Insight into the global phosphorus cycle from apatite in ash from the 2018 Kilauea eruptions

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Volcanic ash eruptions are recognised as an important source of phosporus (P) for the global P cycle, delivering P to soils and the ocean. At volcanoes, P is hosted in *primary phases* such as melt-precipitated apatite, glass and rarely other phases (e.g., sanidine with 5 wt% P at Tolbachik volcano [1]). Data for P in volcanic gases is scarce and suggests concentrations on the order of ~0.1-10's ppm [2-3]. However, some condensates record higher P contents, as do some ash samples that include fragments formed by gas-solid (high T contact metamorphic) reactions in the conduit [4]. Interestingly, at atmospheric pressures and high temperatures P is readily released from P_2O_5 [i.e. it is 'volatile'; 5], but P is reasonably soluble in basaltic melts [6]. Here, we consider the role of P-bearing volcanic gas in condensation and gas/fluid-solid reactions.

We observed apatite crystals attached to sulfate-silica rinds and decorating the interior walls of glass vesicles in ash from the 2018 Kilauea eruptions. These crystals appear to have formed after the primary phases as a result of gas-rich fluid reactions with solid surfaces (rinds or glass). We propose that surface Ca has reacted with P in the gas phase to form these crystals. To test this hypothesis we modelled the formation of apatite using a Gibbs Free Energy minimization approach from a starting composition that included relevant gas and solid phases. The modelling shows apatite is effectively produced from reactions between P-bearing gases and solids. These results indicate that sequestration of P in condensates or products of gas-solid reactions needs to be included in assessing the global P cycle and primary magmatic fluids may have more P than volcanic gases.

References: [1] Shchipalkina et al. 2019 *Phys Chem Minerals* 47, 1. [2] Zelenski et al. 2014 *J Volc Geotherm Res* 285, 136-149 [3] Zelenski et al. 2013 *Chem Geol* 357, 95-116 [4] Obenholzner et al. 2003 in *Volcanic Degassing*, Oppenheimer et al. (ed) Geol Soc Lon Sp Pub 213, 123-148. [5] Muan & Osborn, 1965. *Phase Equilibria Among Oxides in Steelmaking*. Addison-Wesley. [6] Toplis et al. 1994 *Geochim Cosmochim Acta* 58, 797-810.