

## Evolution of micro-porosity during weathering of basalt

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In hydrology and geochemistry, porosity is arguably the most important physical property of a rock because it provides pathways for water flow or infiltration. Chemical reactions induce changes in porosity that change the rates of fluid transport and thus potentially the overall rates of reaction. We investigated porosity evolution during weathering rind formation on basalt clasts. Micro-computed tomography was used to evaluate changes in porosity with weathering down to pore sizes of ~4  $\mu\text{m}$  and reactive transport models were developed that demonstrate the importance of porosity evolution in this system. Small-angle (SANS) and ultra small-angle neutron scattering (USANS) data extend our investigation of porosity evolution during weathering down to nanometer size pores.

SANS and USANS data were collected across the weathering interface of the basalt clasts at the Center for Neutron Research (NIST). The scattering intensity increases by one order of magnitude from the unweathered to weathered samples. Bulk chemical data from electron microprobe analyses and hydrogen concentrations determined using prompt-gamma neutron activation analysis were used to evaluate changes in chemical composition and thus scattering length density with weathering.

To investigate pore distribution we examine scattering curves for each of the samples where scattering intensity is plotted as a function of scattering angle ( $q$ ) on a log-log plot. The fractal nature of these rocks is assessed using the slope of data plotted on the scattering curves. We observe that the fractal nature of the pore system in rocks previously observed is maintained during weathering. A constant slope of -3.3 is observed over the entire range studied (approx. 1nm -5 $\mu\text{m}$ ) in the unweathered basalt and we use a surface fractal model to interpret these results. Scattering data from the weathered basalt show a break in slope. A slope of -3.3 is observed in the high  $q$  region but a slope of -2.6 is observed in the low  $q$  region. This indicates the presence of surface fractality at nanometer length scales and mass fractality in the micron range for weathered basalt.

## Size-driven structural and thermodynamic complexity in Iron oxides

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Iron oxides occur ubiquitously in environmental, geological, planetary, and technological settings. They exist in a rich variety of structures and hydration states. They are commonly fine grained (nanophase) and poorly crystalline. This review summarizes very recently measured thermodynamic data for their formation and surface energies. These data are essential to calculate the thermodynamic stability fields of the various iron oxide and oxyhydroxide phases and understand their occurrence in natural and anthropogenic environments. The competition between surface enthalpy and the energetics of phase transformation leads to the general conclusion that polymorphs metastable as micrometer-sized or larger crystals can often be thermodynamically stabilized at the nanoscale. Such size-driven crossovers in stability help explain patterns of occurrence of different iron oxides in nature.