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Space-time correlations associated with nanoscale dissolution patternsat calcite-water interfaces

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We explore and quantify the complex space-time dynamics of (*i*) surface topography, Z, and (*ii*) reaction rates, R, observed at the nanoscale during calcite dissolution. We rely on a stochastic theoretical framework based on the concept of space-time variogram. The latter has been developed and employed to characterize dynamically evolving correlation patterns of hydrogeological quantities and processes. These include attributes of large-scale (spatially heterogeneous) groundwater systems and temporally varying pressure heads therein. Transferability of the approach to provide a stochastic characterization of nanoscale geochemical phenomena is here assessed for the first time. Our analysis is based on high-resolution experimental data obtained through Atomic Force Microscopy and capturing the evolution of calcite-water interfaces driven by dissolution. Using this extensive dataset, we extract key variability patterns through (*i*) quasi-random Sobol sequence sampling to efficiently cover the spatial domain and (*ii*) a Harmonic Covariance Estimator to model the space-time variogram of Z. The resulting sample variogram reveals distinct periodic oscillations at specific spatial and temporal scales. These are imprinted by interactions between spatial structure and temporal evolution of the diverse mechanistic processes (e.g., etch pits) taking place across the crystal and driving the system dynamics. We then provide a firm theoretical relationship between the variograms of Z and R. As such, our theoretical framework of analysis and analytical developments provide unique insights into spatial and temporal correlations governing calcite dissolution. Our findings establish a link between the space-time evolution of crystal morphology (quantified, e.g., in terms of its spatial topography) and dissolution rates, providing a foundation for predictive modeling of these complex processes at nanoscale resolution. Our approach can be employed to gauge reliability of crystal dissolution models whose mathematical rendering is viewed in a probabilistic context. While typically used models differ in the way one assigns probabilities that dissolution can take place at a given (space-time) location on the simulated crystal surface, our results can assist (stochastic) model calibration and model selection upon constraining these on clearly observable and quantifiable correlation structures.