

# Exploring mineral precipitates at the onset of bulk weathering of crystalline rocks with reactive transport models

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Weathering is the equilibration of minerals formed at high pressure and temperature to the conditions at Earth's surface. At its simplest, the reactions are acid-base and redox in nature, and can be thought of as reactions with CO<sub>2</sub> and O<sub>2</sub>, respectively. In relatively iron-poor granites, oxidation is often the deepest observed reaction under ridgetop locations, occurring deeper than CO<sub>2</sub>-driven reactions. In contrast, in diabase, an iron-rich rock, CO<sub>2</sub>-driven dissolution is the deepest reaction under ridgetops. Additionally, biota act as a throttle or accelerator at Earth's surface because they consume or produce reactive gasses and mediate the flow of waters to depths of mineral reaction: in other words, the nature of microbiota in weathering systems also affects the reactive gasses and relative depths of mineral reactions. Such patterns can be traced by analysis of element-depth patterns in weathering profiles. It is also possible that mineral precipitates during weathering could reflect or record these reactions, even at depths well below the surface.

We have observed that the formation of secondary calcite and FeS may be coupled at the bottom of some weathering profiles. We hypothesize these secondary minerals may mark the transition from an effectively closed to an open system and be the by-product of biota at the initiation of weathering of crystalline rock in humid climates. These tiny carbonates appear to have formed along with Fe-sulfide precipitates, possibly recording where acid-base and redox weathering begin in the profile. When Ca and Fe minerals first begin to dissolve and release Ca and Fe into solution, calcite precipitates apparently form. If this is mediated by microbiota, then this could explain the association of the carbonate minerals with FeS precipitates. We also observed limited evidence that <sup>13</sup>C-calcite is most depleted at the weathered-unweathered rock interface, as if carbon from organic material contributed to the secondary calcite. A possible explanation is that sulfate-reducing bacteria could cause precipitation of this <sup>13</sup>C-depleted secondary calcite and formation of FeS as weathering initiates in the nearly closed, O<sub>2</sub>- and CO<sub>2</sub>-depleted system at the bottom of weathering crystalline rock.