

Supplementary material

High-pressure homogenization of olivine-hosted CO₂-rich melt inclusions in piston-cylinder: insight into the volatile content of primary mantle melts

Roxane Buso, Didier Laporte, Federica Schiavi, Nicolas Cluzel, Claire Fonquernie

Université Clermont-Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, F-63000 Clermont-Ferrand, France

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1. Raman spectroscopy: supplementary figure

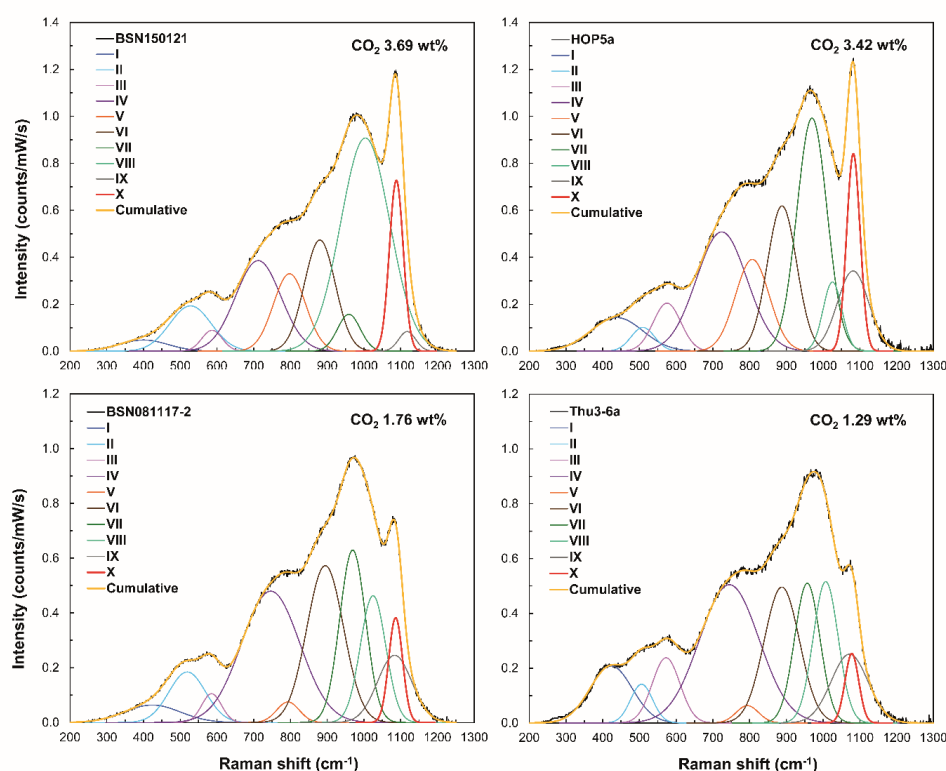


Figure S1. Best fit of the Raman spectra of two CO₂-bearing basanitic reference glasses (BSN150121 and BSN081117-2), an homogenized melt inclusion (HOP#5a) and a natural, unheated melt inclusion (Thu3-6a) by ten Gaussian components labelled (from left to right) I to X: components I to IX correspond to the silicate band, and component X to the CO₃²⁻ peak. The cumulative curves closely match the glass spectra. The chi-square value, χ^2 , is between 0.7 and 0.8 for almost all glasses except for BSN210121 ($\chi^2=1.1$). The intensity is normalized to laser power and acquisition time.

2. Homogenization experiments: textures and phases in presence

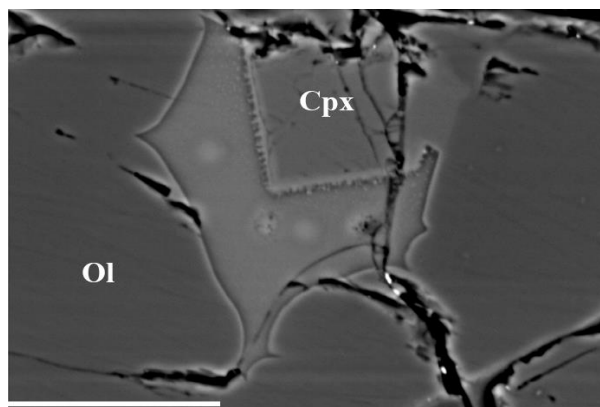


Figure S2. Back-scattered electron microphotograph of a melt inclusion in sample HOP#18 (2.5 GPa, 1275 °C, 30 min): a large, euhedral grain of clinopyroxene grew during the experiment. The brighter areas in the glass (lighter gray) are the traces of the analytical spots. Labels: Ol, host olivine; Cpx, clinopyroxene. Scale bar: 20 μ m.

3. Analytical techniques used to characterize reference glasses

3.1 Elemental analysis: carbon and hydrogen

Carbon and hydrogen contents of the reference glasses used for quantification of H_2O and CO_2 in melt inclusions by Raman spectroscopy were measured with a Thermo Scientific™ Flash 2000 CHNS-O analyzer equipped with a MAS 200R autosampler at Laboratoire Magmas et Volcans. Prior to analysis, small pieces of the reference glasses were selected and carefully prepared: all foreign substances (capsule or assembly pieces) were removed from the glass to avoid contamination during analysis. The mass of reference glasses used for analysis was around 11-13 mg. The weighing of the samples and reference materials was performed in a tin capsule on a microbalance with a 1 μ g resolution. Some milligrams of V_2O_5 were added to the material to optimize the combustion.

Three analytical standards and reference materials were used for calibration: ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), BBOT ($\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_2\text{S}$) and a soil reference (homogeneous batch of soil from Thermo Scientific™) for C, N, and S. The parameters used during analyses were: 2.4 bar helium with a 140 mL/min flow rate of carrier gas and a 120 mL/min flow rate of reference gas; 2.2 bar oxygen with a flow rate of 90 mL/min and an injection end time (duration of O_2 injection) of 11 s. Samples were put by the autosampler into a 950 °C high-temperature reactor consisting of a quartz tube, half-filled with CuO and reduced copper. A fast (flash) combustion of the sample at about 1800 °C is produced by the exothermic combustion of the tin capsule in presence of excess O_2 . The released gaseous products are carried in the helium flow through CuO and reduced copper held at ~ 840 °C. This reduction step converts SO_3 into SO_2 , nitrogen oxides into N_2 , while metallic copper traps excess O_2 .

The gases are separated in a chromatography column (length 2 m, working temperature 70 °C) filled with HayeSep®. At the end of the chromatography column, CO_2 , H_2O , N_2 and SO_2 are analyzed sequentially by thermal conductivity in a detector measuring the difference between reference and carrier circuits. The whole analytical process lasts ~ 600 s for each sample. The instrumental precision of this technique is 2 % relative for CO_2 concentration of 1 wt%. To verify the reproducibility of the measurements and the homogeneity of the samples, we measured three reference glasses in two different sessions. The given CO_2 values used for Raman calibration are average values of these two sessions and the associated error is the largest difference between the CO_2 contents of the glasses obtained for the two sessions (0.05 wt%).

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Measurements of total water content and CO_2 dissolved as carbonate ions (CO_3^{2-}) in the reference glasses were carried out with a Bruker Vertex 70 spectrometer coupled with a Hyperion microscope system using a global light source, a KBr beamsplitter and a MCT (Mercury-Cadmium-Tellurium alloy) detector. Characterization of five of

the seven basaltic reference glasses is described in Schiavi et al. (2018). Two new reference glasses (BSN150121 and BSN210121; Table S1) with higher CO₂ contents were synthesized for this study. Spectra of glasses BSN150121 and BSN210121 were recorded using the OPUS software in the 700-7500 cm⁻¹ range. Plane parallel, doubly polished chips of glasses were placed on a CaF₂ window and analyzed with a beam size of either 25×25 μm or 35×35 μm and 4 cm⁻¹ spectral resolution in transmission mode. For the absorbance and background spectra, 300 and 100 scans were acquired, respectively. Several measurements were done on each reference glass.

The concentrations of the volatile species dissolved in the glass were determined using the Beer-Lambert law (e.g., Stolper, 1982) where: Concentration = (Absorbance × molecular weight)/ (thickness × density × molar absorptivity). Preparation, polishing and accurate thickness measurement of very thin glass chips is challenging. Therefore, the thickness of the glass chips was measured using two methods: 1) by counting the interference fringes on the IR spectra collected in reflective mode on the same spots analyzed in transmission mode (Nichols and Wysoczanski, 2007; von Aulock et al., 2014); 2) by measuring the microscope vertical displacement between the two polished surfaces of the glass chips when Raman laser is focused on them. The glass chips were progressively polished and analyzed until no sign of saturation remained in the spectra. Uncertainty in thickness estimation (± 2 μm) remains one of the principal sources of error for volatile quantification in very thin glasses.

The very small size of the glass chips precluded density measurements by Archimedes' method. Therefore, density was calculated by extrapolating the linear relationship (Fig. S3) between the density and the volatile content (H₂O + CO₂) of the five reference glasses reported in Schiavi et al. (2018). We point out that: (1) no density data are available for basaltic glasses with such high CO₂ contents in the literature; (2) previous studies have showed linear relationships between density and H₂O content (e.g., Schiavi et al. 2018, and references therein) and between density and CO₂ content (Bourgue and Richet, 2001) of silicate melts; (3) small variations of density have a negligible impact on the quantification of the volatile content in the studied samples.

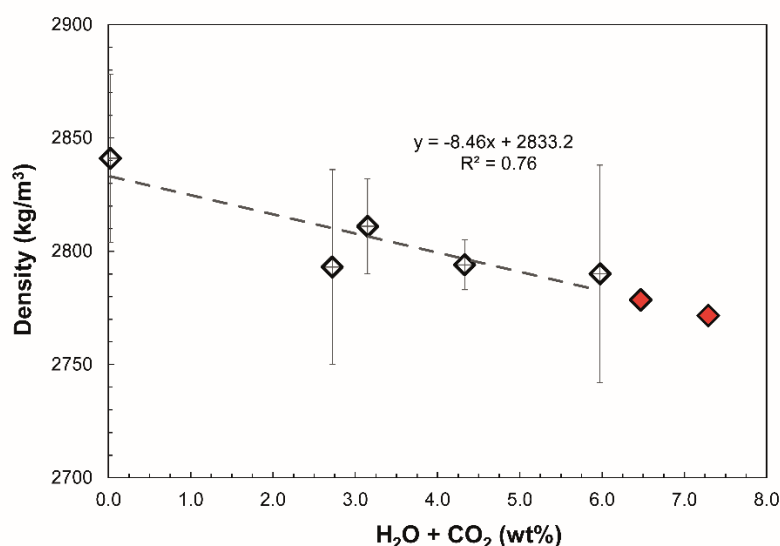


Figure S3. Density versus (H₂O + CO₂) content of the basaltic reference glasses. The density of glasses indicated by empty diamonds was measured by Archimedes' method (Schiavi et al. 2018). The large uncertainties associated to the density measurement of three glasses are caused by the small size of these glass fragments. The density of the two CO₂-richest glasses (BSN150121 and BSN210121; red diamonds) was calculated by extrapolation of the linear regression defined by the other five glasses. The CO₂ and H₂O contents used in this graph were determined by CHNS elemental analysis.

The water and CO₂ contents of the basaltic reference glasses are given in Table S1. Water contents were determined based on the height of the absorbance band at ~ 3500 cm⁻¹ following the procedure described in Schiavi et al. (2018) and using the molar absorption coefficient provided by Shishkina et al. (2014): 57.3 ± 1.8 L mol⁻¹ cm⁻¹. The obtained values match those determined by CHNS within 8 % relative.

Carbon dioxide concentrations were determined from the heights of the absorbance bands centered at approximately 1430 and 1520 cm⁻¹ (Fig. S4), which correspond to the antisymmetric stretching of distorted carbonate groups (e.g., Dixon and Pan, 1995). A splitting of ~ 90 cm⁻¹ separates the two peaks. In the measured spectra, the two carbonate peaks are clearly identified and the baseline below them can be easily drawn because the water band at 1630 cm⁻¹ is absent or very small. The absence of peaks at 2350 cm⁻¹ in the spectra indicates that carbon does not dissolve as molecular CO₂ in these glasses, which is in line with previous studies (e.g., Dixon and Pan, 1995; Shishkina et al., 2014).

To quantify CO₂ dissolved as carbonate ions (CO₃²⁻), we first determined the molar absorptivity ϵ (L.mol⁻¹.cm⁻¹) for our glass compositions using the Beer-Lambert law:

$$\epsilon = 100 \times (\text{MW} \times \text{Abs}) / (C \times t \times \rho) \quad (1)$$

where MW is the molecular weight (44.01 g/mol), Abs is the measured absorbance (peak height), t is the glass thickness (cm), ρ is the glass density (g.L⁻¹ or kg.m⁻³), and C is the CO₂ concentration (in wt%) measured by the elemental analyzer. Values of ϵ_{1430} and ϵ_{1520} were determined from the slope of the linear regression of normalized absorbance vs. bulk CO₂ concentration measured by the elemental analyzer (Fig. S5). The obtained values of molar absorptivity ($\epsilon_{1520} \sim 280 \pm 25$ L mol⁻¹ cm⁻¹, $\epsilon_{1430} \sim 267 \pm 25$ L mol⁻¹ cm⁻¹; Fig. S5) are close to those (281-284 L mol⁻¹ cm⁻¹) provided by Dixon and Pan (1995) for basaltic glasses containing up to 2.5 wt%.

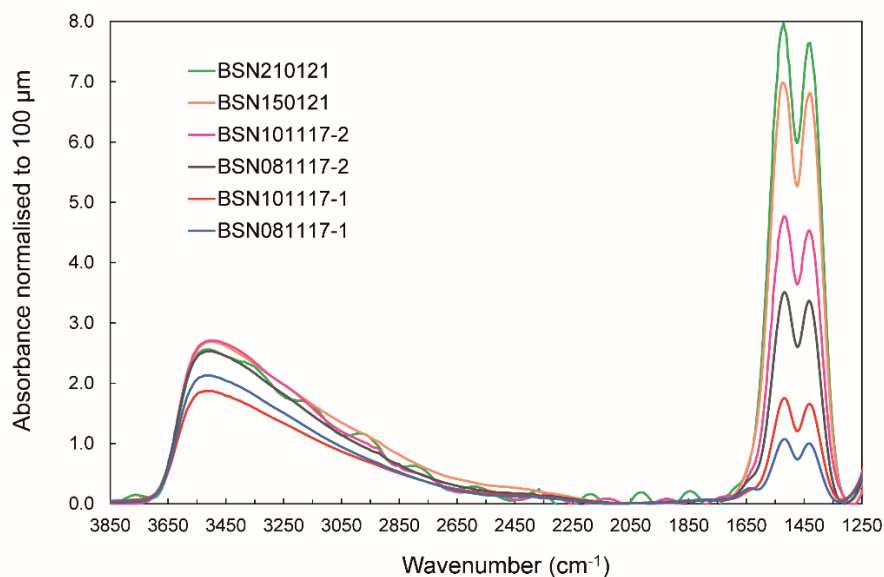


Figure S4. Infrared spectra of the reference basaltic glasses displaying the asymmetric water band at 3500 cm⁻¹, and the two carbonate peaks at 1430 and 1520 cm⁻¹. The CO₂ content of the glasses increases progressively from the bottom spectrum to the top one. The absorbances are normalized to 100 µm thickness. The spectrum of the very thin glass chip of BSN210121 shows interference fringes.

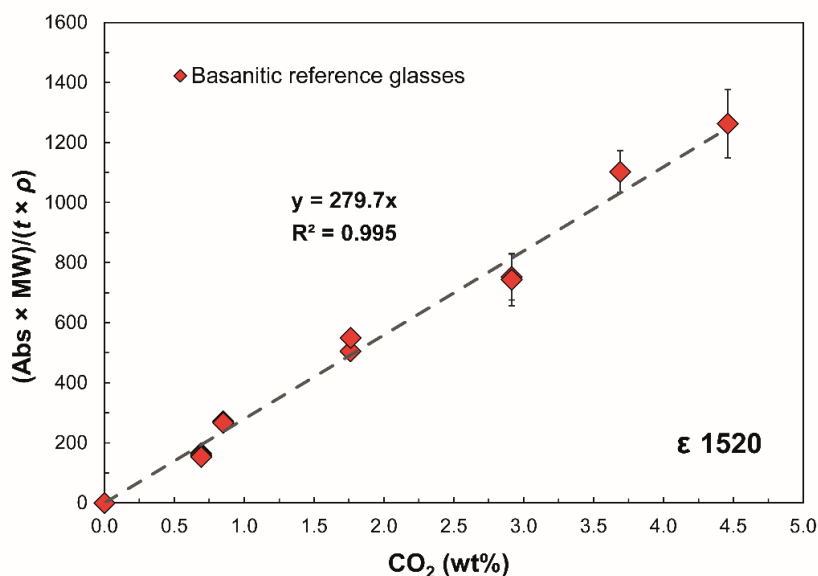


Figure S5. Plot of CO₂ content determined by elemental analysis versus $(\text{Abs} \times \text{MW})/(t \times \rho)$ with regression line passing through the origin (see equation 1). The slope of the regression line indicates the molar absorptivity for the carbonate peak at 1520 cm⁻¹, ϵ_{1520} .

4. Heating stage experiments at 1 atmosphere

Heating stage experiments were conducted at Laboratoire Magmas et Volcans on five olivine grains collected in basanitic tephra from Thueyts volcano (Ardèche, France). Before experiment, these grains were double polished to remove the surrounding glass and allow clear observation of the melt inclusion inside. The melt inclusions and the bubbles were measured and photographed using an optical microscope. A Vernadsky-type heating-quenching stage containing a 1 atm gas-tight sealed furnace cooled by water was used for the heating experiments. In order to maintain reducing conditions during experiment ($fO_2 < 10^{-10}$ atm), He gas purified by Zr metal at 700 °C, was circulated through the furnace. The individual olivine crystals mounted on sapphire discs were progressively heated to a temperature between 1218 and 1230 °C (1305 °C in one case), and then maintained 10 min at this temperature before the quench. The evolution of temperature was recorded by an S-type thermocouple welded to the sample holder. Heating experiments were conducted with a heating rate of 50 °C/min up to ~ 950 °C and then 10 °C/min until the maximum temperature. The total duration of experiments was between 35 and 60 minutes.

For five olivine grains, the bubbles of melt inclusions did not disappear during the runs and in case of multiple bubbles, they coalesced. Even by raising the temperature to 1305 °C, it was not possible to make the bubble disappear. After experiments, most of the bubbles decreased slightly in size (except for the bubbles which coalesced during reheating) and lost their carbonate grains; some contain liquid CO₂ (see supplementary Table S4). After the runs, some melt inclusions show sulfide grains in the glass. For one olivine grain, the melt inclusions exploded during the heating experiment at ~1140 °C (HOP-Thu3-6).

After the experiments, the quenched melt inclusions were exposed, and the H₂O and CO₂ contents were precisely quantified by Raman spectroscopy while the major elements and Cl, F and S contents were obtained by EMPA. The CO₂ contents are in the range of those measured in unheated melt inclusions (see supplementary Table S4). The same conclusion applies to water, indicating a low degree of water loss during the heating experiments at 1 atm. The persistence of bubbles and the CO₂ contents that are comparable to those of unheated melt inclusions, demonstrate that Thueyts melt inclusions cannot be fully homogenized with a heating stage at 1 atm.

5. List of supplementary tables

Table S1. Synthesis conditions and volatiles composition of basanitic reference glasses.

Tables S2, S3 and S4: provided as separate Excel files.

Table S2. Glass compositions measured in unheated melt inclusions from Thueyts: raw EMPA data.

Table S3. Glass compositions measured in melt inclusions from Thueyts after homogenization at high pressure: raw EMPA data.

Table S4. Glass compositions measured in melt inclusions from Thueyts after heating stage experiments at 1 atm: raw EMPA data.

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