

## $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$ chronometry of weathering rinds: Rates of weathering and isotopic record of soil waters

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The interest of  $^{238}\text{U}$ - $^{234}\text{U}$ - $^{230}\text{Th}$  chronometry for constraining time scale of weathering processes is now well established [1]. Here we propose to assess the formation rate of weathering rinds developed on fresh rocks by analyzing U-series nuclides in a weathering rind on a basaltic clast from a 125ka old Costa Rican alluvial terrace [2]. Subsamples were collected along two transects straddling the core-rind boundary by drilling cores into one section of the clast. Variations of major and trace element concentrations along the two transects point out (a) intense loss of alkaline and alkaline-earth elements during the basaltic clast weathering, (b) conservative behaviour of elements such as Zr, Hf and Th, and (c) external input of U into the rind material from soil waters without any evidence of U loss during basalt weathering. In addition, variations in concentrations along the transects show that the main fractionation processes associated with the weathering of the basaltic clast occur at the basalt-rind interface whereas the weathering rind once formed evolves without further secondary chemical modification. These observations permit the development of a closed system evolution model for interpreting  $^{230}\text{Th}$ - $^{238}\text{U}$  disequilibria in the analyzed transect. Model calculations yield to a weathering rate of  $0.5 \pm 0.2$  mm/ka consistent with geological and isotopic evidence constraining the depositional ages for the terraces [2]. The increases of U and Sr isotopic ratios along the analysed transect are best explained by temporal variation of U and Sr isotope ratios of the soil waters brought into the rind. This work highlights how fine U-Th chronological study of weathering rinds can (1) constrain the formation rates of weathering systems, and (2) record the time variation of isotopic composition of weathering fluids.

[1] Chabaux F., Riotte J. & Dequincey O. (2003) *Rev Mineral. Geochem.* **52**, 533-576. [2] Sak *et al.* (2004) *Geochim. Cosmochim. Acta* **68**, 1453-1472.

## $\text{SO}_2$ self-shielding during UV photolysis

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We are investigating the fractionation of sulfur and oxygen isotopes ( $\delta^{33}\text{S}$ ,  $\delta^{34}\text{S}$ ,  $\delta^{36}\text{S}$ ,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ ) caused by photodissociation of gaseous  $\text{SO}_2$ . Isotopic self-shielding of  $\text{SO}_2$ , occurring in Cell #2 (Figure 1), during photodissociation may be a possible mechanism for anomalous sulfur isotope fractionation that occurred in the Earth's early atmosphere. We should see primary isotope effects in Cell #1 as Farquhar *et al.* did in their experiments by using a single gas cell [1].

### Experiment

Using two separate gas cells (Figure 1) will enable us to see the different isotopic compositions that arise from isotopic self-shielding. The gas cells are filled with commercial  $\text{SO}_2$  at pressures of 0.02-0.10 atm, comparable to molecular cloud and volcanic emission column densities, then irradiated for 2-7 days with a deuterium lamp. The use of a broadband source, in contrast to line sources, during isotopic photodissociation gives a closer analog to solar UV radiation. The residual gaseous  $\text{SO}_2$  is collected and converted to  $\text{SF}_6$  and  $\text{O}_2$  via reduction of  $\text{SO}_2$  to  $\text{Ni}_3\text{S}_2$  and  $\text{NiO}$  and subsequent fluorination.

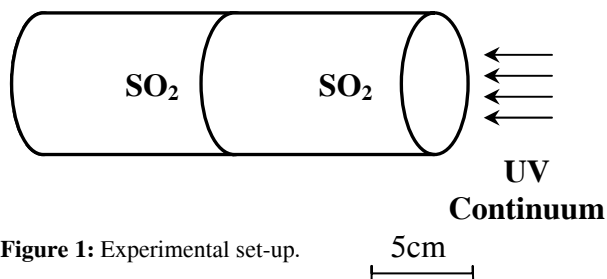


Figure 1: Experimental set-up.

### Results

I will be presenting  $\delta^{33}\text{S}$ ,  $\delta^{34}\text{S}$ ,  $\delta^{36}\text{S}$ ,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  data from the photolysis experiments. From the experimental set-up described above, anomalous fractionations seen in Cell #2 arise from self-shielding and not selective isotopic photodissociation.

[1] Farquhar J., Savarino J., Airieau S. & Thiemens M.H. (2001) *J. Geophys. Res.* **106**, 32829-32839.