

Oxidation-controlled weathering fronts: reaction-driven fracturing vs. oxidative dissolution

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Fe-poor felsic rocks generally weather more slowly than Fe-rich mafic rocks, but their weathering fronts tend to penetrate deeper into the critical zone. This difference may stem from more advective transport of O₂-rich fluids into felsic rock, enabling oxidation of minerals at depth [1]. Alternatively, or in addition, oxidation of the more abundant Fe(II) of mafic rocks may consume more of the O₂ at a shallower depth [2]. Here we investigate incipient weathering of two volcanoclastic rocks of intermediate composition (basaltic-andesite) from the same geologic formation, one of which weathers spheroidally and one that doesn't. Spheroidal weathering has been attributed to oxidation-driven fracturing in which diffusion of O₂ into rock leads to the formation of fractures that permit advective transport [e.g., 3-5].

The rocks investigated come from the Luquillo Critical Zone Observatory, Puerto Rico. Thin sections were analysed using SEM-EDS, electron probe microanalysis, and μ XRF mapping (Diamond Light Source). The spheroidally weathering rock (SR) has a porphyritic texture with much larger pyroxene phenocrysts than the non-spheroidally weathering rock (NSR): ~1030 μ m and 74 μ m diameter, respectively. The NSR has ~10X higher initial porosity and 2X the pyrite content of the SR. The un-weathered SR contains >3X more pyroxene (the main Fe(II) mineral in both rocks) than the NSR and almost 2X more FeO. Pyroxene is largely lost over the 60 mm thick spheroidal zone (SR), and the 12 mm thick rind (NSR), and the pyroxene dissolution rate is similar in both. However, the first detected weathering reaction in the SR is the oxidation of Fe(II) in pyroxene fractures whereas oxidative dissolution of pyrite is the first reaction in the NSR. Both oxidation reaction mechanisms create porosity, but fractures are likely to create larger, more continuous porosity than dissolution, permitting greater advective infiltration of fluids. Hence the mineralogy as well as the FeO content and primary porosity may determine the depth of weathering in oxidation-controlled profiles.

[1] Bazilevskaya *et al.* (2013) *ESPL* **38**, 847–858. [2] Brantley *et al.* (2014) 6.15 *Treatise on Geochem.* pp. 327–352. [3] Fletcher *et al.* (2006) *EPSL* **244**, 444-457. [4] Buss *et al.* (2008) *GCA* **72**, 4488-4507. [5] Behrens *et al.* (2015) *Chem. Geol.* **411**, 283–298.