Multiscale Expression of Apatite Dissolution

Adele Conde & The Department of Geology

AY 2018-2019 Progress Report

Background & Significance

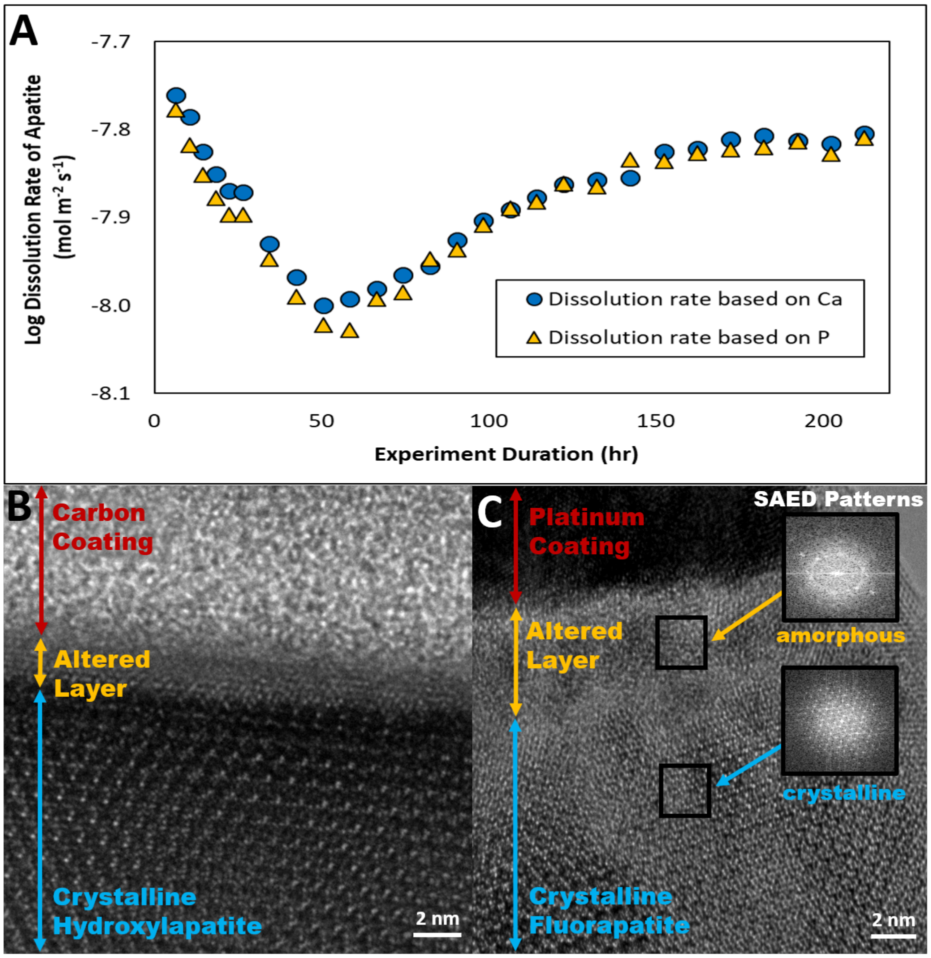
Although phosphate minerals are not the most common minerals on Earth or Mars, they are required for life to occur as phosphorous is the backbone of our DNA. Weathering of the phosphate mineral apatite is the primary source of phosphorus in the environment and composes our bones and teeth. Despite apatite being critical to many biological reactions, little is known about the molecular scale processes driving its breakdown. However, cutting-edge nanoscale observations of weathered silicate minerals have provided compelling evidence of a relatively new chemical weathering mechanism referred to as coupled interfacial dissolution-precipitation (CIDR) which is characterized by the formation of an amorphous surface altered layer (SAL). This SAL represent an interfacial region that would acts as a ‘communication bridge’ between the apatite and the external environment. The mechanistic understanding of this process is necessary to predict chemical weathering at all scales whether on Earth or on Mars.

Project Goals

The primary goals of this project were to determine the nanoscale processes responsible for apatite weathering and the influence of chemical composition and crystal structure on such weathering processes. To fulfill these objectives we formulated two hypotheses, 1) The CIDR weathering model is extendable to phosphate mineral such as apatite and 2) apatite dissolution rates and expression are a function of its chemical composition and crystal structure. To test these hypotheses , two types of apatite with slightly different chemical composition and crystal structure (fluorapatite - $Ca_{10}(PO_3)_4(F,OH)_2$ and hydroxyl-chlorapatite - $Ca_{10}(PO_3)_4(OH,Cl)_2$) were chemically weathered in the laboratory. Before and after weathering the mineral surfaces were observed at the nano- to micro-scale to inform on both structural and chemical transformation of the crystals.

Summary of Key Findings

For the first time, high resolution Transmission Electron Microscope (TEM) imaging and analysis was conducted on partially weathered apatite crystals to determine the presence of a structurally and chemically distinct amorphous SAL. This project provided new evidence that the CIDR weathering mechanism for silicate minerals may extend to phosphate minerals. An amorphous SAL with a structurally sharp interface on both apatites was directly observed via high resolution TEM. The presence of this amorphous SAL combined with preferential weathering of Ca (compared to P) at the macroscale provides substantial evidence that apatite weathering is accompanied by the formation of a Ca depleted amorphous SAL (relative to apatite). Furthermore, we suggest that the SAL is preserved *via* reprecipitation throughout the dissolution process. Observations of the apatites during and after weathering also demonstrate that the primary control of weathering rate and expression lies in the anionic composition. This study consistently showed that hydroxyl-chlorapatite weathered faster than fluorapatite. Additionally, Scanning Electron Microscope (SEM) characterization of the apatite surfaces pre- and post-weathering revealed the development of etch pits during dissolution, however, more pronounced on fluorapatite than hydroxyl-chlorapatite. Apatite solubility and dissolution processes likely depend heavily on the mechanisms by which anionic solid-solution exists. The potential discovery that the CIDR weathering model is extendable to phosphate minerals could transform our understanding of phosphate behavior in medical and environmental fields.



A) Comparison of Ca and P dissolution rates as a function of time. Relatively faster Ca based dissolution rates at the beginning of the experiment (80 hours) indicate a preferential weathering of Ca relative to P leading to the formation of a Ca depleted altered layer. High resolution TEM images of B) hydroxyl-chlorapatite and C) fluorapatite in cross-section shows a sharp interface between crystalline apatite and an amorphous SAL. The blue arrows delineate the crystalline apatite, the yellow arrows delineate the altered surface layer and the red arrows delineate a protective C or Pt coating. C) Selected Area Electron Diffraction (SAED) patterns corresponding to each domain show that the SAL is amorphous and the unaltered fluorapatite is crystalline.