

## Photosensitized aging of succinic acid aerosol

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Ultraviolet or visible light absorbing organic constituents of atmospheric aerosols may act as photosensitizers for a number of processes. Photosensitizers may be primary organics from combustion sources or be formed in situ during oxidation in the atmosphere. The significance of photosensitized processes has been demonstrated by showing enhanced uptake of atmospheric oxidants to organic films or aerosol particles.

A solution containing ammonium sulfate, succinic acid and benzophenone or Benzoyl Benzoic Acid (BBA) was nebulized. The aerosol flow passed through a photoreactor with about 9 min. residence time, which was coupled to a High Resolution Time of Flight Aerosol Mass Spectrometer (AMS) and two Scanning Mobility Particle Sizer (SMPS).

The AMS signal at mass to charge ratio ( $m/z$ ) 44 typically comes from organic acids. During the photooxidation experiments we observed changes to the ratio of  $m/z$  44 to 43 and a loss of organic aerosol mass, while the flow tube was irradiated. We also performed laser photolysis experiments of benzophenone triplet quenching kinetics in solution, confirming that succinic acid reacts with the excited benzophenone triplet.

## Sulfur isotope evidence for microbial sulfate reduction in altered oceanic basalts

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The subsurface biosphere in the basaltic oceanic crust is potentially of major importance in affecting chemical exchange between the ocean and lithosphere. Alteration of the oceanic crust commonly yields secondary pyrite that are depleted in <sup>34</sup>S relative to igneous sulfides. Although these <sup>34</sup>S depleted sulfur isotope ratios may point to signatures of biological fractionation, previous interpretations of sulfur isotope fractionation in altered volcanic rocks have relied on abiotic fractionation processes between intermediate sulfur species formed during basalt alteration. In a recent study, we reported multiple-S isotope (<sup>32</sup>S, <sup>33</sup>S, <sup>34</sup>S) compositions of 165 Ma-old altered basalts at ODP Site 801 in the western Pacific and provided evidence for microbial sulfate reduction within the volcanic oceanic crust. The average  $\delta^{34}\text{S}$  value of -6.8 ‰ for the bulk altered oceanic crust samples further demonstrated that S-based metabolic activity of subsurface life in oceanic basalt is widespread, and can affect the global S budget at the crust-seawater interface.

Here, we report  $\delta^{34}\text{S}$  analysis of secondary pyrite in younger altered oceanic basalt (<3.5Ma) using ion-microprobe (*Cameca 1280*) and LA-MC-ICPMS (*New Wave UP213* laser coupled to *ThermoElectron Neptune*). In-situ  $\delta^{34}\text{S}$  analysis of secondary pyrite in basement rocks from ODP Hole U1301B, located east of the Juan de Fuca Ridge, show a very large range of  $\delta^{34}\text{S}$  values, from 1‰ down to -70‰, although most values are restricted between 0 to -10‰. Similar range has also been found in altered basalts from several DSDP Holes near the Galapagos Rift, with pyrite  $\delta^{34}\text{S}$  values ranging from 10‰ down to -58‰. Such <sup>34</sup>S depletion in pyrite is consistent with previous S-isotope studies of deep-sea sediments showing extreme S-isotope fractionation ( $\alpha \sim 1.077$ ) during single-step microbial sulfate reduction. These new results further support the importance of microbial sulfate reduction during oceanic crust alteration in hydrothermally-active ridge flank settings, but also prompt further work to identify and culture these widespread deep-endolithic sulfate reducing microorganisms.