Fresh glass fragments from the ignimbrites were analyzed at GEOMAR (Kiel, Germany) using JEOL JXA 8200 electron microprobe equipped with 5 wavelength dispersive spectrometers including 3 high-sensitivity ones (2 PETH and TAPH). The analytical conditions were 15 kV accelerating voltage, 6 nA current and 5 μm electron beam size for all analyses. The current/size conditions correspond to the current density of 0.076 nA µm-2, which is within the recommended range (<0.1 nA µm-2) to minimize the Na loss during analysis, especially in a combination with short counting time for Na (Morgan and London, 1996; 2005; Kuehn et al., 2011). Counting times in the latest version of the program are 5/10 s (peak/background) for Na, 20/10s for Si, Al, Mg, Ca, P, 30/15 s for Fe, K, Ti Cl, S, 40/20 s for F and 60/20 s for Mn. Basaltic glass (USNM 113498/1 VG-A99) for Ti, Fe, Mg, Ca, P, rhyolitic glass (USNM 72854 VG568) for Si, Al, Na, K, scapolite (USNM R6600-1) for S and Cl, all from the Smithsonian collection of natural reference materials (Jarosewich et al., 1980), comendite obsidian KN-18 (Nielsen and Sigurdsson, 1991; Mosbah et al., 1991) for F and synthetic rhodonite for Mn were used for calibration and monitoring of routine measurements. Two analyses of all standard glasses and scapolite were performed at the beginning of analytical session, after every 40 analyses of unknown samples and at the end. Typically, 20-22 glass shards were analyzed for every sample. The data reduction included on-line CITZAF correction and small drift correction for systematic deviations (if any) from the reference values obtained on standard materials. Data on reference glasses analyzed along with the samples in this study are provided in Supplementary table XX.

Trace element analyses were obtained at the Institute of Geosciences, CAU Kiel, Germany using using ICP-MS Agilent 8900 and a Coherent GeoLas ArF 193 nm Excimer LA system operated with a fluence of 5 J cm-2, at a repetition rate of 10 Hz and a 15-24 μm ablation craters. Analyses were performed using a large volume ablation (Fricker et al., 2011) modified for fast washout. Helium (0.7 L min-1) with addition of 14 mL min-1 H2 was used as carrier gas. The carrier gas was mixed with Ar (~1 L min-1) prior to introduction to the ICP-MS. Ten major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) and 31 trace elements were analyzed. Analyses included 20 s background (laser-off) and 30 s signal (laser-on) measurements. Dwell time for different elements varied from 5 to 20 ms depending on their abundance. One complete measurement cycle lasted 0.607 ms and initial data reduction was performed in Glitter software (Griffin et al., 2008), that included manual selection of integration windows and preliminary calibration. The typical integration intervals for tiny tephra shards were 6-10 s and included 10-17 cycles. The intensities corrected for background and averaged over the selected intervals were normalized to the intensity of 43Ca isotope and converted to concentrations by matching the sum of major element oxides to 100 wt% (Liu et al., 2008; Pettke et al., 2004). The calibration and correction of instrumental drift used data on ATHO-G reference glass (Jochum et al., 2006), which was measured in duplicate after every 18 points on unknown samples. Typically, 7-10 glass shards were analyzed for every sample. Data on reference glasses analyzed along with the samples in this study are provided in Supplementary table XX.

Further analytical details of the major and trace element analyses can be found in (Portnyagin et al., 2020).

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