Ostwald's step rule: a consequence of growth kinetics and nano-scale energy landscape

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In his 1897 article on the formation and transformation of solid phases, Friedrich Wilhelm Ostwald described the phenomenon that hydrous sodium chlorate precipitates from an oversaturated solution, despite the fact that this phase is much more soluble than the non-hydrous salt. The fundamental concept, also known as Ostwald's step rule, is best summarized on page 307 of his article (here translated to English):

“... Such phenomena also frequently occur during melting and condensation of steam and even in homogeneous chemical reactions, and I would like to summarize the previous experiences with this matter in the single phrase that during departure from any state, and the transition to a more stable one, not the under given circumstances most stable state is reached, but the nearest one.”

Despite its major importance for mineral formation under Earth's surface conditions, this concept is still not fully understood on a mechanistic level. While Ostwald's step rule is commonly explained with the classical nucleation theory, there are several inconsistencies, especially the conundrum that sometimes stable phases, such as dolomite or quartz, do not form as long as a metastable phase is supersaturated. I propose an alternative interpretation that would be consistent with Ostwald's (1897) original formulation as well as with several observations from natural environments and laboratory experiments. If “nearest” (in German: “nächstliegend”) is not understood as “thermodynamically most similar”, but as the phase with the lowest kinetic barrier, Ostwald's step rule should be always valid. The kinetic barrier is surface specific and independent of supersaturation, but it depends on the atomic scale interfacial energy landscape. This concept would better represent the power of Ostwald's step rule to explain mineral formation processes and how they are affected by chemical and biological influences. New nano-scale analytical techniques in combination with advanced molecular dynamic modelling bear great potential to explain and appreciate the importance of Ostwald's step rule.