Effect of Solution Chemistry on the Kinetics of Step Growth

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Crystal growth from solution propagates through the attachment of atoms/molecules (in the classical theory) to the growing surfaces or aggregation of nano building clusters (in the non-classical approach) to each other. While the thermodynamic driving force for the growth is well-understood and can be precisely determined via the saturation level of the solution, our grasp of the effect of other solution chemistry parameters, such as ionic strength and stoichiometry, on the growth kinetics remained loose. In the classical approach, the net growth rate of mono-molecular layers (ie, step velocity v_s) is assumed to to determined by the difference between fluxes of species attaching to and detaching from kinks along step edges. Such treatment leads to the development of the wide used relationship of $v_s = \beta[(a-a_e)/a_e]$ which states that v_s scales linearly with the solute activity a relative to its equilibrium value a_e (the kinetic coefficient β characterizes the enthalpic and entropic barriers for solute incorporation, including desolvation of growth sites and solute particles). It then follows that v_s should be controlled solely the solution saturation under similar T and P conditions. Yet, literature data from numerous cases argued strongly against this supposition. In this study, we conducted a series of in situ AFM experiments to interrogate the effect of solution chemistry parameters other than supersaturaiton on step kinetics using calcite as a model system. We found step kinetics were strong affected by solution pH, ionic strength SI, and the $[Ca^{2+}]/[CO_3^{2-}]$ ratio, and the impact differs in different directions (obtuse va. acute steps on the {104} cleavage faces). For example, while the v_s of acute steps decreased with increasing pH, the obtuse step rate showed little response to pH change. More interestingly, both sides exhibited a sharp trend transition (varied degree of positive v_s – pH dependence) starting at pH ~9.5. In addition, step velocity in both directions decreased with increasing SI, but the trend became significantly weakened in the acute direction when SI > 0.1. The effect of cation-anion ratio on step kinetic appeared to be more complex. A maximum speed was achieved at different values of $[Ca^{2+}]/[CO_3^{2-}]$ for obtuse and acute steps, and the ratio seemed to decrease with increasing pH. These observations strongly suggest that, although supersaturation is the driving force for aqueous phase crystallization, solution chemistry plays critical roles in controlling the actual growth rate and needs to be taken into consideration in kinetic studies of crystallization.

Are molybdenum concentrations and isotopes a tracer for anthropogenic pollution in the atmosphere?

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The trace metal molybdenum (Mo) is not very abundant in the environment but has found numerous applications in anthropogenic activities. For instance, in the form of Mo sulphide (MoS_2) it is a component of diesel fuel. Mo is used as a catalyst in many engines and is believed to be the most efficient catalyst for the hydrocracking of bitumen [1]. Molybdenum has even been suggested as a fertilizer additive [2] and has also been found in coal-fired power plant emissions [3]. Hence, anthropogenic activities may release Mo in larger amounts to the environment that may affect terrestrial and aquatic ecosystems (e.g. via its coupling with the N cycle). We have therefore investigated the potential of Mo concentration and isotope ratio measurements as a tracer of anthropogenic emissions.

We measured the molybdenum (Mo) isotopic composition of aerosols collected on Teflon air filters [4]. Airborne Mo was collected at selected locations including a residence in the city of Calgary, Canada, the isotope laboratory at the University of Calgary, the University of Calgary weather station, and the City of Calgary Transit bus garage where the city buses start and idle for extended periods. Concentrations ranged from 0.07 ng/m^3 in the laboratory to 19.0 ng/m^3 in the bus garage. The $\delta^{98/95}Mo$ values measured for the different urban sampling sites (reported relative to SRM 3134) ranged from –0.18 to +0.94 ‰. The results of this investigation suggest that measurements of Mo concentrations and isotopic compositions have the potential to trace anthropogenic emissions in an urban environment.

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