Goldschmidt 2021 Abstract
https://doi.org/10.7185/gold2021.6303

Nanoscale imaging of mineral growth through a non-classical nanoparticle pathway

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Modern analytical imaging techniques, including atomic force microscopy (AFM) and scanning and transmission electron microscopies (SEM and TEM), have enabled observations of processes occurring at mineral surfaces *in situ* at a nanoscale in real space and time and hence giving the possibility to elucidate reaction mechanisms. Classical crystal growth theories are well established and while they can still be applied to explain crystal growth in many growth scenarios, we now know that these models are not always an accurate description of the mechanism of all crystal/mineral growth processes, especially where nanoparticle formation is observed. Here we describe experimental observations of non-classical crystallization processes at the nanoscale. Using AFM, we demonstrate that many minerals commonly grow by the attachment of nanoparticles on an existing mineral surface, often resulting from the coupling of dissolution of a parent phase and the precipitation of a new product mineral. Using the example of crystal/mineral growth of phosphate minerals as well as calcite and calcium oxalate, we show the importance of the mineral-fluid interface and the aqueous fluid interfacial (boundary) layer in the control of crystal growth. Whether a crystal will grow by classical monomer attachment resulting in step advancement or by the formation, aggregation and merging of nanoparticles, will be controlled by the aqueous fluid composition at the mineral-fluid interface. The processes described also allow for the development of porosity within the new mineral and hence have important consequences for fluid movement and element mobility within the Earth, as well as applying to processes occurring in other scenarios of mineral growth, such as bone, teeth and pathological stone formation.