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A model for the kinetics of high-temperature reactions between polydisperse volcanic ash and SO_2 gas

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Abstract

Rapid calcium diffusion occurs in rhyolitic volcanic ash particles exposed to hot SO_2 atmospheres. Such chemical transport is important immediately following fragmentation, during proximal transport in eruption plumes and during percolative gas transport through a permeable volcanic edifice. Here we analyze published results of experiments designed to constrain the kinetics of this process. The experiments involve crushed rhyolitic glass particles tumbled in SO_2-bearing atmospheres at a wide range of relevant temperatures. We find that the particle-gas reaction is fed by calcium diffusion from the bulk to the particle surfaces where calcium-sulfate crystals grow. The calcium flux is accommodated by local iron oxidation state changes. This process results in time-dependent concentrations of surface calcium that are leachable in aqueous solutions. Those leachate concentrations represent a proxy for the diffusive flux of Ca^{2+} out of the particle to form the surface deposits. We formulate a mathematical framework to convolve the starting particle size distributions with the solution to Fickian one-dimensional diffusion to find a weighted polydisperse result. Using this framework, we minimize for a temperature-dependent calcium diffusivity and compare our results with published calcium diffusivity data. We demonstrate that calcium diffusivity in rhyolite can be decomposed into two regimes: (1) a high-temperature regime in which the diffusivity is given by the Eyring equation and (2) a low-temperature regime more relevant to rhyolite volcanism and these gas-ash reactions. As a further test of our model, we compare the output against spatially resolved data for the calcium gradients in the experimental particles. Our analysis suggests that surface reaction rates are rapid compared with the diffusion of calcium from the particle to the surface, such that full diffusion models must be solved to predict the rhyolite-SO_2 reaction. We conclude by suggesting how this framework could be used to make quantitative predictions of sulfur budgets and iron oxidation during rhyolitic eruptions.

Keywords: Scavenging, scrubbing, gas-ash reactions, volcanic eruption