How crystalline matter dissolves: Contours of a comprehensive stochastic model

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In the 1950's Burton, Cabrera and Frank developed BCF theory for crystal growth and some specific cases of crystal dissolution, e.g. the formation of etch pits along screw dislocations. Subsequently, we have struggled with attempts to develop a comprehensive theory and model that will describe and correctly predict how crystalline matter dissolves.

Today, we can point to a large pool of experimental and field data and a correspondingly large number of so-called rate laws that mainly attempt to fit these data. At the same time, we have identified a number of obstacles that potentially prevent us from understanding fundamental problems, including the measured discrepancies between field and laboratory data, 'reactive' surface area, and related issues. This situation cripples our ability to quantitatively predict how crystalline matter dissolves, and thus has significant consequences for important decisions involving, e.g. the licensing of repositories for nuclear waste, the treatment of hazardous waste, and regulations to ensure groundwater and aquifer quality during the 'fracing' process used by the energy industry to generate shale gas.

As an alternative we have developed a new approach that treats the dissolution and growth of crystalline matter stochastically as a many-body problem. Laboratory studies using vertical scanning interferometry and atomic force microscopy demonstrate that computer simulations of reaction kinetics based on parameterized Monte Carlo simulations are increasingly capable of correctly predicting how a specific surface or an entire crystal dissolves.

Our study shows that variations of up to 2.5 orders of magnitude in dissolution rates are likely real and not an experimental artifact. Thus, the concept of an intrinsic dissolution rate, i.e. the 'rate constant' as a material constant, is indeed fiction. Even if we postulate that the development of a steady-state surface is possible for dissolving crystals, this scenario would not be realistic for most natural processes under ambient conditions.

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^{17}O anomaly of dissolved O_2 in the deep Atlantic Ocean

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It is well established that oceanic dissolved O_2 contains an excess of ^{17}O ($^{17}\Delta$) with respect to atmospheric oxygen [1, 2]. This excess originates from newly produced O_2 by marine photosynthesis. $^{17}\Delta$ is unaffected by respiration and therefore behaves conservatively in the deep sea. In contrast, air-sea gas exchange drives $^{17}\Delta$ towards zero in surface water. As a result, $^{17}\Delta$ is low (20-40 per meg) in the oceanic mixed layer, but high values (up to ~200 per meg) are typical in the seasonal thermocline, where exchange with air is slow and new production of O_2 by photosynthesis is the main factor affecting $^{17}\Delta$. Below the seasonal thermocline, in layers that originate in winter at high latitudes, $^{17}\Delta$ tends again toward low values indicating the dominance of gas exchange over photosynthesis in the source areas. Yet, there is no information on $^{17}\Delta$ below 300 m.

Here we report results of the first measurements in the deep sea. In the Sargasso Sea, $^{17}\Delta$ is ~50 per meg at 500 m and gradually declines to ~30 per meg at 4700 m. These values are expected according to the explanation above and the high latitude origin of the water in this depth range. In contrast, high $^{17}\Delta$ values (79 to 97 per meg) were measured over the depth range of 1250 to 5000 m in two stations in the S. Atlantic (~35° and ~39°S). Such high values in both NADW and AABW are unexpected and we will discuss possible explanations for their origin.

[1] Luz&Barkan (2000) *Science* **288**, 2028–2031. [2] Luz & Barkan (2009) *AME* **56**, 133–145.