## Control of leaching intensity on weathering and non-linear changes in soil chemistry

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Rainfall and the amount of water available to leach ions from soil are among the most important features determining mineral weathering, secondary mineral synthesis and soil chemical properties. Along an arid to humid climosequence on Kohala Mountain, Hawaii, we found that weathering and soil properties change in a non-linear fashion with increased rainfall. The lava soils are influenced by a strong rain shadow with mean annual precipitation (MAP) averaging 160 mm near the coast and rising to > 3000 mm near the summit. The temperature decline from 24 to 15 °C with increasing elevation is matched by a decline in evapotranspiration (ET).

A water balance model (monthly precipitation minus monthly ET) is combined with the porosity in the top meter of soil to provide a leaching index. The index reaches 1 (total filling of the pore space on an annual basis) at about 1400 mm MAP. Index values > 1 imply intense leaching conditions because of pore water dis- and re-placement. In these 170 ka soils leaching losses of soluble base cations and Si are nearly complete at index values > 1, whereas only 60% of Al has been lost. At index values < 1 leaching losses are progressively lower with the lowest rainfall sites having lost 10 to 20% of the original base cations and Si and none of the Al. At all sites, the secondary clay mineral assemblage is dominated by metastable non-crystalline weathering products; humid soil profiles contain very few crystalline minerals whereas the arid profiles contain halloysite, hematite, gibbsite and small amounts of carbonates. Soil surface exchange properties are strongly influenced by climatic conditions and show a dramatic threshold in base cation saturation, pH, and effective cation exchange capacity (ECEC) at leaching index of 1. Soils with leaching index of < 1 have high base cation saturation, neutral pH and high ECEC, whereas those that are > 1 have lost their buffering capacity leading to low pH and low ECEC.

The non-linear decline in ECEC is irreversible under natural conditions; base cation depleted soils will remain so even if the climate shifts to drier conditions. In contrast a climate shift to wetter conditions can drastically modify surface chemical properties existing in the drier soils as weathering depletes primary minerals, elements are lost to leaching and surface chemistry is modified. Loss of buffering capacity through leaching leads to a transfer of biological acidity deeper into the vadose zone or into the aquatic system. The details of this transfer depend on present and past climate, and the age and erosional stability of landscapes.

## A diffusion model for calculating magma residence times using trace element zoning in plagioclase

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Lifetimes of magma chambers and time scales of igneous differentiation are important parameters in understanding the thermal and chemical evolution of the crust. Further, these are key concerns in volcanic hazard management and mitigation. Isotopic methods have been used to assess these parameters but short time scales on the order of a few thousand years to a few days are not ideally suited for the resolution of isotopic methods. A tool that is complementary to these techniques is kinetic modelling. Modelling the differing degrees of modification of compositional zoning of various elements in one crystal provides a unique tool to constrain time scales of processes in magma reservoirs, and in this regard, plagioclase is perhaps the most important group of mineral, i.e., it is widespread, it crystallizes practically over the entire temperature and compositional range of igneous differentiation and, it shows pronounced compositional zoning. However, the compositional variability and large range of diffusion rates also imply that special care is required in kinetic modelling using plagioclase compositions. In particular, an adequate kinetic model needs to consider the following: (i) under any given ambient condition, the chemical potential of trace elements (e.g. Mg) in plagioclase crystals of different anorthite contents are very different, (ii) the diffusion rates of trace elements in plagioclase depend on the anorthite content, (iii) the choice of proper boundary conditions, that closely reflect natural conditions, and (iv) possible 2-D diffusion effects in elongate prismatic grains, depending on grain size. We have developed a set of generalized equations for kinetic modelling that incorporates these considerations using the specific example of Mg in plagioclase. We show that contrary to intuition, diffusive fluxes of trace elements may be strongly coupled to major element concentration gradients and ignoring such coupling can lead to incorrect estimates of time scales. We illustrate the application of the model to plagioclase crystals from gabbroic xenoliths found within Holocene dacitic lava flows of Volcán San Pedro (Chilean Andes, 36 °S). The inferred time scales of metasomatism of the xenoliths on the order of a hundred years serve to illustrate how this approach provides a window into time scales inaccessible by isotopic or other methods.