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Volcanic controls on ash iron solubility: thermodynamic modeling of gas-ash interaction in the hot core of volcanic plumes

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Recently it has been shown that volcanic ash can act as a fertilizer for phytoplankton bloom by injecting bio-available iron into the surface ocean. However, it is also well known that iron in volcanic ash at least at its generation point (i.e. magma) is mostly in insoluble form, i.e. not bio-available. Although different volcanic and atmospheric processes are assumed to contribute to the transformation of insoluble iron into soluble salts, the causes of iron mobilization in volcanic ash are poorly constrained. Here we explore the volcanic control on the mobilization of iron in volcanic ash in the hot core of volcanic plumes ($T>600^\circ C$) based on thermodynamic equilibrium considerations. A conceptual box model is considered for the hot core in which 1000˚C magmatic gas, ash and 25˚C ambient air are mixed. The initial composition of volcanic gas and ash are parameterized based on three types of tectonic settings (convergent plate, divergent plate, and hot spot) and basaltic to rhyolitic magmas. The effect of the initial oxidation state is also considered by changing the oxygen fugacity.

First, magmatic oxides (i.e. SiO_2, FeO, MgO etc) are titrated into the magmatic gas at constant temperature and fugacity in order to generate the initial iron carrying minerals. Since the alteration of ash composition is mainly diffusion controlled, we assume that inside the hot core of the volcanic plume the Fe speciation is only affected at or near to the ash surface. Results show that the main initial iron carrying minerals are usually ilmenite and fayalite with some addition of pyhrrotite at reduced conditions in divergent plate and hot spot settings.

Then the 1000˚C magmatic gas-ash mixture is mixed with the 25˚C air (N_2 79%, O_2 21%) until a temperature of 600˚C is reached. Results demonstrate that the hot core functions as an oxidizing reactor for the ash surface transforming the whole Fe^{2+} minerals to Fe^{3+} species while being cooled to 600˚C. However, in reduced scenarios in divergent plate and hot spot volcanoes the iron remains in Fe^{2+} form (i.e. fayalite, pyhrrotite). Under such conditions bio-available iron production appears more likely because iron is in a more soluble oxidation state (i.e. Fe^{2+}). The role of the “ash iron” in sulfur and halide scavenging is negligible but alkali metals and also Ca can scavenge up to 37% of the erupted sulfur.

Albeit the hot core does not produce any bio-available iron directly (e.g. chloride, fluoride, sulfate), the oxidation state of the iron at or in the vicinity of the surface of volcanic ash can significantly control mobilization processes in the colder parts of the volcanic plume. Divergent plate and hot spot settings seem to be more favorable for the iron fertilization but the atmospheric controls need to be studied too.