

# The influence of crystallinity on high-temperature syn-eruptive gas uptake by volcanic ash

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## Abstract

Formation of surficial sulfate- and halide-bearing salts by syn-eruptive ash-gas interactions is known to occur during volcanic eruptions. For reactions between aluminosilicates and the gas SO<sub>2</sub>, at high temperature regimes ( $T \approx 600$  °C), the controlling mechanism is the outward chemical diffusion of alkalis and alkaline earth metals, predominantly Ca<sup>2+</sup>, that result in sulfate salt formation, mostly CaSO<sub>4</sub>, on glass surfaces. However, most of the experimental research has been conducted for SO<sub>2</sub>-reactions with pure crystal-free, aluminosilicate glass, to simplify the complexities of crystal-bearing systems. Here, we tested high temperature SO<sub>2</sub>-reactions using particles of a rhyolitic, crystal-bearing dome material from a 2013 eruption of Santiaguito volcano (Guatemala), by exposing 2 g of particles to 25 sccm of SO<sub>2</sub>; at 600–800 °C, for 5–60 min each time. We then compare our results with those of previous studies using pure glass particles, aiming to determine the influence of crystal fraction and type on the occurrence and efficiency of gas-ash reactions. We conducted chemical and microscopic analysis of pre- and post-treated samples and observed that diffusion of Ca<sup>2+</sup> is reduced in crystal-bearing samples relative to crystal-free samples at the same conditions. The rate of slow-down of the diffusion process appears to be dependent on the crystal volume fraction, providing a mechanism to account for this effect a priori. SEM images also showed that surface componentry strongly affects presence of CaSO<sub>4</sub>, as salts appear to be absent on specific surface spots corresponding to crystal phases. Our results illustrate the need for ash-gas reaction studies to further consider both the effect of bulk- and surface-componentry, in order to more accurately assess syn-eruptive gas uptake by ash.



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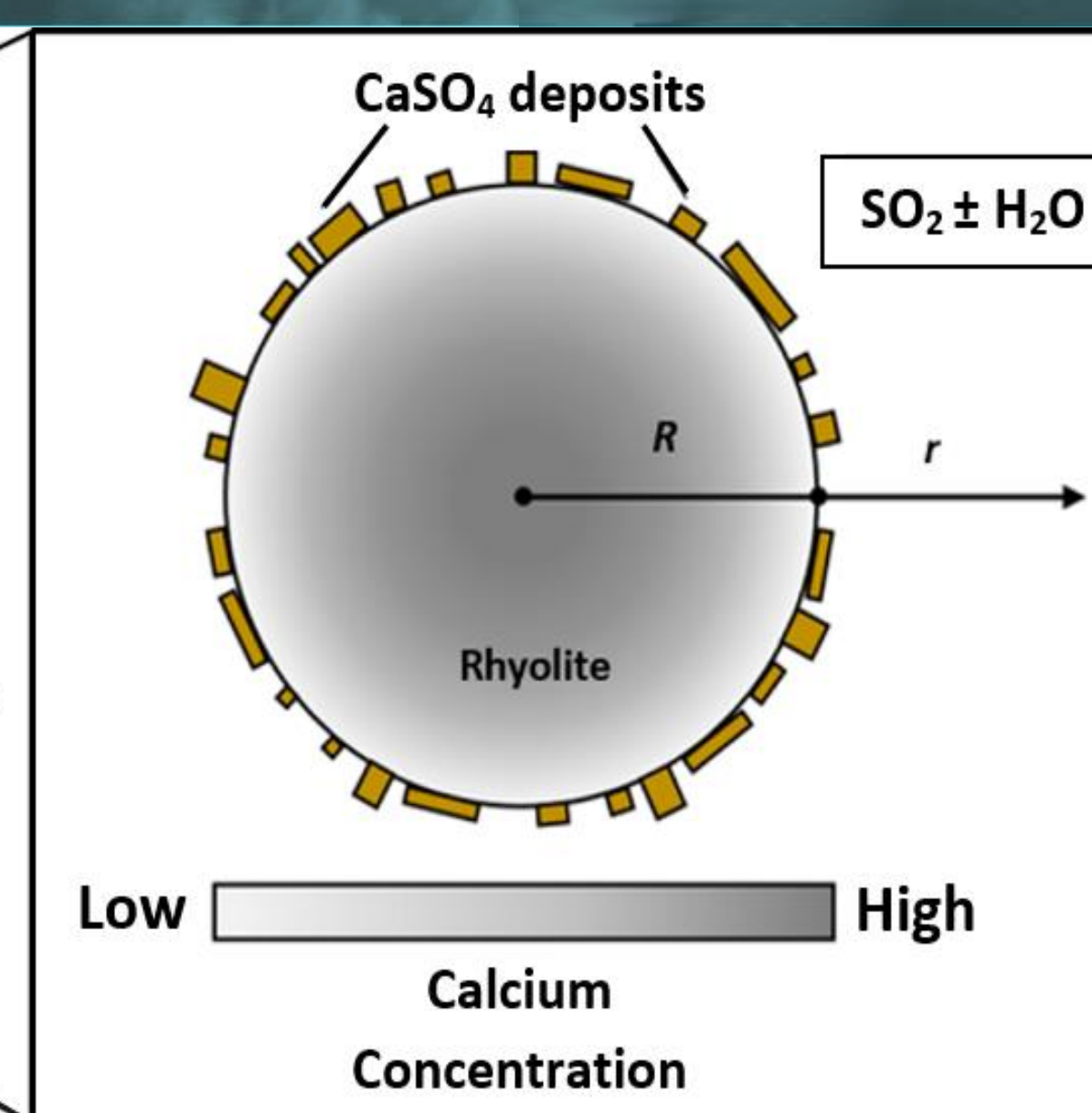
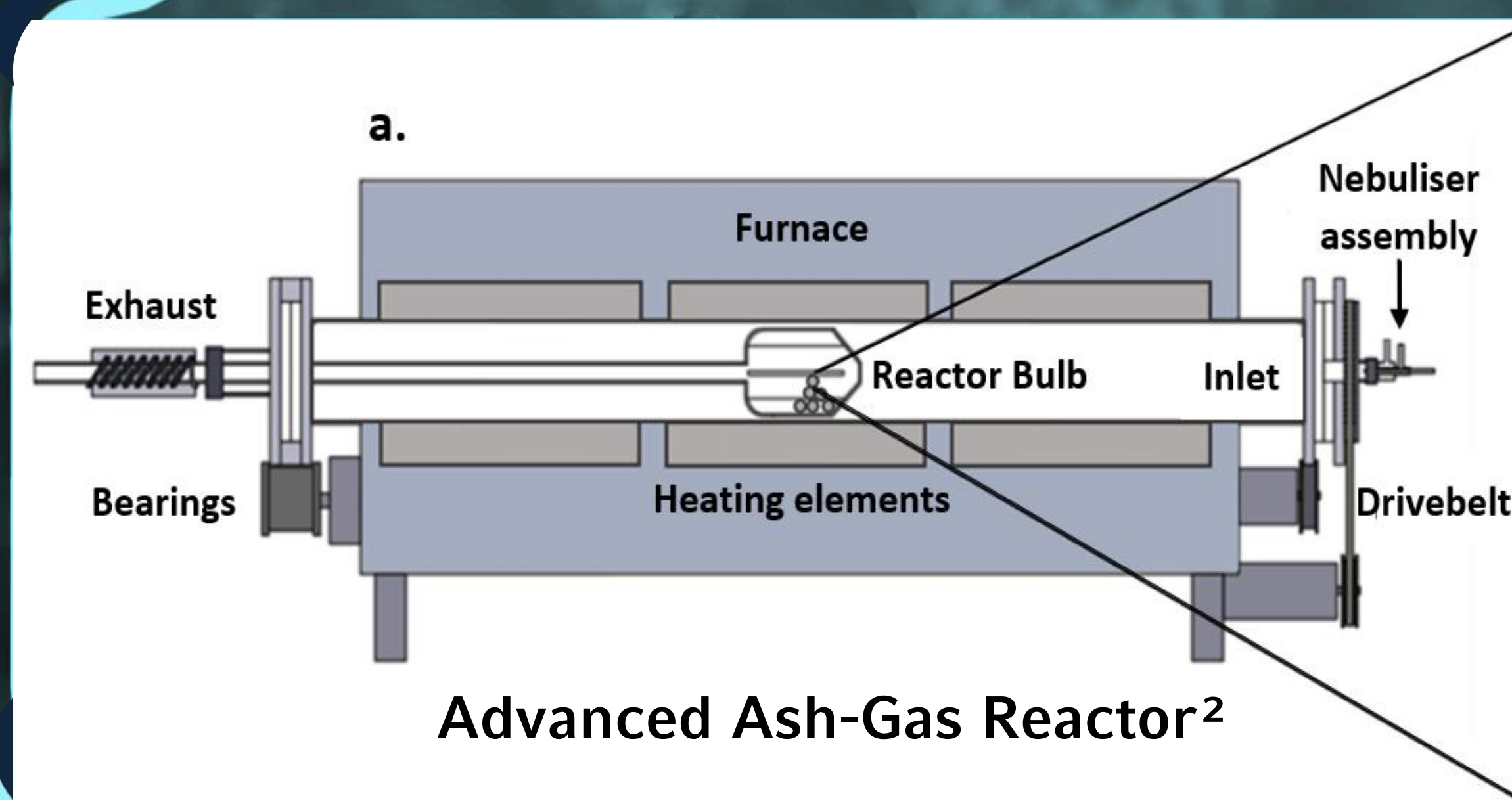
## 1 Introduction

The presence and nature of crystalline phases in pyroclasts (i.e., ash, bombs, lapilli), bear first-hand information about pre- and syn-eruptive magma conditions. For instance, crystal grain size pertains to cooling rate estimations during both magma storage in the chamber and magma ascent through the conduit. Changes in the eruptive style, magma degassing and magma fluid dynamics have also been linked to nucleation and growth of crystalline phases, yet, the influence of the crystallinity of pyroclasts on post-eruptive processes has been given little attention.

Here, we tested the reaction potential of various natural volcanic samples (crushed to fine-ash GSD) by exposing them to a SO<sub>2</sub>-Ar gas mixture (1 mol.% in 99 mol.%) at high temperatures, and characterized the samples prior and after gas treatments.

Using a natural volcanic bomb, we could test, for the first time, the role that a more complex ash-componentry performs in SO<sub>2</sub>-ash reactions, in particular that of the mineral phases in high temperature calcium diffusion that results in surficial salt formation, thus in sinking SO<sub>2</sub> emissions during explosive volcanic eruptions.

## 2 Methods: high temperature SO<sub>2</sub>-glass interactions



### Samples

- 1) **Santiaguito bomb** (2013 eruption)
- 2) **Tungurahua ash** (2014 eruption)

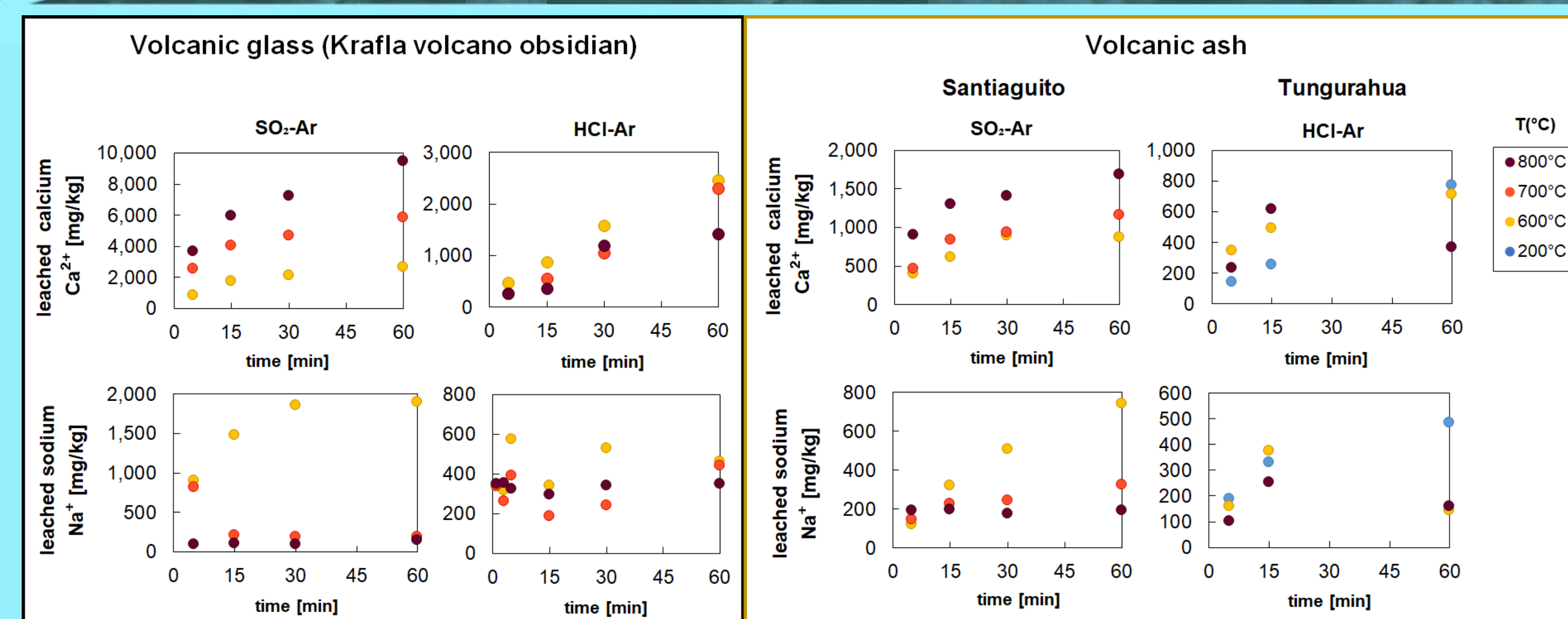
### Variables

Temperature (°C)	200, 600, 700, 800
Gas mixture	SO <sub>2</sub> -Ar and HCl-Ar (1 mol.% in 99 mol.%)
Exposure time (min.)	5, 15, 30, 60

### Characterization

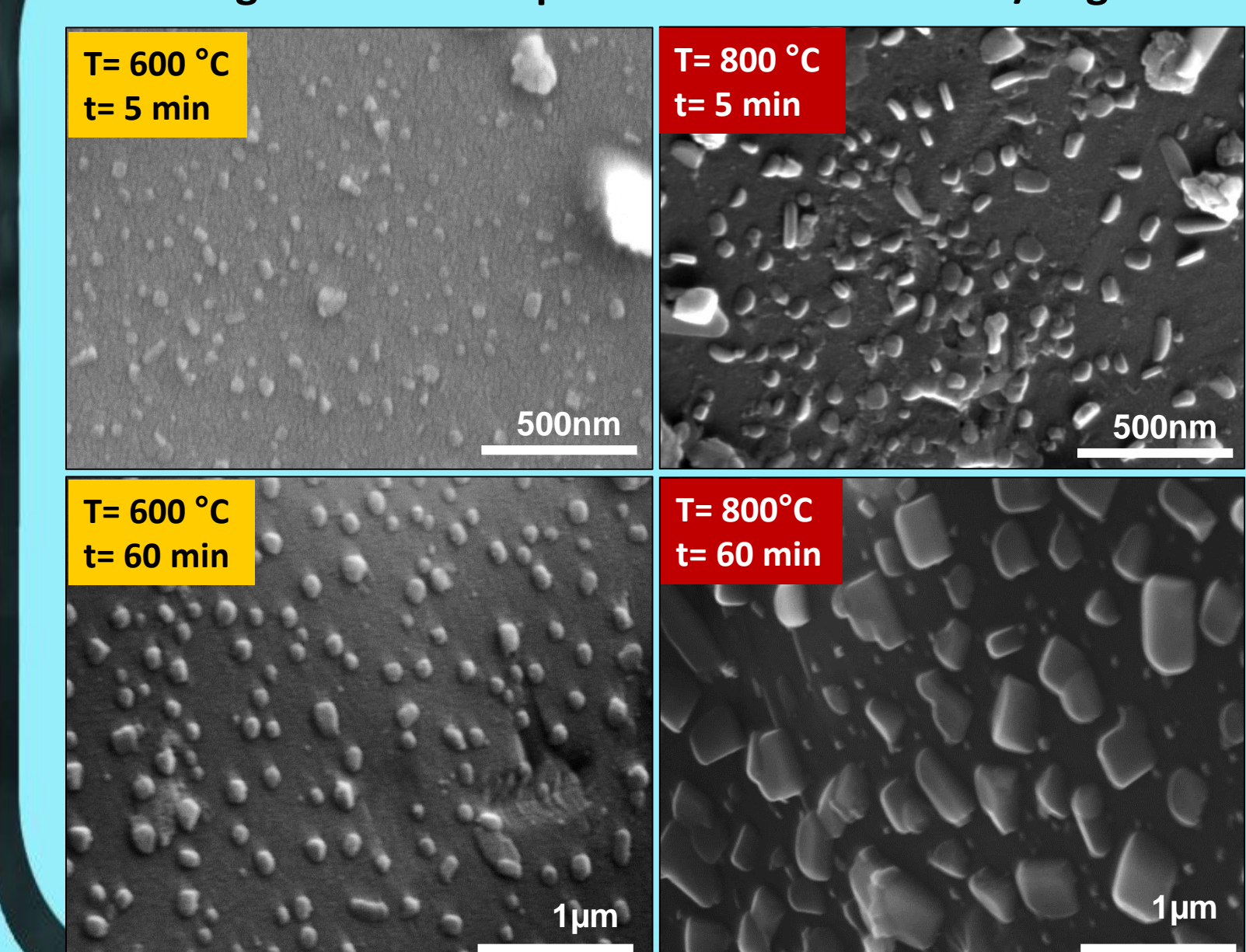
Leaching (1:250 ratio)	Microprobe analysis
IC analysis	Fe <sup>3+</sup> /Fe <sup>2+</sup> ratio determination
Particle size distribution	Potentiometric K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> titration
SEM, BET analysis	

## 3 Results: Leachate analysis



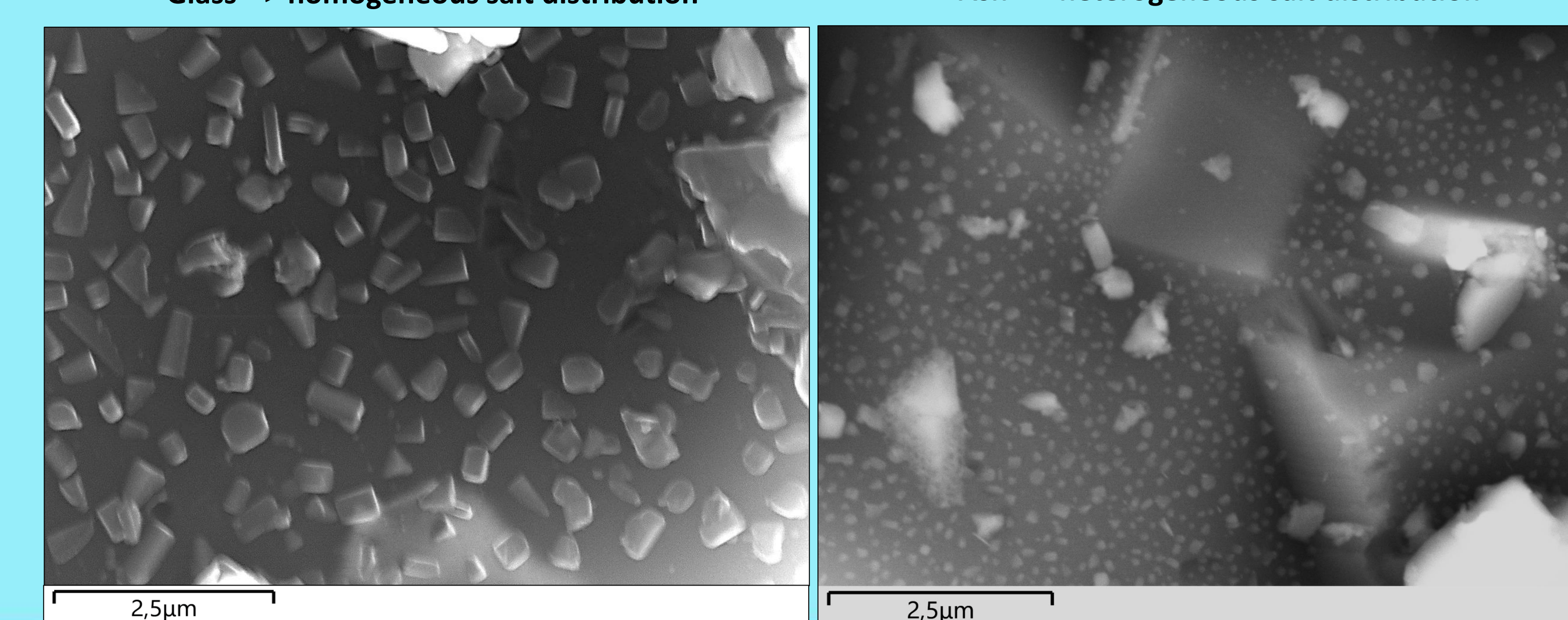
## 4 SEM-BSE images

Increasing time and temperature results in more/larger salts

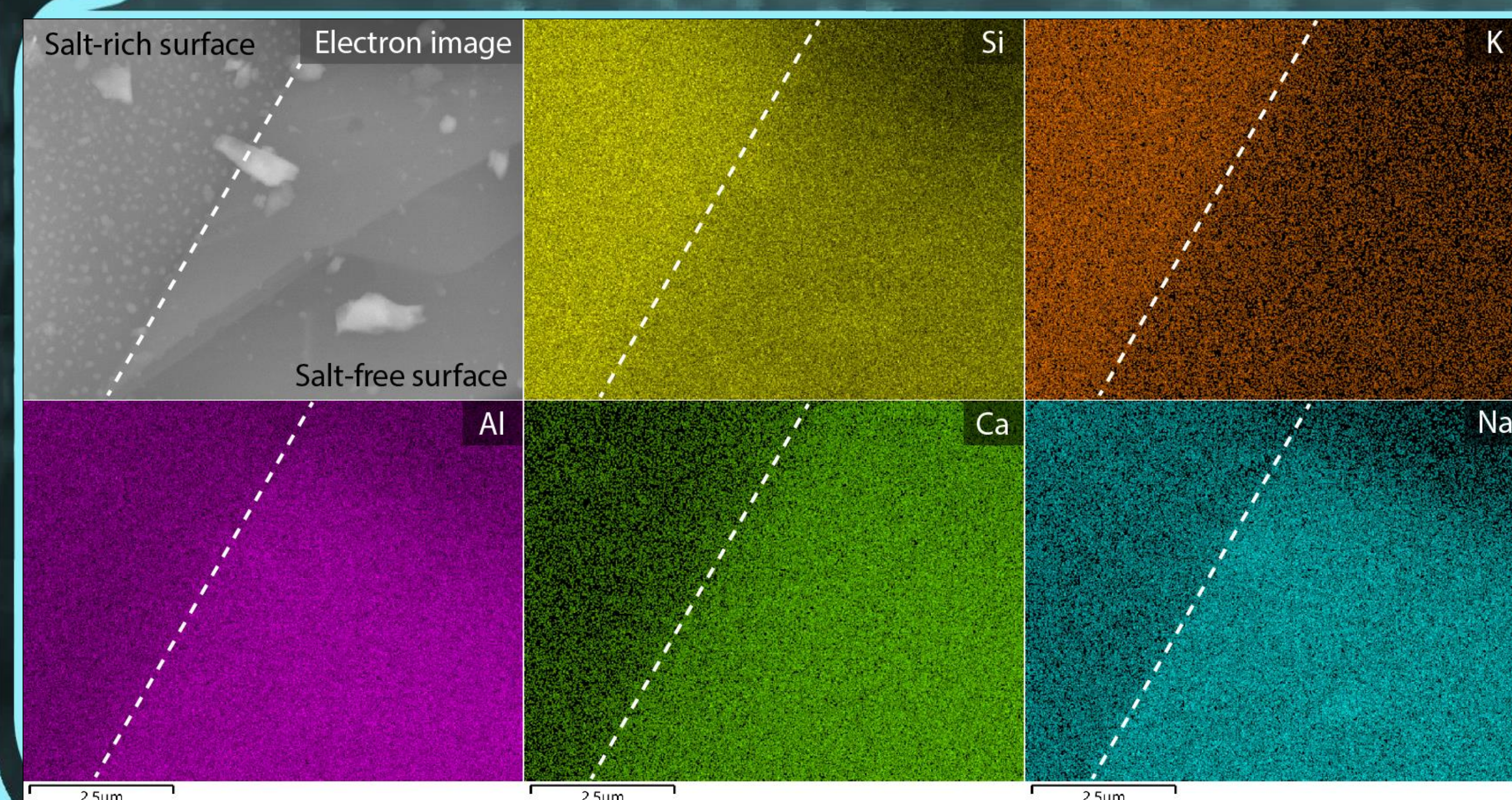


Glass → homogeneous salt distribution

Ash → heterogeneous salt distribution



## 5 SEM-EDS element mapping



Salts formed almost exclusively on Si- K-rich surfaces (amorphous glass), and were absent formed on Al-, Ca-, Na-rich surfaces (plagioclase, pyroxene)

## 6 Discussion

We here observed that, while, exposure temperature, reaction time and bulk composition strongly influence salt formation (nucleation-, growth-rates), the surface chemistry and componentry is a critical parameter that governs solid-gas reaction in the first place; chemisorption of gas molecules (HCl, SO<sub>2</sub>) is perhaps unlikely to occur on pre-existent surficial mineral phases as it is on glass network surfaces. This could be due to the strong crystalline bonding in mineral structures, which prevents atoms, to act as sorbents for gas molecules, thus depriving the surface from reactive adsorption sites. Absence of salts on crystal-rich surfaces, was observed for both HCl- and SO<sub>2</sub> experiments, which implies that regardless of the solid-gas chemisorption mechanism (different for SO<sub>2</sub> and HCl), gas uptake is less likely to occur on surficial mineral phases, thus nucleation, and growth of surficial salts, and high temperature gas scavenging will be less for crystall-rich ash, than for glassy ash.

## 7 Future work

Our final goal is enable the modelling of high temperature volcanic gas uptake for any given eruption. Knowing the mechanisms and variables controlling Calcium diffusion, we can modify the model of Suzuki et al. (2005) and predict the mass of gas uptaken.

This image is an example of a volcanic plume simulation, where the size particle distribution of ash is been tracked in 3 spatial coordinates, for an eruption of the magnitude of Pinatubo, 1991. Courtesy of Yujiro J. Suzuki.

