

Apatite nanoresponse to acidic dissolution

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Phosphorus uptake by plants and organisms is one of the most important life-sustaining processes occurring in the critical zone (CZ). Because 95% of Earth's P reserves is relatively immobile in the form of apatite, plants and organisms rely on molecular scale solubilization process to extract available P. As the world experiences a global P shortage, influencing food production, it becomes increasingly important to understand apatite dissolution. The detailed study of chemically weathered apatite surfaces at the μm to nm-scale is key to understanding P solubilization and uptake in the CZ, allowing for better crop management and efficient fertilization.

Apatite weathering is generally viewed in terms of a pH-dependent process where protons weaken atomic bonds, this leading to the disintegration of the apatite structure. A general feature of apatite weathering in acid and near neutral pH conditions is an apparent non-stoichiometric dissolution characterized by $[\text{Ca}/\text{P}]_{\text{aq}} > 1.66$ in both fluorapatites (FAP) and hydroxyapatites (HAP). This process leads to the formation of a surface altered layer (SAL) with a different composition from the bulk, which many have argued is a Ca-depleted "leached layer".

We investigated apatite weathering at the nanoscale using FIB-prepared TEM-foils. Our preliminary results based on laboratory-altered FAP at ambient T and pH 3 show the formation of amorphous SALs with a maximum thickness of ~ 10 nm. High resolution chemical mapping and profiling using STEM-EELS and STEM-EDXS indicate that the SALs are generally, but not always, depleted in Ca and enriched in P. These results provide an alternate view of the mechanism of apatite dissolution with stoichiometric breakdown of the apatite structure, followed by the reprecipitation of an amorphous surface layer depleted in Ca.

This mechanism can be described in terms of coupled interfacial dissolution-reprecipitation (CIDR), which is increasingly viewed as a universal mechanism of silicate mineral and glass dissolution. Our observation that apatite may dissolve similarly to silicates implies not only that apatite weathering may be more complex than originally thought, but also that the CIDR mechanism may extend beyond silicates.