

Investigating the effects of hydrologic fluctuations on organic sulfur speciation in boreal peatlands

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Sulfur has a complex biogeochemical cycle in peatlands due to its chemical reactivity, wide range of oxidation states, and importance to bacterial metabolism [1]. In sulfur-limited systems sulfate plays a synergistic role in the production of monomethylmercury (MeHg), the bioaccumulative form of mercury [2]. Therefore an understanding of how sulfate is incorporated into and released from peat soils may improve prediction of MeHg production within, and export from, peatlands. Climatic variability can cause large changes in oxidation-reduction potentials within peatlands by influencing the position of the water table. Wetlands are often considered to be sinks in the landscape for sulfate because sulfate inputs to saturated systems are readily consumed by sulfate-reducing bacteria. However, following droughts wetlands have been found to be significant sources of sulfate to downstream aquatic ecosystems [3].

This research compared sulfur speciation in peat from a boreal peatland during and after an historic drought in northern Minnesota. Greater than 95% of sulfur in each peat sample was in an organic form making traditional, wet-chemical sulfur fractionation methods uninformative about a large portion of the total sulfur pool. As an alternative, sulfur speciation in peat was measured at the micron scale by X-ray fluorescence mapping at six incident energies spanning the sulfur 1s absorption edge. Composite maps were fit with reference spectra. X-ray absorption spectroscopy is being used to verify sulfur speciation maps. At naturally occurring sulfur levels, we are able to obtain high quality data. Our goal is to develop a data analysis protocol providing quantitative, spatially resolved sulfur speciation.

[1] Urban *et al.* (1989) *Biogeochem* **7**, 81-109. [2] Gilmour *et al.* (1992) *Environ. Sci. Technol.* **26**, 2281-2287. [3] Eimers *et al.* (2007) *Environ. Monit. Assess.* **127**, 399-407.

Magma degassing timescales from vesicle size distribution and bubble composition heterogeneity in MORB glasses

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Vesicle size distributions (VSD), the number of bubbles of a given size plotted against the size interval are classically used to model the growth rate of vesicles by assuming continuous vesicle nucleation and growth (as for crystal size distributions [1]). However, VSD data in MORB samples are sparse, due to the difficulty in making representative measurements in low vesicle density samples. Here, we use direct 3D images in order to calculate vesicle sizes and their distributions.

The images were obtained by X-ray microtomography (resolution of 5µm or less) of small pieces (some mm³) of glassy pillow lava rims sampled along the mid-Atlantic ridge and the East Pacific Rise. The observed trends allow us to discuss several key issues such as the duration of the vesicle-magma segregation and the link between magma initial volatile content and the vesicle growth rate. Atlantic MORBs and Icelandic glass samples show VSDs that have a distinct kink in the VSD at 100 – 200 µm micron vesicles, showing that there are (at least) two different episodes of vesicle generation: smaller vesicles result from decompression during the final stages of eruption while larger bubbles likely represent magma chamber processes. Vesicle-poor samples such as those from the East Pacific Rise tend to only have a single episode of vesicle generation.

In order to constrain these degassing processes, the trapped glass vesicles were subsequently opened by laser ablation and their volatile contents (He, Ar, CO₂) analysed vesicle by vesicle. The different vesicles preserved in the final glass nucleated at different stages in the magma history, and thus preserve more or less degassed stages of the magmatic volatile evolution. In some samples, the analysed vesicles have homogeneous compositions, while other samples show systematic inter bubble variations consistent with a solubility-controlled Rayleigh distillation. There is no evidence for kinetic fractionation of volatiles in the majority of our samples. These key observations allow the degassing mechanisms to be modeled, as well as the timescales involved in the preservation of such millimetric heterogeneities.

[1] Marsh, B. D. (1988) *Contrib. to Mineralogy and Petrology* **99**, 277-291