Dissolution of apatite: Micro and Nanoscale insights

NICO PERDRIAL[1],ADELE CONDE[1], ROLAND HELLMANN[2], LIZ RAMPE[3], ROY CHRISTOFFERSEN[3], MITSUHIRO MURAYAMA[4]

[1]Department of Geology, University of Vermont, VT, USA
[2]ISTerre, Universite de Grenoble, France
[3]ARES, NASA Johnson Space Center, Houston, TX, USA
[4]NanoEarth, Virginia Tech, VA, USA

Apatite is the most abundant phosphate mineral on Earth. In addition to being the foundation of the global phosphorus cycle, it is the most abundant mineral in the human body and is thought to have played a crucial role in the development of life. Despite its key role, little is known about its dissolution behavior at the atomic scale. Based on recent studies [1,2], there is strong evidence that dissolution of multi-cation silicate minerals are controlled by a coupled interfacial dissolution-reprecipitation (CIDR) process- we hypothesize that the same process controls phosphate mineral alteration.Determining what controls apatite weathering can impact many areas of environmental and medical mineralogy such as dentistry, contaminant scavenging, geochronology or paleoenvironment studies.

To test our hypothesis, we acid-reacted crystals of fluorapatite (FAp) and hydroxylapatite (HAp) in flow-through devices with pH 2 HNO_3 solutions. Determination of the mechanisms of dissolution was carried at multiple scales using aqueous chemistry (macroscale), SEM-EDS (microscale) and STEM-HAADF-EELS on FIB liftouts (nanoscale).

At the macroscale, we observed that the anionic composition of the apatite controls its weathering rate with, unsurprizingly, faster dissolution rates for HAp compared to FAp. SEM characterization of the crystal surface pre- and post-dissolution revealed the development of etch pits during dissolution, which were more pronouced for FAp than HAp. Observation of the mineral/solution interface at the nanoscale using STEM-HAADF revealed the development of a nanometric amorphous layer depleted in Ca compared to P.

The observation of a sharp crystalline/amorphous transition of just a few nanometer, associated with sharp depletion in Ca, suggests that, similar to silicate, apatite is controlled by a CIDR mechanism. This discovery has the potential to transform our understanding of phosphate behavior in medical and environmental mineralogy.

[1] Hellmann et al., 2012, Chem Geol, 294
[2] Daval et al., 2018, EPSL, 498