

Dynamics of sulfur degassing in alkaline magmas illustrated with melt and fluid inclusions

MARIA LUCE FREZZOTTI¹ AND FRANCESCA TECCE²

¹Dept. Earth and Environmental Sciences, University Milano Bicocca, Italy (maria.frezzotti@unimib.it)

²Istituto di Geologia ambientale e Geingegneria, CNR Roma, Italy (francesca.tecce@cnr.it)

The dynamics of sulfur transfer into the magmatic fluid phase in a long-lived shallow magma reservoir has been investigated using melt and fluid inclusions in syenite xenoliths from the Sabatini K-rich volcanic complex (0.8-0.04 Ma; Roman magmatic province, Italy). Silicate melt inclusions (MI; up to 100 μm) in clinopyroxene and in sanidine have compositions in the phonotephrite-phonolite-trachyte spectrum, similar to erupted rocks. MI in sanidine argue convincingly that the pre-eruptive alkaline melt was oversaturated with respect to a sulfate-rich melt phase, and to a vapor-rich aqueous phase. Most MI show a large bubble/glass ratio and contain several pinkish-yellowish globules (1-5 μm), rich in SO_3 (6-7 wt %), SiO_2 , Al_2O_3 , alkalis, and CaO. Raman spectroscopy of globules reveals an alkali-silicate glass structure containing oxysulfur species dominantly as SO_4^{2-} , with subordinate CO_3^{2-} groups, and absence of S-S bonds. Magmatic vapor-rich brine inclusions have a microthermometric behavior consistent with the presence of up to 25 wt% sulfate in solution. Sulfur species in liquid water include an hydrated double alkali-Ca sulphate \pm anhydrite, $(\text{SO}_4)^{2-}$ and $(\text{HSO}_4)^-$ ions, and SO_2 ; CO_2 is detected in the inclusion bubble.

This case study suggests that during crystallization, sulfur supersaturation in oxidized alkaline magmas induces liquid immiscibility between silicate and sulfate melts. At these pre-eruptive stages, significant amounts of S partition as SO_2 and SO_3 (or H_2SO_4) in magmatic aqueous-rich fluids.

Isotopic constraints for sources and sinks of NO_x in the city of Berlin

M.FRIEBEL¹ AND U. WIECHERT¹

¹Freie Universität Berlin; Germany

(*correspondance: mfriebel@zedat.fu-berlin.de)

Atmospheric NO_x causes various problems in urban environments such as tropospheric ozone production and the formation of secondary aerosols. The isotopic composition of atmospheric nitrates can help to identify the sources of NO_x ($\delta^{15}\text{N}$) [e.g. 1] and to understand its reaction pathways and sinks in the atmosphere ($\delta^{18}\text{O}$) [e.g. 2].

Here, we report the results of isotopic measurements of nitrates from precipitation collected during single storm events in Berlin between March 2007 and January 2008. $\delta^{15}\text{N}_{\text{NO}_3}$ ranges from -11.6 to +2.0; mean = -4.5 (relative to AIR) and $\delta^{18}\text{O}_{\text{NO}_3}$ values range between +8.9 and +67.2; mean = +32.6 (relative to V-SMOW). The $\delta^{15}\text{N}$ values show a high variation between each rain event and can be separated into groups with values of -4.3 to +2.0 (mean = -1.2) and -11.6 to -5.1 (mean = -8.0). The $\delta^{18}\text{O}_{\text{NO}_3}$ values show a bimodal distribution with one maxima in June-July 2007 and the second in January 2008. The measured $\delta^{18}\text{O}$ values are low, especially during the spring of 2007 (+8.9 to +23.4), compared to those reported in other studies [e.g. 2].

The nature of the observed isotopic variations is complex. More positive $\delta^{15}\text{N}_{\text{NO}_3}$ values may represent NO_x originating from fossil fuel combustion (mostly fuel NO_x) and more negative $\delta^{15}\text{N}_{\text{NO}_3}$ values may be related to volatilization of nitrogen compounds from fertilized soils. This variation in the $\delta^{15}\text{N}_{\text{NO}_3}$ values could be associated with long distance transport of air masses from different source regions, since the lifetime of NO_x is approximately one day [e.g. 3] and its deposition as nitrate (residence time of 1-2 days [e.g. 3]) can be hundreds of kilometres from the nitrogen source. $\delta^{18}\text{O}_{\text{NO}_3}$ serves as a fingerprint for the reaction pathways of NO_x to nitrate. High $\delta^{18}\text{O}$ values are consistent with a high proportion of NO_x oxidised by ozone, whereas low $\delta^{18}\text{O}$ values indicate preferential oxidation by peroxy and/or OH radicals [e.g. 2]. The results show that isotope ratios of atmospheric nitrates contribute important constraints in conjunction with local concentration measurements and storm track information on the sources and fate of tropospheric NO_x and O_3 and their dynamics in the urban environment of Berlin.

[1] Hastings *et al* (2003) *JGR* **108**(D24), 4790 [2] Michalski *et al* (2011) *Hand. Env. Iso. Geoch.* 613-635 [3] Liang *et al* (1998) *JGR* **103**(D11), 13,435.