

Phase Transformation of MnCO_3 surfaces within Nanometric Water Films

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Phase transformations at mineral surfaces have been widely investigated in liquid water, yet those that occur within nanometrically-thick water films formed by exposure to atmospheric moisture continue to be misunderstood. The study of reactions within these confined environments is directly relevant to a score of processes in nature, including atmospheric cloud formation, chemical weathering, and vadose zone biogeochemistry.

In this work, we monitored the phase transformation of rhodochrosite (MnCO_3) within the confines of nanometrically-thick water films. We find that $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ -oxides coatings form in water films of no less than ~ 10 monolayers when exposed to ambient conditions of CO_2 and O_2 . Vibrational spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy and Transmission Electron Microscopy collectively provide evidence for the transformation surface Mn(II) species to nanosized hausmannite (Mn_3O_4) and birnessite ($\delta\text{-MnO}_2$), however only in alkaline films. We explain this transformation by the homogenous oxidation of hydrolyzed Mn(II)aqueous species, and their subsequent precipitation to $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ -oxides nanoparticles all within the confines of ~ 10 monolayer-thick water films. Although rhodochrosite is strongly resilient to surface oxidation under ambient conditions, hikes in water film pH during dehydration events in environments exposed to wet-dry cycling, especially at oxic/anoxic boundaries, could produce these new reactive $\text{Mn}^{\text{III}}/\text{Mn}^{\text{IV}}$ -oxides nanoparticle coatings.