

Three-years variations of HCl concentration and chlorine isotopic compositions in fumarolic gases of La Soufrière de Guadeloupe (FWI) reveal key constraints on the scrubbing of HCl(g)

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For volcanoes with large hydrothermal systems, the composition of the magmatic gases are modified by interaction with hydrothermal systems during their ascent through the volcanic edifice. During their ascent from the hydrothermal aquifers to the surface, the altered volcanic gases are affected by partial dissolution of SO₂(g) and HCl(g) in aqueous water (i.e. scrubbing effect). Chlorine is highly soluble in waters and mainly considered as chemically non-reactive (unlike SO₂) and according to current knowledge large Cl isotope fractionations in hydrothermal systems containing HCl should mainly occur during evaporation and/or vapor condensation. Thus we anticipate that Cl concentrations [Cl] and isotopic compositions ($\delta^{37}\text{Cl}$) should inimitably trace interactions between gases and waters.

Here, we investigate for the first time the potential of $\delta^{37}\text{Cl}$ to constrain the evolution of gas-water interactions on a suite of samples from la Soufrière de Guadeloupe summit fumaroles. Under tropical climate, this volcano has developed a large hydrothermal system which is increasingly active since 1992.

Fumarolic gas condensates sampled from January 2018 to June 2021 show extreme variations in [Cl] and $\delta^{37}\text{Cl}$ values (respectively of 1 to 4689 mg/l and -1 to +16‰) that are strongly anti-correlated, with the highest [Cl] associated with the lowest $\delta^{37}\text{Cl}$ values, close to the expected magmatic Cl. Such wide $\delta^{37}\text{Cl}$ range can be explained by HCl(g) partial entrapment in the hydrothermal system that favors the light isotope entrapment (³⁵Cl). More widely, among all the other parameters considered here, we find a rough anti-correlation between $\delta^{37}\text{Cl}$ and CO₂/CH₄ ratio and no covariation between $\delta^{37}\text{Cl}$ and fumarole temperatures, rainfall, or seismic energy. Such features indicate

that even during a non-eruptive period, the intensity of scrubbing might not be primarily controlled by external forcing (i.e. fresh water feeding the aquifer into the edifice), but might instead be primarily driven by internal forcing (i.e. magmatic activity). Moreover, if we make the usual assumption that the H₂O(g) flux emitted by fumaroles is not affected by scrubbing, the slope of the [Cl]— $\delta^{37}\text{Cl}$ correlation suggests that chlorine isotope fractionations between HCl(g) and dissolved HCl may occur out of equilibrium within the hydrothermal system.