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Crystallization via non-classical pathways: Nanoscale imaging of mineral surfaces

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The advancement in analytical imaging techniques, including atomic force microscopy (AFM) and scanning and transmission electron microscopies (SEM and TEM), has allowed us to observe 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 have been established for well over 100 years 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. Consequently there is a current challenge at the forefront of understanding crystal/mineral growth mechanisms. This work describes experimental observations of non-classical crystallization processes at the nanoscale. Using AFM as well as SEM and TEM imaging, 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. Through varied examples of crystal/mineral growth, including calcite and other carbonates, barite, brucite, and apatite, we define 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. Additionally an understanding of natural mineral growth has implications for geomimetic applications for the manufacture of functional engineered materials.