Polyphosphates in volcanic environments: Revisiting Yamagata's 1991 experiment. D. A. Lindsay¹, N. L. La Cruz¹, K. J. Rodzinyak¹, J. M. Sampson¹ and M. A. Pasek*, ¹School of Geosciences, University of South Florida, Tampa, Florida dlindsay1@usf.edu

Introduction: The formation of phosphorylated biomolecules may require reactive phosphates such as polyphosphates. An option often mentioned but not always explored for the origin of polyphosphate energy-currency is the volcanic environment. Yamagata's 1991 experiments and analyses of natural volcanic fumarole exhalations [1] demonstrated that polyphosphates are synthesized by volcanoes and that these may have had an origin from P_4O_{10} gas. Further work has shown that glasses formed by melting rock can indeed polymerize phosphates [2] and these phosphates may have been relevant to the development of life [3].

Yamagata's 1991 experiments had produced several unidentified P species using the methods available at the time. As a result, the pathway leading to phosphate activation was unclear.



Figure 1. Replication of Yamagata et. al.'s (1991) experiment.

Results: We attempted to replicate Yamagata's 1991 experiment using the apparatus picture as Figure 1. The resulting aqueous solutions were analyzed by ³¹P NMR, extracts of the rock were done using EDTA and also analyzed by ³¹P NMR. Finally, HPLC-ICP-MS analyses of the extracts will be performed to investigate trace P species.

Aqueous Chemistry. First runs did not show NMR-detectable polyphosphate resulting from volatilization of P from apatite-basalt rock mixtures. HPLC-ICP-MS results may identify the trace species and these results will be shown.

Rock Chemistry. Apatite did polymerize to form pyrophosphate $(P_2O_7^{4-})$ at about 10% yield when the rock was extracted by the EDTA solution, and the extract analyzed by ^{31}P NMR. These results support some polymerization of phosphate in volcanic environments, but the ubiquity of polyphosphate production and volatilization may not have been widespread.

References:

[1] Yamagata Y. et. al. (1991) *Nature*, 352, 516-9. [2] Cody G.D. et al. (2001) *Geochimica et Cosmochimica*, 65, 2395-2411. [3] Holm N.G (2014) *Geochemical Transactions*, 15:8.