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# Mineral Surface Transformations by Ice Nucleation

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The weathering of minerals is driven by physical, chemical, and biological processes. Chemical and biological weathering impact the chemistry of the mineral surfaces through reactions at the water-mineral interface or deposition of biofilms [1]. Physical weathering can occur through water uptake and ice formation. Understanding ice formation on mineral surfaces is important for cloud formation through ice nucleation in the atmosphere. Ice nucleation is dependent on the chemical composition and topology of the particles [2]. Characterizing the organic material on the surface of the minerals is important to understand how phase transformation processes can occur and impact weathering [3]. We aim to understand the role of physical processes on the incipient weathering of mineral samples through ice nucleation mechanisms.

Rock grains were exposed to ambient conditions in a dry desert scrub ecosystem (Catalina Critical Zone Observatory [CZO]; Arizona, USA), a humid mixed hardwood-pine forest (Calhoun CZO; South Carolina, USA), and an experimental setting (Biosphere 2 model ecosystem [1]). Samples from the Biosphere 2 experiment were exposed to biological weathering in increasing complexity to include: microbes, microbes-vascular plants (Buffalo grass), and microbes-plant-arbuscular mycorrhiza. These exposure conditions define the type and amount of organic matter present on the rock substrate. Imaging of surfaces during ice nucleation events was performed utilizing a custom-built ice nucleation stage interfaced with an environmental scanning electron microscope (IN-ESEM) at PNNL where individual ice nucleation events can be observed in the SEM at high spatial resolution [4]. The ice nucleation experiments were performed at temperatures around 240 K under immersion freezing conditions.

By utilizing energy dispersive X-ray spectroscopy (EDS) under low kV energy and low vacuum conditions in SEM, we observed organic matter as dark patches on the rock surface (Fig. 1). Fungal hyphae are also observable in the Calhoun CZO samples as elongated structure on the rock surface with high carbon and nitrogen content. The IN-SEM experiment shows that at 236 K water is first taken up by the surface organic layer, followed by freezing (Fig. 2). After subsequent ice sublimation from the rock surface, there is substantial change in the physical ordering of the organics, indicative of surface mobilization during the physical weathering process. In the sample from the Calhoun CZO, ice nucleation never initiated on the fungal hyphae but rather originated from areas with an organic film on the surface of the rock. There was an increase in ice nucleation activity for samples exposed to biotic conditions with no preference for exposure type. With large regions of terrestrial surface undergoing periodic freezing, studying ice formation on rock surfaces should be accounted for when conceptualizing and modelling atmosphere-geosphere-biosphere interactions.

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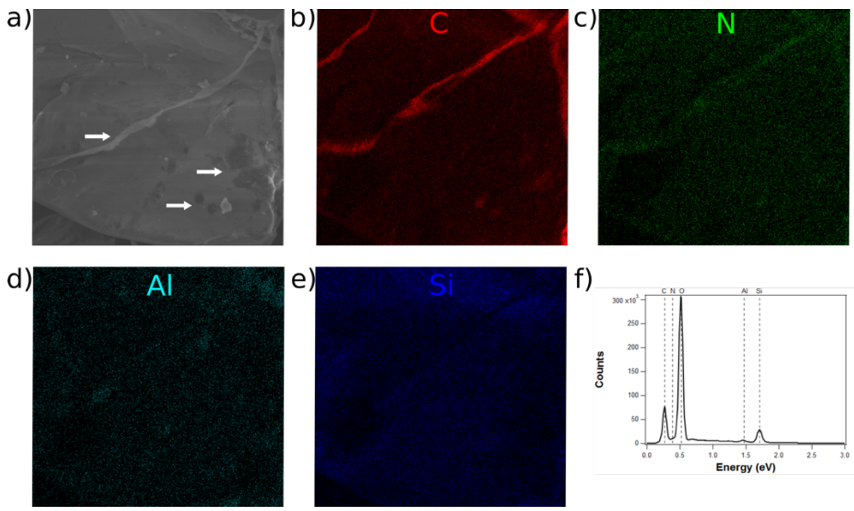


**Figure 1**: Elemental EDS mapping of sample surfaces at 3 kV under low-vacuum conditions demonstrating that the dark patches (a) are correlated with high carbon (b) and nitrogen (c) contents, indicative of surface organic material along with the fungal hyphae on the surface. Aluminum (d) and silicon (e) are from the mineral. f) The EDS spectrum for the mineral substrate.

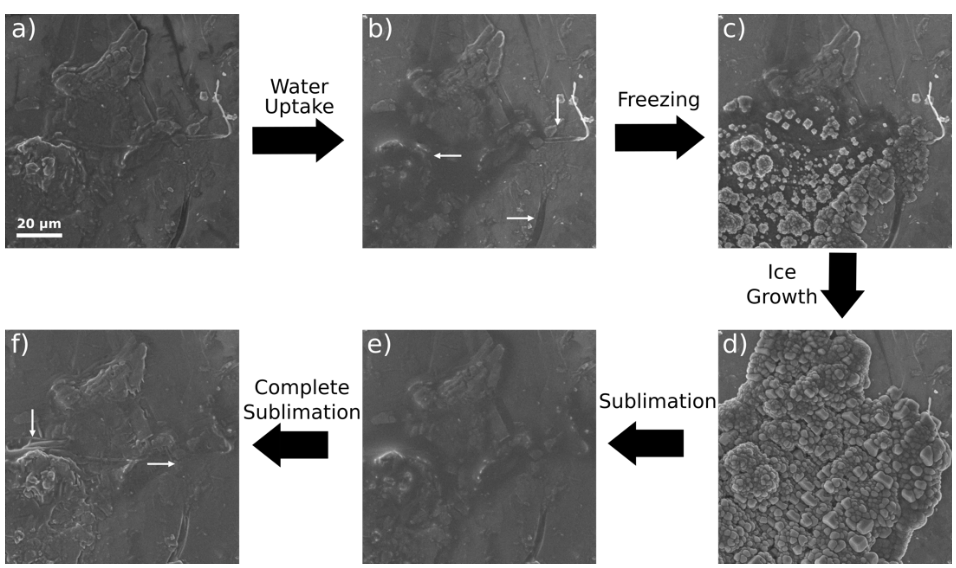


**Figure 2**: Demonstration of immersion freezing on granite surfaces extracted from the Calhoun CZO a) initial at 236 K and with increasing humidity b) water uptake is observed on the carbon rich areas and c) subsequent freezing followed by d) ice crystal growth, e) sublimation of the frozen water, and f) completely dry sample with signs of organic matter migration.

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