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CO_2 driven weathering vs plume driven weathering as inferred from the groundwater of a persistently degassing basaltic volcano: Mt. Etna

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At Mt. Etna the presence of a persistent volcanic plume provides large amounts of volcanogenic elements to the bulk deposition along its flanks. The volcanic plume consists of solid particles, acidic droplets and gaseous species. After H_2O and CO_2, S, Cl and F represent the most abundant volatile elements emitted as gaseous species from the craters. During rain events acidic gases interact rapidly with droplets lowering the pH of rain. This process favors the dissolution and dissociation of the most acidic gases. Under these conditions, the chemical weathering of volcanic rocks and ashes is promoted by the acid rain during its infiltration. Subsequently during groundwater circulation, chemical weathering of volcanic rocks is also driven by the huge amount of deep magmatic carbon dioxide (CO_2) coming up through the volcanic edifice and dissolving in the water. These two different weathering steps occur under very different conditions. The former occurs in a highly acidic environment (pH < 4) and the reaction rates depend strongly on the pH, while the latter usually occurs under slightly acidic conditions since the pH has been already neutralized by the interaction with volcanics rocks. The high content of chlorine is mainly derived from interactions between the plume and rainwater, while the total alkalinity can be completely ascribed to the dissociation of carbonic acid (H_2CO_3) after the hydration of CO_2. The relative contributions of plume-derived elements/weathering and CO_2-driven weathering has been computed for each element. In addition, the comparison between the chemical compositions of the bulk deposition and of groundwater provides a new understanding about the mobility of volatile elements. Other processes such as ion exchange, iddingsite formation, and carbonate precipitation can also play roles, but only to minor extents. The proposed approach has revealed that the persistent plume strongly affects the chemical composition of groundwater at Mt. Etna and probably also at other volcanoes characterized by huge open-conduit degassing activity.