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How predictable are dissolution rates in natural and industrial systems?

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The large discrepancy between field and laboratory measurements of mineral reaction rates is a long-standing problem in earth sciences, often explained by factors extrinsic to the mineral itself. However, differences in reaction rate also exist within well-constrained laboratory measurements, raising the possibility of intrinsic variation as well. At their core, these variations involve the distribution of surface reactivity, a problem which has in the past been pursued in terms of definition and measurement of so-called *reactive surface area*.

In a simple experiment involving a single crystal and its polycrystalline counterpart, we demonstrate the sensitivity of dissolution rate to grain size, and show how this sensitivity is related to the fundamental variance of the rate. We also show how these complex distributions are further confused by the common practice of surface area normalization. Moreover, comparison of these findings with published AFM step velocities [1] and single crystal dissolution data [2] provide further indication of a fundamental variability in surface reactivity. Together with related considerations involving the distribution of surface reactivity [3], we argue these results are consistent with the following hypothesis: *the dissolution of crystalline materials cannot be adequately characterized by a material constant*.

This hypothesis reflects our understanding that crystal structures undergoing dissolution influence their neighbours in a classic many-body problem, and thus the dynamics of these populations are not predictable in the manner implied by a rate constant. In place of such invariant parameters there must appear terms that contain probabilistic information. Despite some past resonance in the literature, this problem is currently largely unrecognised and has no accepted treatment, an unhappy situation that handicaps our ability to make critical predictions involving natural and industrial systems. We argue that its resolution will require a fundamentally new approach, one that begins by first recognising the probabilistic nature of the dissolution process.

[1] Jordan & Rammensee (1998) *Geochimica et Cosmochimica Acta* **62(6)**, 941–947. [2] Busenberg & Plummer (1986) *Studies in Diagenesis, U. S. Geological Survey Bulletin* **1578**, 139–168. [3] Fischer & Lüttge (2007) *American Journal of Science* **307(7)**, 955–973.