Chemical and isotopic composition and mineral chemistry of products from the 79 CE eruption of Somma-Vesuvius

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1. Samples and Analytical technique

1.1 Sample preparation

Samples representative of each unit of the 79 CE pyroclastic sequences were sampled at Cava Pozzelle (40.796935°N, 14.467026°E), Terzigno, on the eastern flank of Mt. Somma-Vesuvius (Campania region, Itay). Approximately 1-2 kg of material were collected for each eruptive unit (EU2 to EU8). All samples are pumices from individual layers. Each analysed sample comprised pumice clasts which were similar in colour, texture and crystal content. Bulk major and trace elements, isotopic (Sr and Nd) and mineral chemistry analyses were carried out on pumice samples and two mafic cumulates (samples VT-C1 and VT-C2 sampled in EU3fC base unit) vertically from the whole stratigraphic sequence (Table 1).

Table 1

Pumice colour	Eruptive Unit	Sample	Whole rock analyses	Sr-Nd isotopic ratios	Mineral chemistry	Compositional profiles in Cpx	Noble gases and CO_2
	EU8	VT-79 EU8	x				
	EU7	VT 79 EU7 base	x	x			
	EU6	VT-79 EU6	x				
	EU4	VT-79 EU4pf					
	EU3pftot	VT-79 EU3pftot base	x				
	EU3f	VT-79 EU3fC top	x	x	x		x
	EU3f	VT-79 EU3fC base	x				
	EU3pf	VT-79 EU3pf top	x				
	EU3pf	VT-79 EU3pf base	x				
Grey p.	EU3f	VT-79 EU3fB	x	x	x	x	
Grey p.	EU3f	VT-79 EU3fAtop					
Grey p.	EU3f	VT-79 EU3fAbase	x				
	EU2/3pf	VT-79 EU2/3pf					
White p.	EU2f	VT-79 EU2f top	x	x	x	x	
White p.	EU2f	VT-79 EU2f mid	x				
White p.	EU2f	VT-79 EU2f base	x	x	x		
White p.	EU1	VT-79 EU1					
M. cum.	EU3f	VT-C1		x	x		x
M. cum.	EU3f	VT-C2			x		x

List of the 79 CE Eruptive Units (EU) and related samples. The analyses performed on each sample are shown. Grey p.= grey pumices; White p.= white pumices; M. cum.= mafic cumulates.

Moreover, $^{3}He/^{4}He$ and $\delta^{13}C$ isotopic analyses were performed on fluid inclusions in minerals from mafic cumulate fragments and from the grey pumices.

Pumices of each sample were sieved and a large number of centimetre-size pumice fragments were washed in distilled water multiple times, and then dried overnight at 110°C. The pumices were successively distinguished, based on their colour, in a grey and white fraction. An aliquot of about 500 grams of pumice was then crushed to lapilli-size particles, ground and homogenized in an agate mortar. An aliquot of the obtained sample powders was used for major and trace element analyses; a different aliquot for isotopic (Sr and Nd) analyses.

Another portion of the selected pumice fragments was used for density measurements. A different part was gently crushed through a jaw crusher and sieved. The granulometric classes ranging between 0.025 mm and 1 mm were examined under a stereo-microscope to hand-pick and separate the most abundant mineral phases (e.g. clinopyroxene, K-feldspar, phlogopite, olivine). Crystals (in the range 0.5–1 mm) were mounted in epoxy resin and polished for electron microprobe analyses (EMPA). Other aliquots of crystals were utilized for noble gases, CO_2 and Sr isotopic analyses.

1.2 Whole-rock major and trace elements

Whole rocks major and trace elements analyses were performed on samples belonging to eruptive units EU1 to EU8 (Table 1). Analyses of whole-rock major and trace elements were obtained by ICP-OES and ICP-MS at the Centre de Recherches Petrographiques et Geochimiques (CNRS-CRPG) in Nancy (France). Analytical uncertainty (1σ) is <2% for SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O and K_2O, <5% for MnO, and TiO_2, 5–10% for P_2O_5, and <5% for all trace elements except U (<8%).

1.3 Sr and Nd isotopic analyses on whole rocks and minerals

Sr-Nd isotopic analyses, were carried out on whole rocks and mineral grains of K-feldspar, clinopyroxene, olivine and phlogopite from selected samples of white (VT-79 EU2f base and top) and grey (VT-79 EU3fB, VT-79 EU3fC base) pumices (Table 1). The $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios were determined at the Radiogenic Isotope Laboratory of the Istituto Nazionale di Geofisica e Vulcanologia, sezione di Napoli-Osservatorio Vesuviano. An aliquot (0.1 g) of powdered whole rocks and mineral concentrate were leached with HCl for 10 min before dissolution. Sr and Nd were separated, following HF-HNO_3-HCl suprapur acid dissolution, using standard chromatographic methods of column. The isotopic composition of Sr and Nd was determined in the mass spectrometry laboratory of the Osservatorio Vesuviano through Thermal Ionization Mass Spectrometry (TIMS) techniques using a Thermo Scientific Triton Plus® mass spectrometer. In-run isotopic fractionation was corrected through normalisation of measured $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios to $^{88}Sr/^{86}Sr$ =

8.37521 and $^{146}Nd/^{144}Nd$ = 0.7219 ratios, respectively. During the period of analysis, replicate measurements of NIST–SRM 987 ($SrCO_3$) and JNdi–1 international reference standards were carried out to check for external reproducibility, 2σ (where σ is the standard deviation of the standard results). The following mean values were obtained: $^{87}Sr/^{86}Sr = 0.710246 \pm 0.000019$ (2σ, n = 171) for NIST–SRM 987; $^{143}Nd/^{144}Nd = 0.512105 \pm 0.000007$ for JNdi-1 (2σ, n=60). The measured Sr and Nd isotope ratios were normalized to the recommended values (Zhang and Hu, 2020) of NIST–SRM 987 ($^{87}Sr/^{86}Sr = 0.710248 \pm 0.000012$ (σ)) and JNdi–1 ($^{143}Nd/^{144}Nd = 0.512107 \pm 0.000012$ (σ)) standards, respectively.

1.4 Mineral chemistry

Minero-chemical analyses were carried out (Table 1) on crystals (feldspars, clinopyroxene and olivines) from EU2 (samples VT-79 EU2f base, VT-79 EU2f top), EU3 (samples VT-79 EU3fB and VT-79 EU3fC base) and mafic cumulates (VT-C1 and VT-C2). All the separated crystals were observed under a polarizing microscope for a preliminary inspection. Compositional core-to-rim traverses were acquired on clinopyroxenes belonging to the EU2f and EU3f eruptive units. The quantitative compositional profiles were measured on 35 crystals showing optical evidence of compositional zoning.

Mineral compositions were obtained at the HP-HT Laboratory of Experimental Volcanology and Geophysics of the Istituto Nazionale di Geofisica e Vulcanologia in Rome (Italy), using a Jeol-JXA8200 electron microprobe equipped with five wavelength dispersive spectrometers and performing single spot analyses on both unzoned and zoned crystals and core-to-rim transects on zoned clinopyroxene crystals. Crystals were analysed under high vacuum conditions, using an accelerating voltage of 15 kV and a beam current of 7.5 nA. Spot dimension varies between 2 and 3 microns in diameter. The compositional transects in zoned clinopyroxenes were realized with 3 to 6 μm spots separation and a spot dimension of 2–3 microns in diameter, length of transects varies between 18 and 300 μm depending on the zoning pattern. Elemental counting times were 10 s on the peak and 5 s on each of two background positions. Corrections for inter-elemental effects were made using a ZAF (Z: atomic number; A: absorption; F: fluorescence) routine. The range of standards for calibration was taken from Micro-Analysis Consultants (http://www.macstandards.co.uk, n.d.) (MAC) and variable diffraction devices: albite (Si-PET, Al-TAP, Na-TAP), forsterite (Mg-TAP), augite (Fe-LIF), apatite (Ca-PET), orthoclase (K-PET), rutile (Ti-PET) and rhodonite (Mn-LIF). Accuracy was better than 1%–5% except for elements with abundances below 1 wt.%, for which it was better than 5%–10%. Precision was typically better than 1%–5% for all analysed elements.

1.5 Isotopic analyses of noble gases and CO_2

The isotope composition of helium ($^3He/^4He$ ratio), neon (^{20}Ne) and argon ($^{40}Ar/^{36}Ar$) has been analysed in fluid/melt inclusions hosted in olivine and clinopyroxene crystals from mafic cumulates (samples VT-C1 and VT-C2) and from grey pumice (sample VT-79 EU3fC top; Table 1). In clinopyroxenes from the VT-C1 cumulate, we also carried out one measurement of carbon isotopes of CO_2, together with a second estimation of CO_2 concentration (Table 1). Isotopic analyses of noble gases and CO_2 in clinopyroxene and olivine hosted fluid inclusions were carried out in the laboratories of Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo (Italy). Approximately 0.3–1.0 g of crystals was hand-picked and then cleaned in an ultrasonic bath under nitric acid, deionised water and acetone. For noble gases isotopic analyses, the crystals were loaded into a single-step crusher and backed under pumping to achieve ultra-high vacuum conditions. Following the crushing and release of fluid inclusions, CO_2 concentration in the gas mixture was first quantified manometrically. The gas mixture was then purified following the methods reported by Rizzo et al. (2018, 2021). The isotopic analyses of helium (^3He and ^4He) and ^{20}Ne were realized independently through two distinct split-flight-tube mass spectrometers (Helix STF-Thermo), while a multicollector mass spectrometer (GVI Argus) was used to measure stable argon isotope (^{36}Ar, ^{38}Ar, ^{40}Ar). The ^{20}Ne has been corrected for isobaric interferences at m/z values of 20 ($^{40}Ar^{2+}$) (Rizzo et al., 2018).

The $^3He/^4He$ ratios are stated in Rc/Ra units, where Ra represents the $^3He/^4He$ of atmospheric air (1.39×10^{-6}) and Rc is the air corrected $^3He/^4He$ ratio of the sample, calculated using the $^4He/^{20}Ne$ ratios. The Rc/Ra value is equal to:

$$[(R_m/Ra)(He/Ne)_m–(He/Ne)air]/[(He/Ne)_m–(He/Ne)air]$$

where “m” and “air” are measured values and air, respectively.

The argon ^{40}Ar was corrected for atmospheric contamination. Assuming that that all the ^{36}Ar in the fluid inclusion is atmospheric in origin, in the samples with $^{40}Ar/^{36}Ar > 300$, the ^{40}Ar concentration can be corrected:

$$^{40}Ar^* = {}^{40}Ar_m - [(\,{}^{40}Ar/^{36}Ar)air \times {}^{36}Ar_m]$$

where m is the measured value and $^{40}Ar^*$ is the corrected isotope value.

The analytical error for the ^{20}Ne (1σ) was <0.8 %, the $^3He/^4He$ measurements had an uncertainty (1σ) of less than 1.4 % (except for olivine from VT-C2), and the stable argon isotope measure have analytical uncertainty of $^{40}Ar/^{36}Ar < 0.2\%$.

After noble gas analysis, and taking into account those samples with the estimated highest CO_2 concentration, an aliquot of 3.0 g of crystals was selected for the determination of the carbon isotopic composition of the fluid inclusion ($^{13}C/^{12}C$). The carbon isotopic composition is reported as $\delta^{13}C$ notation in parts per mil (‰) relative to the Vienna Pee Dee Belemnite (V-PDB) international standard. Samples for carbon isotopic analyses were extracted from a single-step crushing process using an on-line glass trap and frozen under liquid nitrogen. After purification in a glass line to prevent adsorption and fractionation of CO_2, the CO_2 was trapped in a glass sampler for subsequent IRMS measurements. Further details of the extraction and analytical protocol can be found in Gennaro et al. (2017), Rizzo et al. (2018, 2021), Sandoval-Velasquez et al. (2023, 2024) and references therein. The analytical error, estimated as 1σ, was better than 0.3 ‰.

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