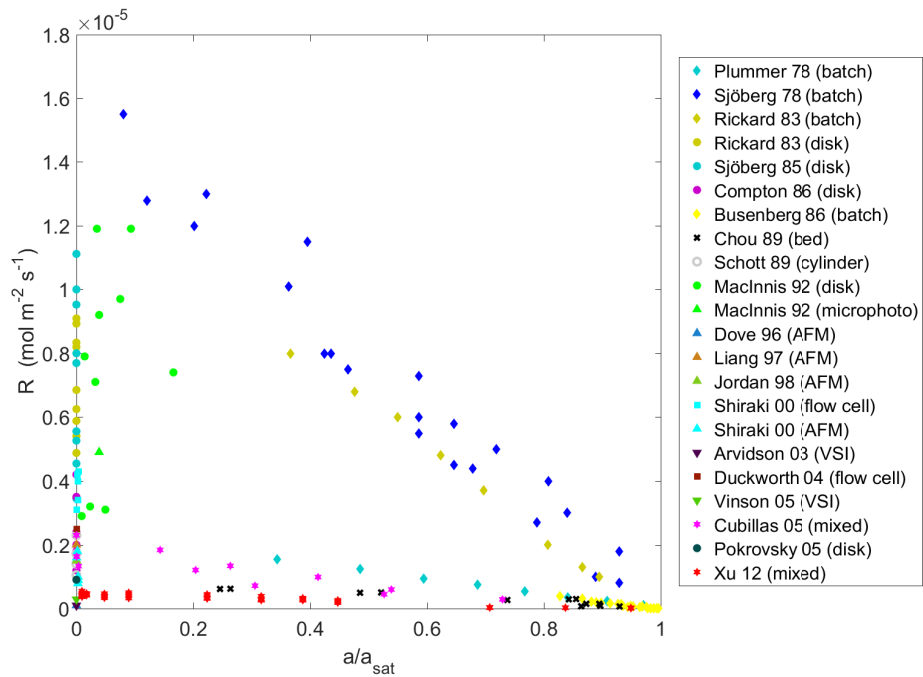


Figure 2: Published alkaline dissolution rates  $R$  of calcite versus under-saturation  $a/a_{\text{sat}}$ . The measurements have been performed with a batch reactor (diamond-shape dots) by Plummer *et al.*,<sup>4</sup> Sjöberg,<sup>5</sup> Rickard & Sjöberg<sup>10</sup> and Busenberg & Plummer,<sup>11</sup> with a rotating disk (circular dots) by Rickard & Sjöberg,<sup>10</sup> Compton *et al.*,<sup>12</sup> Sjöberg & Rickard,<sup>13</sup> MacInnis & Brantley<sup>14</sup> and Pokrovsky *et al.*,<sup>15</sup> with a fluidized bed (cross-shape dot) by Chou *et al.*,<sup>6</sup> with a rotating cylinder (open circular dots) by Schott *et al.*<sup>16</sup>, with microphotographs or AFM (upward triangular dots) by MacInnis & Brantley,<sup>14</sup> Dove & Platt,<sup>17</sup> Liang & Baer,<sup>18</sup> Jordan & Rammensee<sup>19</sup> and Shiraki *et al.*,<sup>7</sup> with a flow cell (square dots) by Shiraki *et al.*<sup>7</sup> and by Duckworth & Martin,<sup>20</sup> with VSI (downward triangular dots) by Arvidson *et al.*<sup>2</sup> and Vinson & Lüttge,<sup>21</sup> and with a mixed batch-flow cell reactor (star-shape dots) by Cubillas *et al.*<sup>8</sup> and Xu *et al.*<sup>22</sup> Note that chemical and hydrodynamical conditions vary among studies.

with  $\gamma_X$  the activity coefficient of species X.

This transformation is equivalent to convert all the data to zero ionic strength conditions. Replacing the concentration by the activities for the equilibrium determination as much as for the kinetic behavior measurement amounts to consider only the calcium and carbonate ions really involved in the reaction.

Figure 3 shows all the literature results expressed in the same  $I = 0$  condition, in the  $a/a_{\text{sat}} - R'$  plane, with  $R' = \gamma R$  the dissolution rate of the activities, not of the concentration, and  $\gamma$  the mean ionic activity coefficient. The scales in Figure 2 and Figure 3 are identical to make the comparison easier. We immediately see that the data are much less dispersed than in the  $a/a_{\text{sat}} - R$  plane, spanning now over only one order of magnitude, proof that part of the dispersion of the results was a mere consequence of the variability of the chemical composition among the experiments.

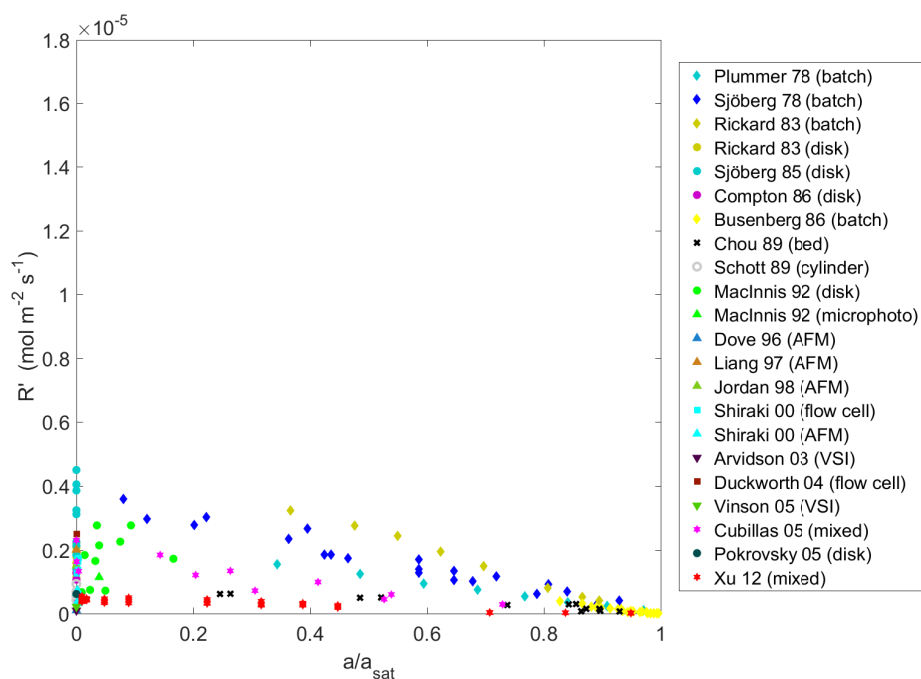


Figure 3: Dissolution rates of Figure 2 in similar chemical conditions ( $I = 0$ ). The rate is  $R' = \gamma R$ .

All the reported experiments have been performed by dissolving calcite powder or crystals in a flowing liquid. The hydrodynamics of the experiments varies with the geometry of the device:

batch (dissolution in a reactor with stirrer),<sup>2,4,5,10,11,21</sup> rotating disk or cylinder,<sup>10,12–16</sup> fluidized bed,<sup>6</sup> flowing cell<sup>7,17–20</sup> or mixed reactor (stirrer + flowing liquid).<sup>8,22</sup>

Unfortunately, the configuration of the flow modifies the measured overall dissolution rate. Some authors have even specified that the results depend on the “suspension load, stirrer form and vessel shape”<sup>23</sup>! Hence no values can be compared without removing the hydrodynamic part of the rate. The dissolution rate must be processed in such a way that it only contains the contribution from the chemical reaction, not from the fluid mechanics. To do so, we have performed a boundary layer analysis.<sup>24</sup> Indeed, as the solvent is flowing along the calcite surface, a diffusional boundary layer of thickness  $\delta$  develops in the vicinity of the solid, where the solution activity evolves from its value  $a_{\text{surf}}$  at the interface to its bulk value  $a_{\text{bulk}}$ . In AFM studies, the influence of the thickness of this layer on the dissolution rate can be directly evidenced in measuring the change of the atomic steps velocity (linked to  $R$ ) with the flow rate in the cell (influencing  $\delta$ ).<sup>18</sup> Our analysis enables to compute the contribution of the species mass transport inside the boundary layer, and to remove it from the measured dissolution rate, in order to access to the pure surface reaction rate  $R'_{\delta=0}$  (see Experimental Methods section).

The pure dissolution rates are shown in Figure 4. Again, to make comparisons easier, the scale has been kept identical to the scale in Figure 2 and Figure 3. We can see that all rates have been slightly shifted upward by the removal of the mass transport contribution. Opposite to the case of gypsum,<sup>24</sup> the reaction kinetics of calcite is significantly slower than the diffusion kinetics, which tends to make it reaction-limited. Therefore the influence of hydrodynamics is not negligible, but remains small.

This assertion is true except for a few experiments for which the removal of the diffusional contribution has induced a large increase of the rate, which stems from a trend of these configurations to be diffusion-controlled. The deduction of a pure chemical reaction rate in these situations where mass transport dominates is too tentative and has led us to discard some of these data.<sup>8,13,14</sup>

The dissolution rate is a flux of matter, so a quantity of ions crossing a given surface. Two choices are usually made for the calculation of the surface area: a surface area measured from a



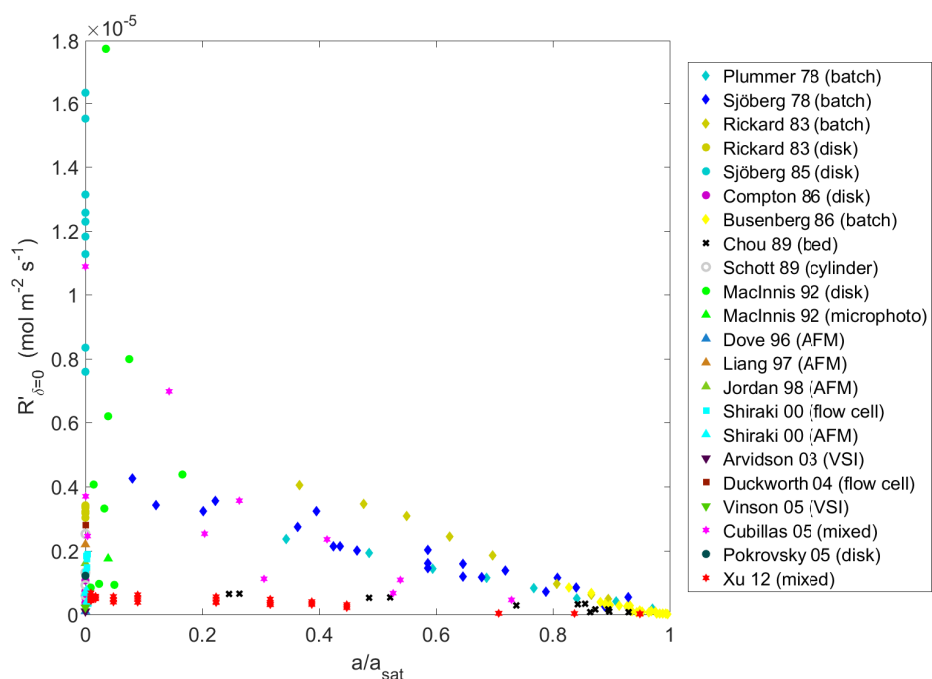


Figure 4: Dissolution rates of Figure 2 in similar chemical and hydrodynamical conditions ( $I = 0$  and  $\delta = 0$ ).  $R'_{\delta=0}$  has been computed from  $R'$  in removing the contribution of Fick diffusion to the rate.

quantity of adsorbed gas (e.g. with the BET method), which is supposed to depict the real reacting surface, or a geometric surface area, which portrays a kind of smoothed surface.

But Fischer *et al.* have demonstrated that the use of BET surface produces large errors in the area-normalization process.<sup>3</sup> Furthermore, ions have to cross the diffusional boundary layer before being captured and measured. Therefore we consider that the only experimentally accessible surface is the outer boundary layer, i.e., the geometric surface, which must therefore always be used to normalize the dissolution flow rate. Only one of all the articles studied here proposes BET-normalized  $R$ , without providing the geometric surface area of its material to enable a conversion, so we had to discard its results.<sup>11</sup>

Finally, we had also to discard some studies because they were performed at  $p\text{CO}_2$  larger than atmospheric  $p\text{CO}_2$  and because they missed the driving atomic mechanism of the dissolution (see Experimental Methods section).

Figure 5 gathers exhaustively the usable experimental dissolution rates found in the literature in comparable conditions, i.e., converted to zero ionic strength and zero contribution of mass transport. An irreducible dispersion of the results of one order of magnitude still persists. To understand the origin of this spreading of the data, a look at the current knowledge of the dissolution mechanisms of calcite appears necessary.

The stepwave model states that etch pits act mainly during dissolution as source of atomic steps.<sup>25</sup> According to this model, validated for calcite experimentally<sup>3,26</sup> as much as numerically,<sup>27</sup> the dispersion of the rate values originates in the variety of the sources of steps for each investigated sample. Thus, the density of dislocations (via the formation of etch pits), the polishing scratches, the grain boundaries, the abundant step and kink sites at the curvature in small grains, etc. all contribute to the availability of atomic steps.

This explains why, in Figure 5, the lower rates stem from the flatter samples<sup>12,21</sup> or largest grains,<sup>22</sup> whereas the higher ones are found for the most polished surfaces<sup>10</sup> or smallest grains.<sup>5</sup> Considering that this large batch of data provides a good statistical averaging of the available types of samples, benchmark values can now be defined. For  $\text{pH} \geq 6$ ,  $\text{pCO}_2 \leq \text{pCO}_2^{\text{atm}}$ , ambient temperature, under-saturation  $\Omega$  and activity coefficient  $\gamma$  (fixed by the ionic strength), the expected dissolution rate of calcite is:

$$R = \gamma^{-1} k_{\text{exp}} (1 - \Omega^{1/2}). \quad (1)$$

If the sample topography is known (by AFM for instance) to be particularly flat,  $k_{\text{exp}} = 0.5 \times 10^{-6}$  mol m<sup>-1</sup> s<sup>-1</sup> should be chosen. If it is highly energetic (due to grinding, etching, polishing ...),  $k_{\text{exp}} = 6 \times 10^{-6}$  mol m<sup>-1</sup> s<sup>-1</sup> should be taken. Values in-between may be chosen in case of intermediate surface state. In case of ignorance of the surface topography, a mean value  $k_{\text{exp}} = 3 \times 10^{-6}$  mol m<sup>-1</sup> s<sup>-1</sup> should be chosen. Finally, if nothing is known concerning the surface, under-saturation and ionic strength, the dissolution rate  $R = 3 \times 10^{-6}$  mol m<sup>-1</sup> s<sup>-1</sup> can be chosen as first estimation. The contribution of mass transport to the observable rate may be neglected, being in the majority of the measurements less than 10%. But in the case where the flow past the mineral is known to be particularly slow, or even nonexistent, a reduction of the rate down to 50%

of its value should be applied.

Finally, scarce results seem to indicate that for  $a_{\text{Ca}^{2+}}/a_{\text{CO}_3^{2-}}$  ratios markedly above one<sup>5</sup> and below one<sup>21</sup> the dissolution rate takes lower values, due to the adsorption of the over-represented ion at kink sites of the atomic steps.<sup>28</sup> The influence of the nature of the background electrolytes has received little attention so far and the only available study comes to the conclusion that the change from  $\text{Na}^+$  to  $\text{K}^+$  has no effect on the dissolution rate.<sup>10</sup>

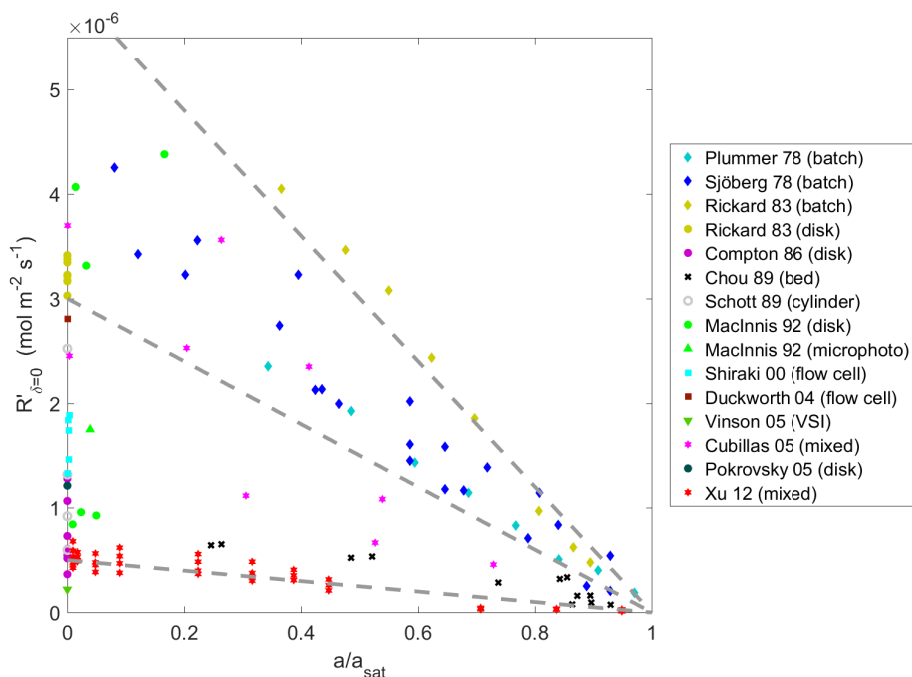


Figure 5: Exhaustive overview of the exploitable published alkaline dissolution rates of calcite versus under-saturation in similar chemical and hydrodynamical conditions ( $I = 0$  and  $\delta = 0$ ). The dashed lines stand for the minimum, average, and maximum rate laws.

We think that these benchmark values of the alkaline dissolution rate of calcite, taking into account the solution chemistry, fluid mechanics and surface physics of the phenomenon, and compatible with all the published values, can be used for every study needing a reliable estimate, in geology as much as in environmental or material science, and may also be used to survey new calcite dissolution measurements.

## Experimental methods

We present here the methodology of the literature data processing.

**Under-saturation.** The rate law for the dissolution of calcite is still a matter of debate. We think that, as long as the atomistic mechanisms of dissolution of calcite are not clearly described, which is still the case, no theoretically established law may surface. Therefore, to represent all the data, we have selected the quantity to represent the under-saturation from its heuristic utility: We have made the choice to express all dissolution rates as a function of  $a/a_{\text{sat}}$ ,  $a$  being the mean ionic activity of  $\text{Ca}^{2+}$  and  $\text{CO}_3^{2-}$  and  $a_{\text{sat}}$  the saturation mean ionic activity, for the only reason that almost all data sets form a straight line in the  $a/a_{\text{sat}} - R$  plane, as shown in Figure 2 (details about the data processing for each experiment can be found in the Supporting Information).

**Boundary layer analysis.** Dissolution proceeds in three stages: (i) the ions detach from the solid with a kinetics described by the rate law  $R'_{\text{diss}} = k(1 - a_{\text{surf}}/a_{\text{sat}})$  (deduced from the linearity of the curves in Figure 2), with  $k$  the dissolution rate constant, (ii) then the ions migrate through the boundary layer by diffusion, following Fick's first law  $R'_{\text{diff}} = D(a_{\text{surf}} - a_{\text{bulk}})/\delta$ , with  $D$  the diffusion coefficient of the ions and  $\delta$  the boundary layer thickness, (iii) and eventually the ions are advected by the flow to the concentration measurement apparatus.

Here, we will not estimate a priori that the literature results are either transport-driven ( $R'_{\text{diff}} \ll R'_{\text{diss}}$ ), or reaction-driven ( $R'_{\text{diss}} \ll R'_{\text{diff}}$ ), or even mixed, but resolve quantitatively the activity gradient inside the boundary layer. With this aim, we apply mass conservation between the bottom and top of the boundary layer. This requirement implies that  $R'_{\text{diss}} = R'_{\text{diff}}$ , which in turn fixes the surface activity:

$$a_{\text{surf}} = a_{\text{sat}} \left( \frac{k\delta + Da_{\text{bulk}}}{Da_{\text{sat}} + k\delta} \right). \quad (2)$$

When Eq. (2) is introduced in Fick's law, the following linear rate law, taking into account the competition of surface reaction and mass transport, is obtained:

$$R'_{\text{diff}} = \frac{1}{\frac{1}{k} + \frac{\delta}{Da_{\text{sat}}}} \left( 1 - \frac{a_{\text{bulk}}}{a_{\text{sat}}} \right). \quad (3)$$

From this, we see that we can deduce the pure dissolution rate constant  $k$  for each dot from:

$$k = - \frac{a_{\text{sat}}}{\frac{1}{\frac{\partial R'}{\partial a_{\text{bulk}}}} + \frac{\delta}{D}} \quad (4)$$

and the experimentally accessible pure dissolution rate, corresponding to the hypothetical case  $\delta = 0$ , can be obtained through:

$$R'_{\delta=0} = k \left(1 - \frac{a_{\text{bulk}}}{a_{\text{sat}}}\right). \quad (5)$$

Details about the computation of  $\delta$  for each device can be found in the Supporting Information.

**CO<sub>2</sub> partial pressure.** The partial pressure of CO<sub>2</sub> above the solution contributes strongly to the chemical equilibrium of dissolved carbonates, which is the reason of the considerable importance of calcium carbonate dissolution in the global CO<sub>2</sub> cycle. We have restricted our study to the case of the atmospheric situation, i.e.,  $p\text{CO}_2^{\text{atm}} = 10^{-3.5}$  atm. As no measurable discrepancy between results for this value and for 0 atm of CO<sub>2</sub> has been noticed,<sup>22</sup> possibly due to the slowness of CO<sub>2</sub> conversion in HCO<sub>3</sub><sup>-</sup>,<sup>29</sup> these values have also been included in the corpus, but all experiments carried out above  $p\text{CO}_2^{\text{atm}}$  have been excluded.<sup>30</sup>

**AFM measurements.** The main mechanism of transfer of matter from solid to liquid during dissolution is the retreat of monomolecular steps at the dissolving calcite surface. So dissolution rates have been deduced from the velocity and numerical density of these atomic steps measured with AFM.<sup>7,17–19,21</sup> Two families of steps have been observed. First, two types of regular steps, one making an acute angle with the surface, and one an obtuse angle, are found enclosing etch pits, their propagation inducing a broadening of the pits.<sup>18</sup> Secondly rough steps, generally stemming from the merging of two straight steps, also migrate across the surface.<sup>21</sup> All the studies have computed the dissolution rate from the velocity of steps enclosing etch pits, which has led to slow dissolution rate values. Unfortunately, Vinson & Lüttge have shown, in comparing AFM and VSI (vertical scanning interferometry) measurements, that the kinetics of the dissolution is driven by the propagation of the rough steps, not the straight ones.<sup>21</sup> This fact may incidentally contribute to explain the absence of correlation between the evolution with pH of the dissolution rate and of the

straight steps velocity.<sup>7,9</sup> We were thus forced to discard all the published AFM dissolution rates, all originating from the scrutiny of the celerity of pits widening or deepening.<sup>7,17–19</sup>

## Supporting information

In the Supporting Information, the measurement technique, origin of the calcite, grain or crystal size, sample preparation protocol, temperature, pCO<sub>2</sub>, pH, composition of the dissolving solution and ionic strength of every study are recalled when available. The stirring rate, when relevant, is provided, and details on the computation of the saturation index of the solution are also given. The reason of the discarding of some studies is also explained.

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