The Influence of Carbonate Alkalinity on Calcite Dissolution Kinetics: An Experimental Study

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There is increasing recognition of the importance of variation in rates of mineral dissolution under otherwise similar conditions. Recent studies have shown conclusively an intrinsic dissolution rate variability of two to three orders of magnitude under identical chemical conditions [1-3]. In this study, we analyze the variability of calcite dissolution kinetics as a function of carbonate alkalinity (particularly the contribution from carbonate ion, CO_3^{2-}), a parameter that has been observed to significantly impact site-specific reaction kinetics of calcite surface (10.4) steps [4] and their sensitivity to inhibition [5]. Here, we focus specifically on the investigation of the spatial heterogeneity of dissolution rate based on high- resolution surface topography data using fast-scanning atomic force microscopy (FS-AFM). During dissolution, point dislocations and screw defects are the source of dissolution stepwaves. Sequences of surface data trace the spatial and temporal evolution and movement of dissolution stepwaves. We compare the FS-AFM data with data collected by vertical scanning interferometer (VSI). VSI data provide a large field-of-view, thus allowing insight into the spatial heterogeneity of surface reactivity. We varied alkalinity in the reacting fluid from 0.5 to 4.4 mM (expressed here as sodium carbonate concentrations), allowing pH to vary in the alkaline range at fixed pCO_2, and generating shifts in carbonate ion concentration over orders of magnitude. The temporal sequences of surface data were used to calculate dissolution rate maps under these conditions. These maps provide direct insight into the spatial heterogeneity of surface reactivity, and furthermore constitute the database for the calculation and analysis of rate contributors that combine to produce an overall surface reaction rate [2,3]. These results provide the quantitative constraints to rate modes for calcite dissolution that are mechanistically sensitive to carbonic acid system variation.

[1] Arvidson et al. (2003) GCA **67**, 1623-1634; [2] Fischer et al. (2012) GCA **98**, 177-185; [3] Fischer & Luttge (2017) EPSL **457**, 100-105; [4] Lea et al. (2001) GCA **65**, 369-379. [5] Vinson et al. (2007) J Cryst Growth **307**, 116-125.