

## 4.5.P24

### A Ge/Si, $^{234}\text{U}/^{238}\text{U}$ , and $^{87}\text{Sr}/^{86}\text{Sr}$ investigation of weathering reactions and flowpaths in a tropical granitoid watershed

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We employ here a multi-tracer approach to understanding granitoid weathering in a tropical environment. The study site is the Rio Icaos watershed in the Luquillo Mountains, a USGS Water, Energy, and Biogeochemical Budgets research watershed in Puerto Rico. In this study we analyze Ge/Si ratios,  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, and  $^{234}\text{U}/^{238}\text{U}$  activity ratios in bedrock primary minerals, secondary minerals, soil porewaters, and streamwaters with the aim of better understanding the mineral transformations, water flow-paths, and chemical changes along those flow-paths through varying hydrological regimes.

Germanium follows silicon through its biogeochemical cycle, but Ge/Si ratios are fractionated by several processes in the weathering environment, potentially providing insight on silicate weathering processes and silica cycling. At the base of the profile soil porewaters have a Ge/Si ratio of 0.3  $\mu\text{mol}/\text{mol}$ , reflecting fractionation during the incongruent weathering of plagioclase (3.1  $\mu\text{mol}/\text{mol}$ ) to kaolinite (5.9  $\mu\text{mol}/\text{mol}$ ) at the soil/rock interface. At intermediate depths soil porewaters have Ge/Si ratios between 2 and 3  $\mu\text{mol}/\text{mol}$ . This is interpreted as reflecting a mixture of both biotite (6.1  $\mu\text{mol}/\text{mol}$ ) and quartz (0.6  $\mu\text{mol}/\text{mol}$ ) weathering reactions taking place at these depths.

Streamwater samples at baseflow have Ge/Si ratios near 0.5  $\mu\text{mol}/\text{mol}$ , indicating that the Si flux under these conditions is dominated by weathering of plagioclase at the base of the soil profile. During high discharge events, the Ge/Si ratio of streamwaters rises to values around 2.3  $\mu\text{mol}/\text{mol}$ , reflecting the value of the intermediate-depth porewaters and suggesting that biotite and quartz-derived Si is flushed from the profile during these events.

$^{234}\text{U}/^{238}\text{U}$  activity ratios in soil, saprolite, and soil porewaters have also been analyzed to further elucidate the weathering history. Preliminary data show soil  $^{234}\text{U}/^{238}\text{U}$  activity ratios close to 1.00 at the top of the profile. Saprolite from the base of the profile has  $^{234}\text{U}/^{238}\text{U}$  activity ratios between 1.10 and 1.15. Uncertainties on this data are 0.005 (2  $\sigma$ ). U concentrations in soil porewaters are highest at the top of the profile (~40 ppt) and decrease with depth. Initial sampling of streamwaters show extremely low U concentrations (~1 ppt), suggesting removal earlier in the flowpath.

## 4.5.P25

### Weathering products trapped in pure platform limestones: Geochemical picture of magnetic susceptibility and gamma-ray variations

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The magnetic susceptibility and gamma-ray spectrometric ( $\chi$  and  $\gamma$ ) section in open-sea platform carbonates (M. Devonian, Givetian; Moravian Karst) was correlated with carbonate sections from other parts of the world. The patterns in the logs are nearly identical and must widely correspond to climate evolution. The EMP and TEM investigations suggest that colloidal forms of trapped material prevailed. Analyses concern 45 representative nodes of the section (ICP-MS, INAA, etc.).

For assessment of REE sources, hypothetical "trapping coefficients" were derived from mean recent REE fluxes to the ocean [1] by means of fitting of "trapping patterns (TPs)" to the observed REE-variation field. The optimum coefficients for separate REE numerically correspond to  $\sim 1/\sqrt{\tau}$  [ $\tau$  = mean seawater residence time]. Ce required further correction (~0.3). The TPs represent four "ideal components" from seawater solutes, atmospheric, riverine and remineralization sources.

Comparison of these TPs with REE distributions revealed strong correlations with atmospheric source (AS) and seawater solutes (SS), alternatively, whereas the riverine and remineralization sources have small or no influence. If ordered and plotted, the AS vs. SS curves are mirror-shaped, both (0.9; -0.3). "Relative AS factor" (AS minus SS): Th/U (INAA) correlates well (0.5), as well as total  $\gamma$  equivalents (0.55) and  $\chi$  (0.47) [ $\gamma$  with  $\chi \sim 0.7$ ]; Al, Cs, K, Fe, Cu, Th, Rb, Pb, As, U, Y and Zn correlations decrease from 0.6 to 0.4, respectively, Ba, Tl, Cr, Co correlate slightly and Be, Mn, Sr, Cd, Mg and V yielded about zero values. "Total organic carbon": Surprisingly, Cd yielded zero and V  $\sim -1.7$ ; Th, As and Fe typically  $\sim 0.2$  to 0.3, but U  $> 0.4$ . The  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values show slight positive correlations. "Total mass of trapped compounds": The  $\delta^{13}\text{C}$  yielded zero value, but  $\delta^{18}\text{O}$  correlates significantly (0.45).

Main conclusions: The major part of weathering products trapped in the Givetian limestones of Moravian Karst originated from atmospheric sources and seawater solutes. The relevant elements (Fe, Th, U, etc.) are approx. close to the place of trapping but the partial early diagenetic geochemical pathways are extremely variable. {Project: A3013209; ICP-MS L. Strnad, INAA J. Frána}.

#### References

- [1] Nozaki Y. (2001) Rare earth elements and their isotopes. Encyclopedia of Ocean Sciences, AP London, 2354-2366.