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New method for initial composition determination of crystallized silicate melt inclusions

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ABSTRACT

Silicate melt inclusions (SMI) trapped in minerals and carried up to the surface by volcanism are routinely studied in order to determine the pre-eruptive volatile budgets of volcanic systems. The volatile contents of SMI that are affected by post-entrapment processes, such as crystallization (PEC) and/or bubble nucleation during cooling, are generally difficult to interpret. Therefore, there is a general preference to select the melt inclusions that experienced minimal post-entrapment effects. Conversely, SMI can be homogenized at high temperature and quickly quenched. This method is controversial because heating may induce leakage of water

from the silicate melt during experiments in addition to loss by diffusion. Here, we propose a new multi-disciplinary method to study crystallized SMI. This method involves the following processes: (1) X-ray microtomography for measuring phase proportions; (2) NanoSIMS for measuring C and H concentrations in glass as a proxy for CO₂ and H₂O; (3) EPMA (electron probe microanalyzer) for major and volatile element concentrations in all phases; and (4) thermodynamical modeling using Rhyolite-MELTS for volatile saturation determination. To test this approach, we studied the Los Humeros (East Trans Mexican Volcanic Belt) volcanic complex SMI. Three-dimensional (3D) petrographic observations of the studied SMI demonstrate that minerals inside the SMI were crystallized from the trapped silicate melt and were not trapped with the silicate melt (protogenetic). Accordingly, the mathematical reconstruction of the SMI is performed with the following equation: $X_{SMI} = \sum [V_{Mineral(i)} * X_{Mineral(i)}] + [V_{Glass} * X_{Glass}] + [V_{Bubble} * X_{Bubble}]$. Bubbles are associated with a heterogeneous trapping of a melt+fluid mixed phase. The PEC of large minerals inside SMI is consistent with slow cooling rates of the SMI, meaning that exsolved volatiles diffused toward the bubble in equilibrium with the melt before the glass transition. The volatile pressure determined in X_{SMI} and using Rhyolite-MELTS is therefore equal to the pressure of the bubble. The volatile mass in the bubble is determined and added to the bulk volatiles of the silicate melt. This method can be used for a wide range of samples and may significantly improve our knowledge of volatile degassing processes.

Key words: Silicate melt inclusions, mathematical composition determination, X-ray microtomography, geochemistry, thermodynamic modeling.

1- INTRODUCTION

The style, frequency and intensity of volcanism are affected by volatile contents. The characterization of the magmatic system and its volatile content evolution is therefore

significant to constrain volcanic history (e.g., magma ponding) and magma sources (e.g., Frezzotti, 2001; Lowenstern, 2003; Métrich and Wallace, 2008). However, pre-eruptive volatile contents can be difficult to determine because volatiles can be lost when magma approaches the surface and pressure decreases (Dixon et al., 1995). In these cases, bulk-rock and volcanic glass samples rarely reflect the pre-eruptive volatile contents.

Over the last 20 years, the interest in silicate melt inclusions (SMI) has been growing, particularly as a way to determine the pre-eruptive volatile budgets of volcanic systems and to study a wide variety of magmatic processes (e.g., Sobolev and Danyushevsky, 1994; Szabó et al., 1996; Kamenetsky et al., 1997; Roggensack et al., 1997; Bureau et al., 1999; Sobolev et al., 2000; Métrich et al., 2001; Frezzotti, 2001; Hauri, 2002; Bodnar and Vivo, 2003; Wallace, 2005; Métrich et al., 2014; Moore et al., 2015).

Post-entrapment modifications of the SMI may occur between the time of trapping, eruption onto the surface, and analysis in the laboratory (Roedder, 1979; Roedder, 1984). Modifications can be associated with the formation of a bubble or to post-entrapment crystallization (PEC, Steele-macinnis et al., 2011). These modifications will affect the composition of the melt (glass) into the SMI and make the analysis and interpretation challenging. The combined effects of post-entrapment modifications produce trends in the H₂O-CO₂ content of the glass phase that could be mistaken for those produced as a result of magma degassing (Gaetani et al., 2012). To avoid this problem, samples are generally specifically collected to obtain the most rapidly quenched samples (e.g., Bureau et al., 1998a, b; 1999; Spilliaert et al., 2006; Métrich and Wallace, 2008); incomplete information about the magmatic processes is therefore inevitable if the slowly cooled volcanic products, such as lavas, are not studied.

When only bubble-bearing SMI are available for study, some authors have addressed potential contributions from the bubble by stating that the CO₂ contents and pressures determined from

the glassy SMI (FTIR, SIMS) are minimum values (Anderson and Brown, 1993; Cervantes and Wallace, 2003; Spilliaert et al., 2006; Kamenetsky et al., 2007; Johnson et al., 2008; Vigouroux et al., 2008; Ruscitto et al., 2010; Esposito et al., 2011). Some have attempted to homogenize and quench bubble-bearing SMI in order to eliminate the bubble and produce a homogeneous glass before analysis (Skirius et al., 1990; Yang and Bodnar, 1994; Student and Bodnar, 2004; Tuohy et al., 2016). Others report that bubbles are present but do not further discuss their potential contribution to SMI volatile abundances (Lowenstern, 1994; Roggensack et al., 1997; Walker et al., 2003; Liu et al., 2006; Mangiacapra et al., 2008; Lloyd et al., 2013). More recently, studies have demonstrated that the CO₂ contents of bubbles can be estimated (Anderson and Brown, 1993; Shaw and Dingwell, 2008; Steele-macinnis et al., 2011; Wallace et al., 2015) or determined by measuring the CO₂ density in the bubble using micro-Raman spectroscopy (Esposito et al., 2011; Moore et al., 2015).

In some cases, the experimental homogenization at high temperature allows the elimination of any bubble and/or crystals (if present) and the melting of any post-entrapment crystallization at the rims of the host-crystal in the cavity of the inclusion during natural cooling. It therefore produces a homogeneous glass that can be analyzed (e.g., Sobolev and Kostyuk, 1975; Roedder, 1984; Schiano et al., 1992; Student and Bodnar, 2004). However, experimental homogenization is not always effective. In the case of forsteritic olivines trapping H₂O-rich melts, it may be impossible to dissolve the bubble completely just by heating, and high-pressure and controlled fO₂ conditions are usually required. In this case, the methodology can be complex. Moreover, high-temperature treatment of SMI, either to estimate the temperature of entrapment or to obtain homogenized inclusions, may cause irreversible chemical or textural changes, possibly water loss, and overestimation of the homogenization temperature (e.g., Sobolev et al., 1983; Kamenetsky et al., 1997; Bureau et al., 1998a, b; Gioncada et al., 1998; Massare et al., 2002). Another method consists of the calculation of the post-

entrapment crystallization of the host crystal in the inclusion using a mineralogical equilibrium (Bureau et al., 1998a, b; 1999). When applied to bubble-free inclusions, this method is reliable.

Regarding this issue, we propose a mathematical method for SMI homogenization combining 3D X-ray microtomography, major and volatile element geochemistry and thermodynamic modeling devoted to the reconstruction of the initial amounts of volatiles of the SMI. To do so, we use natural SMI from Los Humeros, a volcanic complex from the Trans Mexican Volcanic Belt (TMVB, Mexico).

2- SAMPLE DESCRIPTION & GEOLOGICAL SETTING

The TMVB is well-known for its large diversity of volcanism. Indeed, Gómez-Tuena et al. (2016) recently reviewed the large heterogeneous range of the volcanic products, from alkaline intraplate-like to calc-alkaline subduction-related compositions. Eruptive products from the Los Humeros volcanic complex (LHVC) also exhibit this heterogeneity (from basaltic to trachytic volcanic rocks; see supplementary material) and are therefore good products to study SMI with variable compositions with and without evidence of post-entrapment modifications. Post-entrapment processes may also be due to the quenching rate (a low quenching rate allows the formation of relatively large minerals to occur inside the SMI). The eruptive history of the LHVC had originally been grouped by Ferriz and Mahood (1984) into four main eruptive stages. Nevertheless, Carrasco-Núñez et al. (in press) recently proposed a scenario with three main stages based on new geochronological data: pre-caldera, caldera (including two large caldera-forming eruptions, with a plinian phase in between) and post-caldera, each including several episodes. Four volcanic deposits derived from the lower Plio-Pleistocene pre-caldera eruptive episode (1.55 ± 0.1 My, Ferriz & Mahood 1984), the upper Pleistocene pre-caldera episode (190 ± 20 ky, Carrasco-Núñez & Riggs 2008), the

second caldera episode (69 ± 16 Ky, Carrasco-Núñez et al. in press), and the post-caldera stage (8.91 ± 0.03 Ky, 6.4 ± 0.1 Ky, Carrasco-Núñez et al., in press and Dávila-Harris & Carrasco-Núñez, 2014) were sampled for the presence of SMI. Minerals carrying melt inclusions having experienced (or not) a natural rapid quenching were hand-picked for study. Sample HK14-44, formed during the pre-caldera Plio-lower Pleistocene event at 1.55 My, is a porphyritic lava containing phenocrysts of plagioclase, olivine, orthopyroxene and clinopyroxene. Sample HK14-26, formed during the pre-caldera upper Pleistocene event at 190 ky, is a basaltic lava. It is a black porphyritic rock with plagioclase, olivine, clinopyroxene and orthopyroxene phenocrysts in a glass matrix. Sample LH4a, formed during the second caldera event at 69 Ky, is a pumice deposit from the Zaragoza ignimbrite. A few centimeter-diameter pumices are white and contain plagioclase phenocrysts. Two samples were collected from the post-caldera events at 6.4 ky (HJ14-31) and 8.91 ky (HK14-05) in porphyritic lavas. Sample HJ14-31 is trachyandesite and contains plagioclase, olivine and clinopyroxene phenocrysts. The HK14-05 sample is trachyandesite and contains plagioclase, olivine, orthopyroxene and clinopyroxene phenocrysts together with large vesicles and a glass matrix.

The SMI used to develop the new method for SMI initial composition determination are trapped in olivine and plagioclase crystals from different volcanic materials of the Los Humeros volcanic complex. Some of these inclusions contain bubbles and/or large minerals (Table 1). In current SMI studies, rapidly quenched samples are usually specifically collected in order to avoid post-entrapment processes. However, in this study, with the exception of the caldera event sample (LH4a), none of the collected samples show evidence of rapid quenching (lavas). Olivine and plagioclase host phenocrysts were targeted and hand-picked after whole rock crushing. They are 0.5-2.0 mm in size. Olivine phenocrysts from HK14-44, HJ14-31 and HK14-05 (pre-caldera I and post-caldera) samples commonly contain isolated,

round melt inclusions up to 230 μm in size, with a single or several shrinkage bubble(s). For HK 14-44 and HK14-05, euhedral minerals are observed inside the SMI. Plagioclases from LH4a (caldera event) contain isolated, rounded to pseudomorphic melt inclusions up to 100 μm in size, with no shrinkage bubble or mineral.

3- ANALYTICAL PROCEDURES

3.1- X-ray microtomography

X-ray microtomography has been used extensively in the past two decades for characterizing Earth materials (Ketcham and Carlson, 2001; Cnudde and Boone, 2013). X-ray microtomography has been successfully applied to reveal the shape, orientation and 3D distribution of minerals, porosity and cracks in various rocks showing complex textures such as sedimentary rocks (Noiriel, 2015), metamorphic rocks (Sayab et al., 2015), magmatic rocks (Baker et al., 2012), mantle rocks (Créon et al., 2017) and ores (Kyle and Ketcham, 2015). Since the pioneering study of Nakashima et al. (1997), inclusions have been the subject of only a few studies by X-ray microtomography, even with more recent and powerful equipment (Kyle et al., 2004; Kyle and Ketcham, 2007a, b, 2008, 2015; Nowecki, 2014; Pamukcu et al., 2013, 2015; Gaetani et al., 2015; Créon et al., 2017). Those studies showed that X-ray microtomography allows the imaging of isolated inclusions, inclusion clusters and trails as well as discriminating and quantifying different phases within the inclusions in transparent (e.g., olivine) and opaque (e.g., pyrite) minerals. The fifteen samples analyzed consist of an individual or cluster of SMI hosted in individual minerals (0.5-2.0 mm diameter). The internal part of the minerals was observed and studied through laboratory X-ray micro-tomography at the *Laboratorio Universitario de Microtomografía de Rayos X* (Centro de Geociencias, UNAM, Querétaro, Mexico) on a ZEISS Xradia 510 Versa.

The detector used was a CCD ANDOR camera with 1080*1080 pixels and 32-bit resolution. Polychromatic microtomography with 30 to 40 keV radiation was performed on the minerals. The sample-detector source-sample distances were optimized for a pixel size equal to 1.01 to 3.37 μm with magnifications of 0.4x to 4.0x. Typically, the 3D images obtained are composed of 885×885×999 voxels (elementary image volume) with 32-bit gray-scale resolution. Acquisition time ranged from 2 to 8 hours for 1601 projections together with approximately 200 reference images (blanks). A correction of the ring artifacts was done directly during the analysis using specific filters.

Tomographic volume reconstructions were performed at the *Laboratorio Universitario de Microtomografía de Rayos X* (Centro de Geociencias, UNAM, Querétaro, Mexico) using ZEISS XRM software. Petrographic data treatments were performed using ImageJ[®] and Avizo 9.2[®] software. Each phase was individualized by segmentation of the volumes corresponding to the relative density range of each individual phase. Once the thresholds had been well defined, the volumes of the phases were segmented and quantified.

3.2- NanoSIMS microanalyses of C and H

After X-ray microtomography acquisition, the SMI were one-side polished, and grains were mounted into epoxy for the Nano-SIMS and EPMA analysis (see supplementary material).

3.2.1- Analytical procedure

Due to the very small sizes of the inclusions (from 30 to 230 μm), water and CO₂ contents in melt inclusions were determined using the Cameca NanoSIMS 50 installed at MNHN, Paris, France following the procedure of Bartoli et al. (2014) and Créon et al. (2017). The sample surface was sputtered by a Cs⁺ primary beam, set at 20 pA and rastered over 4 × 4 μm^2 surface area. We only collected ions from the inner 2 × 2 μm^2 (electronic gating using the

beam blanking mode) to reduce surface contamination (Stephant et al., 2014). An electron-flooding gun was used for charge compensation. Secondary ions of $^{12}\text{C}^-$, $^{16}\text{OH}^-$, $^{28}\text{Si}^-$, $^{27}\text{Al}^{16}\text{O}^-$ and $^{56}\text{Fe}^{16}\text{O}^-$ were collected in multicollection mode. Mass resolving power was set at minimum 6000, sufficient to resolve interferences on $^{16}\text{OH}^-$. A single analysis comprises a stack of 200 cycles, each cycle being 1.024 s long. Before each acquisition, we applied a presputtering over $6 \times 6 \mu\text{m}^2$ during 4 minutes using a high beam current (300 pA) in order to remove the gold coating (approximately 20 nm), surface contamination and to reach sputtering steady state (Thomen et al., 2014). The vacuum in the analysis chamber remained below 5×10^{-10} Torr during the session of water and CO_2 measurements.

3.2.2- Calibrations

Water and CO_2 concentrations were determined through the measurement of $^{12}\text{C}^-/^{28}\text{Si}^-$ and $^{16}\text{OH}^-/^{28}\text{Si}^-$ ratios, respectively. These ratios were converted into concentrations using calibration curves (see supplementary material) that had been determined using standards of known compositions. We used two sets of standards for the determination of water concentrations: three leucogranitic glasses with well-known H_2O concentrations (Acosta-Vigil et al., 2016) and four trachyandesitic glasses from the Stromboli volcano (Bureau et al., 2009). The leucogranite glasses are as follows: glass DL reported in Acosta-Vigil et al. (2003) with $\text{H}_2\text{O} = 6.5$ wt. %; glass LGB1 from Behrens and Jantos (2001) with $\text{H}_2\text{O} = 4.9$ wt. %; and the almost anhydrous glass B from Morgan and London (2005) with $\text{H}_2\text{O} = 300 \pm 42$ ppm. The trachyandesitic standards (STR 9, 10, 11 and 13) are glass fragments of shoshonite lava from the Stromboli volcano that were experimentally doped in carbon and water by Bureau et al. (2003). The water concentration of these standards was measured by elastic recoil detection analysis (CEA Saclay, France) and by SIMS (Cameca IMS 1280 at Centre de Recherche en Pétrographie et Géochimie, Nancy, France). The carbon concentration of the

four trachyandesite glasses were measured by nuclear reaction analysis (CEA Saclay, France) following the procedure described in Malavergne et al. (2014) and using a Cameca IMS 1280 at CRPG (Deloule et al., 1995). The analysis results of the samples are presented Table 2.

Data corrections using the aforementioned calibration and error calculations were performed using the R program following the procedure described in Créon et al. (2017). The errors reported in Table 3 combine counting statistics and the uncertainty of the calibration curves; the contribution from the latter dominates the reported uncertainty.

3.3- Electron Microprobe analyses

The major element composition of host minerals and glasses and minerals contained in SMI was analyzed in the 15 selected samples using a Cameca SX100 at CAMPARIS (Jussieu, Paris, France). The glass and minerals were analyzed with a 15-kV accelerating voltage. Calibrations were performed using international standards of minerals (e.g., diopside for Si, Mg and Ca, orthoclase for Al and K and apatite for P). Standard minerals were analyzed in order to test the accuracy of the analysis. For the glasses (SMI), we used a 4-nA defocused beam and a counting time of 10 s. The concentrations of S and Cl were determined with a 30-nA defocused beam and a counting time of 120 s on peak. The analysis accuracy was cross-checked against well-known glassy samples (see supplementary material): ALV981R23 tholeiitic glass fragments (Métrich and Clocchiatti, 1989; Mosbah et al., 1991), Ke12 pantellerite from Eburu (Kenya; Métrich and Rutherford, 1992), Cfa 47 trachytic obsidian from Italy (Métrich and Clocchiatti, 1989), and Vg2 basaltic glass (Thordarson et al., 1996; Métrich et al., 2001). The detection limits are <73 ppm for S and <44 ppm for Cl. Minerals were analyzed with a focused beam, with a beam current of 10-30 nA and a counting time varying from 10 to 20 s.

3.4- Mathematical initial composition determination of the SMI

The mathematical initial composition determination methodology developed in this study can be divided into 5 steps:

(1) X-ray microtomography acquisition of each mineral and its hosted SMI to determine the volume of each phase of the SMI (glass, bubble and the different mineral phases). (2) Observation in 3 dimensions (3D) of the SMI in order to validate if the mineral crystallization and bubble formation originate from the trapped melt or if they are due to a heterogeneous trapping. (3) Polishing of the minerals until the crosscut of the inclusion and NanoSIMS experiments on the glass phase to determine the dissolved CO₂ and H₂O contents. (4) Microprobe analyses to analyze the major and volatile (S, Cl) elements of the host mineral and of the mineral and the glass phases present in the SMI. (5) Mathematical homogenization following equation (1):

$$X_{SMI} = \Sigma[V_{Mineral(i)} * X_{Mineral(i)}] + [V_{Glass} * X_{Glass}] + [V_{Bubble} * X_{Bubble}], (1)$$

where X and V represent the composition and the volume, respectively. Volumes were obtained by X-ray microtomography, X_{Mineral} and X_{Glass} were determined by microprobe and NanoSIMS analysis, and X_{Bubble} was derived from the NanoSIMS analyses and thermodynamic modeling.

4- RESULTS

4.1- Petrographic observation in 2 dimensions

Olivine (pre- and post-caldera events) and plagioclase (caldera event) crystals were hand-picked from 0.5- to 2.0-mm grain size. SMI, first studied under an optic microscope, are rounded (except in plagioclase host-minerals where they are elongated following mineral rims), variable in size from 30 to 230 µm in diameter, are trapped as primary inclusions (Roedder, 1979) and are not co-trapped with any other fluid or mineral inclusions. SMI show

different evolution regarding the post-entrapment processes (Figure 1). Indeed, some SMI present no bubbles and no post-entrapment crystallization (PEC, Figure 1a,c) when others show bubbles and a high degree of PEC (up to 91 vol. % of PEC; Table 1, Figure 1b,e,f). The secondary minerals inside the SMI have small (nanometer) to large ($\sim 80 \mu\text{m}$) sizes and are euhedral.

4.2- Description of the solid phases

4.2.1- EPMA analysis

Host-mineral chemistry – The analyzed host-minerals are olivine ($\text{Fo}_{73.3-84.5}$, $n=12$) and plagioclase ($\text{An}_{28-47} \text{Alb}_{50-68} \text{Or}_{2-5}$, $n=3$) phenocrysts. EPMA analyses of the core, middle and rim parts of the host minerals show that the minerals are not zoned chemically (Table 4).

Glass (major and volatile elements) – All analyzed glasses, though the volcanic column, and trapped as SMI in olivine and plagioclase phenocrysts show basalt to trachyte compositions (Table 3). Pre- and pre-caldera II crystallized SMI have trachytic glass compositions; caldera non-crystallized SMI have trachytic to rhyolitic glass composition; and post-caldera crystallized SMI (HK14-05) and non-crystallized SMI (HJ14-31) have basaltic trachyandesite to trachyandesite and basalt to trachyandesite glass compositions, respectively (Figure 2). H_2O contents are highly variable between 0.40 and 4.65 wt. %, and CO_2 concentrations are also highly variable but in lower abundance, with 95 to 1867 ppm dissolved in glass (Table 3).

Clinopyroxene daughter crystals – Clinopyroxenes were analyzed in eight of the SMI host samples (pre- and early post-caldera events, Table 5). One similar Ca-rich clinopyroxene composition is observed in all the clinopyroxene-carrying SMI. A second composition family of Fe-rich clinopyroxenes is observed in HK14-44-1 (pre-caldera I event), HK14-05-1 and

HK14-05-9 (early post-caldera event) samples. In the following text, the first clinopyroxene composition will be named CpxI, and the second family will be named CpxII.

Plagioclase daughter crystals – In the early post-caldera event in sample HK14-05-3, a plagioclase daughter crystal family is present (Table 5).

Spinel daughter crystals – Spinel was analyzed in only four samples because of their very tiny dimensions (pre-caldera II event and early post-caldera event, Table 5). The spinels are magnetites with FeO* rich (68.1-74.2 wt. %) and Cr-poor (0.0-0.8 wt. %) compositions. MgO and Al₂O₃ in the spinels are more variable, with 5.4 to 10.2 wt. % and 4.2-12.4 wt. %, respectively.

4.2.2- Melt, minerals and retraction bubble volume measurements

The volumes of the different phases of the SMI are reported in Table 1 and will be used for initial composition determination of the SMI in *section 5*.

4.2.3- X-ray absorbance and density

Density is directly linked to the composition of the phases. The density variation between phases will therefore be highlighted by different local attenuation of the X-ray beam in the 3D images. Six various X-ray absorbance are observed in the SMI. Thanks to phase compositions (obtained by EPMA) and 3D images (obtained by X-ray microtomography), the association between composition and X-ray absorbance is direct, and the phases can be named as follows:

Very high absorbance/“very high” density – Spinel. Spinel has high density and Fe-rich composition (68.1-74.2 wt. %).

High absorbance/“high” density – Fe-rich clinopyroxene (CpxII). CpxII are Fe-rich; therefore, a higher density than Ca-rich clinopyroxene is expected. This variation in

composition is clearly observed in X-ray absorbance too. The segmentation of both minerals is therefore direct.

Medium high absorbance – Ca-rich clinopyroxene (CpxI). Ca-rich clinopyroxenes are less rich in FeO and less dense than CpxII. The X-ray absorbance is therefore lower.

Medium low absorbance – Plagioclase. Plagioclase and glass have similar X-ray absorbance, which can complicate the segmentation somewhat. Plagioclases are Al-rich and Fe-poor, and therefore the X-ray absorbance is “medium low”.

Low absorbance/“low” density – Glass. Similar to plagioclase, glass will have a low X-ray absorbance due to its composition.

Very low absorbance/“very low” density – Bubble. Bubbles are the less-absorbent phase, as the density is assumed to be very low or at least much lower than the glass-phase.

Laboratory X-ray microtomography does not allow the determination of phase density from the X-ray absorbance in contrast to synchrotron X-ray microtomography. However, phase density is not required for the mathematical SMI reconstruction described here.

4.2.4- Grain morphology and location

2D and 3D observations highlight that the minerals inside SMI are euhedral. CpxI are relatively small crystals, located at the rim of the SMI and in direct contact with the olivine host mineral. Spinels are tiny crystals also located at the host-mineral and SMI contact. Plagioclase is very large and occupies almost half of the total SMI. It is in direct contact with host-olivine. CpxII have larger diameter than CpxI and are located at the rim as well as at the center of the SMI and are often observed in contact with the bubble and following the bubble-shape.

4.3- Order of appearance of the different phases into the SMI

Crystallization sequences of different daughter minerals make a strong argument that microtomography is a valuable technique for studying melt inclusions. Indeed, 3D observations allowed us to determine that CpxI and spinel were the first to crystallize. This is consistent with their location at the SMI rim. Plagioclase mineral crystallization is slightly more problematic, as it occupies half of the whole SMI. Moreover, there is no evidence of a heterogeneous trapping, and an early crystallization of that mineral is expected. 3D observations show its importance with the CpxII family. Indeed, CpxII is a second generation of clinopyroxene, which crystallized after first generation clinopyroxenes and spinel. It is also observed that CpxII follow in most of the samples the shapes of the bubble (SEM images, Figure 1e).

5- DISCUSSION

5.1- Origin of the SMI daughter minerals and bubbles

The daughter minerals present in SMI are euhedral and do not have evidence of a spongy rim or other indicators of disequilibrium with the SMI-glass host. Moreover, the daughter minerals are located at the rim of the SMI or at the border of the bubble and follow their shapes. These observations confirm that daughter minerals were formed within the inclusions after the SMI trapping.

The bubble volumes are controlled by the difference in thermal expansion between the trapped melt and the host phenocryst during cooling from the trapping temperature to T_{glass} rather than by the amount of CO_2 contained in the bubble (Moore et al., 2015). Therefore, the vol. % vapor to be expected in any melt inclusion in which the volume change of the host and the glass are known as a function of temperature may be estimated. We calculated the volume change of the melt and host mineral as a function of temperature for SMI hosted by olivine

following the method described by Moore et al., (2015). Bubble volumes associated with the thermal expansion in SMI are significantly low in comparison with bubble volumes measured by X-ray microtomography. Indeed, the measured bubble volumes vary between 5.2 and 10.2 vol. % with an average volume of 7.5 vol. %, while the volumes associated with the thermal expansion in SMI vary between 1.5 and 4.0 vol. % with an average volume of 2.6 vol. % (Table 9). This observation was to be expected, as the rate of cooling can have a profound effect on shrinkage bubble volume, and an “ideal” shrinkage bubble volume may not be representative in some cases (e.g., Lowenstern 1994b). Molar volumes can differ between the glass and crystal phases, and that could explain those differences. To test this hypothesis and to verify if the differences between bubble volumes are too large to have formed after trapping, SMI-masses of the theoretical non-crystallized SMI and of the crystallized analyzed SMI were calculated. The densities of the theoretical bubbles were determined between 9.4 and 78.1 g.cm³. Those densities are obviously too high to be correct and highlight the trapping of a heterogeneous melt + fluid mixed phase.

Raman analyses were performed on the bubbles (see supplementary material for information), and no measurable volatile contents were found. The absence of measurable volatile content within the shrinkage bubble can be explained by the potential presence of micro/nano fractures formed during eruption, as suggested from models (Tait, 1992), weathering or sample preparation; it is also possible that crystallized SMI may scatter most of the incident light used in Raman analyses and make it impossible to analyze the bubbles.

Large minerals crystallized from the trapped melt in the SMI are strong evidence of a low quenching rate of the volcanic product and of the tardive crystallization of at least the second generation of clinopyroxenes (after bubble formation, Figure 1c).

5.2- First step of the mathematical reconstruction of the original SMI compositions, the daughter phases crystallization correction

The SMI with evidence of post-entrapment crystallization have been homogenized mathematically following equation 1 (see Table 1 and section 5.1). The compositions of the SMI after the post-entrapment crystallization (PEC) correction exhibit less evolved glass compositions, from basanite to basaltic trachyandesite, than non-corrected SMI (basaltic trachyandesite to trachyte; Table 3, 6).

5.3- Second step of the mathematical reconstruction, the chemical equilibrium

In SMI studies, chemical equilibrium can be verified between the trapped SMI and the host olivine if $Kd^{Mg-Fe} = 0.3$ (Roedder and Emslie, 1970). A constant value of Kd^{Mg-Fe} provides a simple and practical way to assess equilibrium in natural mineral–glass pairs. The extent to which Kd^{Mg-Fe} is truly constant has been the subject of debate (e.g., Mysen et al., 1975). Since the work of Roedder and Emslie (1970), the number of olivine saturated experiments reported in the literature has increased steadily, and a compilation of data shows that published values of Kd^{Mg-Fe} cover at least the range 0.17 to 0.45. Diverse origins for these variations have been discussed (see Toplis, 2005 and references therein). However, in this study, it is considered that the possible variability of the Kd is less significant regarding the uncertainty associated with the mathematical reconstruction of the SMI. Therefore, in this study, a Kd^{Mg-Fe} of 0.3 has been used to test chemical equilibrium between the trapped SMI and the host olivine. The chemical equilibrium is considered verified if the olivine host crystal and initial SMI compositions are the result of a single-source process and/or if SMI is not modified by mineral crystallization or elemental diffusion (with host olivine). Considering that minerals and SMI are the result of a single-source process, a Kd^{Mg-Fe} of 0.3 would allow us not only to

verify the validity of the mathematical homogenization method but also to correct the SMI compositions for host mineral (olivine) post-entrapment crystallization at the SMI rim.

Once the post entrapment crystallization is corrected through the mathematical approach, the chemical equilibrium between the melt and the host olivine has been verified using the K_d^{Mg-Fe} . The K_d^{Mg-Fe} values vary between 0.03 and 0.47 (Table 6) and therefore do not satisfy an equilibrium between the melt and the host olivine for the main part of the samples. There is little constraint on the redox conditions of the Los Humeros volcanic products, and we thus used a range of fO_2 and Fe^{3+} proportions (Table 6). For a temperature of 1150°C and a K_d^{Mg-Fe} value of 0.30 (Toplis, 2005), the extent of olivine post entrapment crystallization is calculated to be below 6.5%. The PEC of olivine has therefore been corrected in order to satisfy the chemical equilibrium between the melt and the olivine host ($K_d^{Mg-Fe} = 0.3$). Two samples (pre-caldera I HK14-44-1 and pre-caldera II HK-14-26-1 SMI) are not in agreement with this equilibrium ($K_d^{Mg-Fe} = 0.45$ and 0.47). The absence of equilibrium can be related to various effects, such as the microprobe resolution for the analysis of the very tiny minerals inside the SMI (<10 μm diameter), the microtomograph resolution, and the influence of the composition on the K_d , or can be due to the 2D limitation of the chemical analysis of the minerals (as opposed to the mineral volume determination in 3D). Plagioclase PEC at the SMI rim was not corrected, as no evidence of post-entrapment modification was observed. There is no volatile saturation, even if the volatile content is high, and no mineral crystallization inside. A fast quenching is expected for plagioclase, which is in agreement with the pumice host. The corrected SMI compositions are given in Table 6 and are located within the compositional range of the host bulk-rocks (see supplementary material for whole rock compositions). These compositions illustrate a dilution of the measured volatile element compositions (NanoSIMS) due to the mathematical “dilution” of the minerals inside the melt.

The $K_d^{\text{Mg-Fe}}$ of 0.3 obtained for the large majority of the SMI and with extent of olivine PEC below 6.5%, together with the similitude between the reconstructed SMI and the host bulk-rock composition (see supplementary material), are a first strong validation of the SMI mathematical homogenization method.

5.4- Melt saturation pressures and SMI trapping pressures

The quenching rate has a strong influence on the volatile diffusion from the melt to the bubble. Indeed, if the quenching rate is too fast, it could avoid having the exsolved CO_2 in the trapped melt to diffuse into the bubble to produce an equilibrium concentration (pressure). The petrographic observations provide evidence of a low quenching rate that allowed the formation of relatively large minerals (clinopyroxenes and spinels) to occur inside the SMI (Figure 1). Regarding this petrographic evidence, an equilibrium concentration (pressure) between the melt and the bubble can be concluded for almost all the crystallized samples (1.6-3.5 Ma, 220 Ka, 30 Ka).

To assess the conditions of melt super-saturation, mixed-vapor ($\text{H}_2\text{O-CO}_2$) saturation isotherms (Table 6) were calculated for the different melt compositions reconstructed from the present samples for a temperature of 1150°C (estimated trapping temperature for olivine-hosted SMI and for basaltic melt composition) using Rhyolite-MELTS software (version 1.2.0, Gualda et al., 2012; Ghiorso and Gualda, 2015) and following the methodology described in Créon et al. (2017). This model is suitable for the calculation of thermodynamic equilibrium of mafic to felsic systems with H_2O and CO_2 over a pressure range of 0–3 GPa, corresponding to the expected conditions of the magma path in Los Humeros. Saturation pressures were estimated for each SMI composition, as Rhyolite-MELTS takes in account the melt composition for volatile solubility calculations (Gualda et al., 2012; Ghiorso and Gualda, 2015). Based on vapor-saturation isotherms, bubble-melt equilibrium pressures were

calculated from the CO₂ and H₂O contents of melts determined by NanoSIMS (Table 3). These saturation pressures at 1150 °C vary between 0.23 and 1.94 kbars (Table 7). Melt saturation pressures of 0.23 to 1.94 kbars were converted to CO₂-H₂O density using the program MacFlinCor[®] 8.93 from Brown and Hagemann (1994), and fluid composition was obtained with the Rhyolite-MELTS program (Table 8). The densities obtained vary between 0.068 and 0.328 g.cm⁻³.

The volatile/glass mass ratio corresponding to the melt + bubble system was calculated following equation (2):

$$\frac{M(\text{volatile})}{M(\text{glass})} = \frac{V(\text{volatile})}{V(\text{glass})} \frac{\rho(\text{volatile})}{\rho(\text{glass})}, \quad (2)$$

where M is mass, V is volume, and ρ is density. V(volatile) and V(glass) were obtained by X-ray microtomography, $\rho(\text{glass})$ was calculated with the method of Dixon et al. (1995) using the major element and H₂O compositions of the melts, and $\rho(\text{volatile})$ was derived from the NanoSIMS analyses and thermodynamic modeling (Rhyolite-MELTS, Gualda et al., 2012; Ghiorso and Gualda, 2015) as described in (Créon et al., 2017).

The calculated volatile/melt mass ratios range from 0.54 to 2.00 wt. % H₂O and from 1579 to 6260 ppm CO₂ (Table 6). These ratios would correspond to a single-phase system at pressures of 3.0 to 17.1 kbars (Table 6). The 6.42 Ka samples show no PEC; therefore, we cannot conclude on an equilibrium concentration (pressure) between the melt and the bubble that requires slow quenching rates. However, a minimum estimation from the volatile content dissolved in the melt (considering no volatile in the bubble) can be given. The pressures range between 0.29 and 0.55 kbars, (Table 6). We note that HK14-05-8 presents a very important trapping pressure (17.1 kbars) which may be surprising given the forsterite content of its host olivine (~80%).

6- Methodological advances

SMI affected by post-entrapment processes, such as crystallization (PEC) and/or formation of a bubble, are generally more complicated to interpret. Indeed, in some cases, it may be impossible to dissolve the bubble completely just by heating, and high-pressure and controlled fO_2 conditions are usually required. Therefore, a general preference to select melt inclusions for analysis that have experienced minimal post-entrapment effects is done.

Here, we propose a new multi-disciplinary method to study crystallized SMI in order to better constrain the initial SMI compositions.

Moore et al. (2015) recently demonstrated that vapor bubbles are a strong contribution to melt inclusion volatile budgets; the new method developed here takes that into account by the addition of the volatile phase exsolved in bubbles to the bulk volatile content of the inclusions thanks to the accurate 3D measurements of the bubble volume.

In common SMI studies, crystallized SMI are less studied, and samples are mostly collected to obtain the most rapidly quenched samples. This sampling strategy was until now the best option to estimate the initial SMI compositions. The new mathematical approach developed here can be used for samples having experienced a long quench such as lavas. It can be applied to a wide range of volcanic products. This will significantly improve the knowledge of volcanic processes, including melt migration and degassing in the lithospheric mantle and the crust.

The presented approach is a major improvement in the methodology for the study of SMI. This approach will not replace the well-known methods but can be used as a refinement for more complex samples such as crystallized SMI.

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Figure captions:

Figure 1 : a- Optic microscope picture of LH4a-5 SMI in transmitted light, SMI presents no post-entrapment modification ; b- Optic microscope picture of HK14-05-9 SMI in transmitted light, SMI presents PEC and bubble ; c- SEM picture of LH4a-5 SMI presenting no post-entrapment modification ; d- SEM picture HJ14-31-6 SMI presenting non post-entrapment crystallization and bubble formation ; e- SEM picture of HK14-05-9 SMI presenting PEC and bubble ; f- X-ray microtomography 3D images of HK14-44-1 SMI illustrating minerals repartitions inside the SMI.

Figure 2 : TAS diagram illustrating analyzed silicate melt inclusion compositions (diamonds) and reconstructed silicate melt inclusion compositions (circles)

Age	Episode	Sample	Host mineral	Bubble	PEC (vol. %)	SMI phases
1.6-3.5 My	Ante-caldera	HK14-44-1	Olivine	Yes (11.3 vol. %)	49.6	Cpx I (18.6 vol. %) + Sp (0.3 vol. %) + Cpx II (30.7 vol. %) + Glass (50.41 vol. %)
190 Ky	Ante-caldera	HK14-26-1	Olivine	Yes (8.7 vol. %)	90.9	Cpx I (4.5 vol. %) + Sp (78.5 vol. %) + Glass (8.3 vol. %)
190 Ky	Ante-caldera	HK14-26-3	Olivine	Yes (5.2 vol. %)	58.3	Cpx I (47.8 vol. %) + Sp (0.3 vol. %) + Glass (49.7 vol. %)
190 Ky	Ante-caldera	HK14-26-7	Olivine	Yes (9.9 vol. %)	44.9	Cpx I (40.1 vol. %) + Sp (0.3 vol. %) + Glass (49.7 vol. %)
69 Ky	Caldera	LH4a-5	Plagioclase	No	0.0	Glass (100 vol. %)
69 Ky	Caldera	LH4a-6	Plagioclase	No	0.0	Glass (100 vol. %)
69 Ky	Caldera	LH4a-8	Plagioclase	No	0.0	Glass (100 vol. %)
8.9 Ky	Post-caldera	HK14-05-1	Olivine	Yes (6.3 vol. %)	16.6	Cpx I (4.3 vol. %) + Sp (0.0 vol. %) + Cpx II (12.3 vol. %) + Glass (83.4 vol. %)
8.9 Ky	Post-caldera	HK14-05-3	Olivine	Yes (7.3 vol. %)	54.1	Cpx I (5.9 vol. %) + Sp (2.7 vol. %) + Pl (41.5 vol. %) + Glass (42.6 vol. %)
8.9 Ky	Post-caldera	HK14-05-8	Olivine	Yes (7.8 vol. %)	27.3	Cpx I (22.0 vol. %)+ Sp (5.3 vol. %) + Glass (72.7 vol. %)
8.9 Ky	Post-caldera	HK14-05-9	Olivine	Yes (6.3 vol. %)	28.8	Cpx I (22.9 vol. %) + Sp (5.3 vol. %) + Cpx II (0.6 vol. %) + Glass (71.2 vol. %)
6.4 Ky	Post-caldera	HJ14-31-1	Olivine	Yes (1.2 vol. %)	0.0	Glass (98.8 vol. %)
6.4 Ky	Post-caldera	HJ14-31-3	Olivine	No	0.0	Glass (100 vol. %) - Nano-PEC
6.4 Ky	Post-caldera	HJ14-31-5	Olivine	Yes (5.2 vol. %)	0.0	Glass (94.8 vol. %) - Nano-PEC
6.4 Ky	Post-caldera	HJ14-31-6	Olivine	Yes (7.0 vol. %)	0.0	Glass (93.0 vol. %) - Nano-PEC

Table 1: Petrographic description of the silicate melt inclusions. SMI- Silicate melt inclusions. Ol- Olivine, CpxI- Clinopyroxene first generation, CpxII- Clinopyroxene second generation, Sp- Spinel, PEC- Post-entrapment crystallisation

	Leucogranitic glasses			Trachyandesitic glasses			
Sample	DL†	B	LGB/1	STR9	STR10	STR11	STR13
SiO ₂	73.81 (0.37)	77.95	73.95	50.2	50.2	50.2	50.2
TiO ₂	0	0	0.09	1	1	1	1
Al ₂ O ₃	12.01 (0.13)	12.78	12.4	18	18	18	18
FeO	0	0	0.93	7.2	7.2	7.2	7.2
MnO	0	0	0.04	0	0	0	0
MgO	0	0	0.1	5.6	5.6	5.6	5.6
CaO	0.02 (0.02)	0.02	0.84	11.3	11.3	11.3	11.3
Na ₂ O	4.15 (0.12)	4.51	3.74	2.7	2.7	2.7	2.7
K ₂ O	4.49 (0.11)	4.73	4.25	2.2	2.2	2.2	2.2
P ₂ O ₅	0	0	0	0	0	0	0
F	0	0	0	0	0	0	0
Cl	0	0	0	0	0	0	0
H ₂ O	5.52	0.03	4.86	0.48	0.38	0.94	4.59
CO ₂	n.d.	n.d.	n.d.	556	664	632	864

Table 2: Nano-SIMS standard compositions. † Mean composition after 80 analyses. Numbers in parentheses refer to 1-sigma standard deviations. H₂O in % determined by ERDA. CO₂ in ppm determined by SIMS.

	HJ14-31-1	HJ14-31-3	HJ14-31-5	HJ14-31-6	HK14-05-1	HK14-05-3	HK14-05-8	HK14-05-9	HK14-26-1	HK14-26-3	HK14-26-7	HK14-44-1	LH4a-5	LH4a-6	LH4a-8
Age	6.4 Ky	6.4 Ky	6.4 Ky	6.4 Ky	8.9 Ky	8.9 Ky	8.9 Ky	8.9 Ky	190 Ky	190 Ky	190 Ky	1.6-3.5My	69 Ky	69 Ky	69 Ky
SiO ₂	46.54	58.23	57.15	57.98	58.97	61.23	61.91	55.94	64.57	60.20	61.55	60.64	69.31	64.92	66.80
TiO ₂	0.04	1.62	1.36	1.55	0.76	0.53	0.85	0.46	0.46	0.33	0.25	0.55	0.36	0.53	0.38
Al ₂ O ₃	33.09	20.37	21.30	20.39	22.81	22.96	20.32	25.23	19.46	21.85	23.11	21.36	14.13	15.10	14.92
FeO*	1.33	1.95	3.10	2.86	2.08	1.28	1.63	1.55	1.41	1.16	0.86	1.33	1.82	2.77	2.22
Cr ₂ O ₃	0.04	0.00	0.00	0.03	0.01	0.02	0.02	0.02	0.03	0.03	0.01	0.01	0.01	0.03	0.04
MnO	0.00	0.17	0.13	0.05	0.05	0.02	0.05	0.07	0.03	0.05	0.02	0.05	0.02	0.05	0.05
MgO	0.07	0.45	0.66	0.78	0.87	0.18	0.89	0.49	1.02	0.13	0.16	0.36	0.21	0.52	0.31
NiO	0.00	0.08	0.04	0.07	0.03	0.03	0.03	0.01	0.15	0.00	0.04	0.01	0.02	0.03	0.08
CaO	16.29	6.34	7.29	6.89	6.24	7.06	3.76	8.37	1.87	3.02	1.65	2.18	0.93	1.58	1.29
Na ₂ O	1.97	5.13	5.02	5.21	4.94	5.06	5.37	4.93	6.08	7.93	6.83	8.79	3.94	4.72	4.50
K ₂ O	0.05	2.54	2.27	2.58	1.82	1.78	2.35	1.34	3.23	3.43	5.68	2.24	4.73	3.91	4.22
P ₂ O ₅	0.20	0.45	0.37	0.62	0.42	0.31	0.37	0.24	0.82	0.55	0.38	1.71	0.03	0.12	0.06
H ₂ O	0.45	0.40	0.45	0.49	1.06	1.39	2.47	1.09	1.00	4.33	2.19	1.35	4.31	4.52	4.65
σ 1 (H ₂ O)	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
CO ₂	165	115	174	144	322	334	259	247	655	1867	96	204	95	95	306
σ 1 (CO ₂)	12	11	12	12	15	21	14	14	17	57	12	12	14	12	16
SO ₂	0.00	0.05	0.06	0.06	0.17	0.06	0.14	0.07	0.37	0.20	0.10	0.00	0.01	0.02	0.01
Cl	0.00	0.09	0.07	0.09	0.07	0.06	0.08	0.05	0.13	0.08	0.06	0.06	0.10	0.09	0.11
Total	265.06	212.87	273.28	243.51	422.29	435.96	359.24	346.85	755.64	1970.61	198.61	304.93	194.72	194.30	405.86

Table 3: Analyzed glass major and volatile element compositions in silicate melt inclusions. Concentration in wt.% (except for CO₂ in ppm). σ 1- sigma standard deviations for H₂O and CO₂ are given for information.

Comment	HJ14-31-1_C	HJ14-31-1_M	HJ14-31-1_R	HJ14-31-3_C	HJ14-31-3_M	HJ14-31-3_R	HJ14-31-5_C	HJ14-31-5_M	HJ14-31-5_R
SiO₂	37.49	38.37	38.12	38.27	38.81	38.99	38.71	39.14	38.78
TiO₂	0.16	0.11	0.05	0.02	0.00	0.02	0.07	0.00	0.00
Al₂O₃	0.00	0.00	0.00	0.08	0.00	0.04	0.00	0.00	0.00
FeO*	21.72	22.43	21.35	19.53	19.88	19.24	17.61	18.61	17.88
MnO	0.18	0.20	0.33	0.17	0.20	0.21	0.27	0.42	0.39
MgO	39.65	39.41	39.39	41.71	41.60	40.91	42.22	41.81	42.18
CaO	0.14	0.14	0.17	0.15	0.18	0.23	0.16	0.13	0.24
Na₂O	0.00	0.03	0.00	0.04	0.00	0.00	0.00	0.00	0.00
K₂O	0.04	0.01	0.01	0.01	0.02	0.00	0.00	0.00	0.02
P₂O₅	0.00	0.01	0.05	0.00	0.05	0.00	0.04	0.00	0.18
Cr₂O₃	0.00	0.07	0.07	0.00	0.16	0.01	0.00	0.00	0.00
NiO	0.01	0.21	0.13	0.00	0.13	0.27	0.13	0.31	0.05
Total	99.49	101.00	99.67	100.06	101.09	99.92	99.23	100.45	99.74
Te	0.19	0.22	0.36	0.18	0.22	0.22	0.29	0.46	0.42
Fo	76.19	75.49	76.22	78.89	78.50	78.69	80.63	79.51	80.18
Fa	23.42	24.10	23.18	20.72	21.05	20.76	18.86	19.85	19.07

Table 4: Major element compositions for melt inclusion host minerals. Concentration in wt.% – Part 1

Comment	HK14-05- 8_C	HK14-05- 8_M	HK14-05- 8_R	HK14-05- 9_C	HK14-05- 9_M	HK14-05- 9_R	HK14-26- 1_C	HK14-26- 1_M	HK14-26- 1_R
SiO₂	38,58	39,53	39,46	37,07	37,23	38,13	39,12	38,73	39,41
TiO₂	0,00	0,02	0,00	0,02	0,02	0,14	0,00	0,00	0,00
Al₂O₃	0,11	0,00	0,00	0,00	0,10	0,00	0,05	0,25	0,00
FeO*	19,53	18,85	17,69	20,10	19,66	19,66	16,11	15,01	14,81
MnO	0,27	0,11	0,19	0,33	0,17	0,18	0,14	0,26	0,45
MgO	41,72	40,80	40,62	41,19	40,51	40,67	44,60	44,87	45,71
CaO	0,13	0,15	0,19	0,18	0,17	0,14	0,24	0,34	0,30
Na₂O	0,00	0,00	0,06	0,00	0,00	0,00	0,02	0,03	0,01
K₂O	0,06	0,00	0,05	0,00	0,05	0,00	0,02	0,00	0,01
P₂O₅	0,00	0,02	0,03	0,00	0,00	0,07	0,03	0,00	0,00
Cr₂O₃	0,10	0,15	0,15	0,04	0,00	0,00	0,03	0,00	0,02
NiO	0,34	0,03	0,23	0,03	0,17	0,29	0,08	0,17	0,23
Total	100,85	99,72	98,67	98,98	98,09	99,33	100,44	99,65	100,95
Te	0,29	0,13	0,21	0,36	0,18	0,20	0,15	0,27	0,47
Fo	78,84	79,16	79,97	78,04	78,26	78,36	82,76	83,59	83,89
Fa	20,70	20,51	19,54	21,36	21,31	21,25	16,77	15,68	15,25

Table 4: Major element compositions for melt inclusion host minerals. Concentration in wt.% – Part 2

Comment	LH4a-5_C	LH4a-5_M	LH4a-5_R	LH4a-6_C	LH4a-6_M	LH4a-6_R	LH4a-8_C	LH4a-8_M	LH4a-8_R
SiO₂	60,68	59,44	61,23	54,86	54,89	56,76	60,45	60,27	60,20
TiO₂	0,05	0,14	0,00	0,00	0,05	0,00	0,05	0,02	0,00
Al₂O₃	25,07	26,28	25,41	27,73	26,22	27,53	25,09	25,85	25,07
FeO*	0,38	0,52	0,31	0,36	0,37	0,20	0,36	0,37	0,41
MnO	0,01	0,00	0,00	0,05	0,00	0,07	0,03	0,07	0,03
MgO	0,00	0,00	0,02	0,06	0,03	0,03	0,01	0,00	0,00
CaO	5,62	6,80	6,22	9,63	8,72	9,61	6,58	6,92	6,62
Na₂O	7,60	7,04	7,10	5,81	6,63	5,66	7,16	7,33	7,19
K₂O	0,81	0,68	0,74	0,29	0,44	0,37	0,77	0,67	0,78
P₂O₅	0,02	0,04	0,05	0,20	0,06	0,10	0,03	0,08	0,04
Cr₂O₃	0,05	0,13	0,00	0,08	0,06	0,00	0,00	0,00	0,05
NiO	0,16	0,00	0,05	0,00	0,00	0,00	0,00	0,07	0,00
Total	100,52	101,08	101,14	99,07	97,47	100,37	100,52	101,65	100,40
An	27,63	33,43	31,18	46,99	41,02	47,36	32,18	32,99	32,22
Ab	67,60	62,62	64,42	51,33	56,49	50,49	63,32	63,24	63,27
Or	4,77	3,95	4,40	1,68	2,49	2,15	4,50	3,78	4,50

Table 4: Major element compositions for melt inclusion host minerals. Concentration in wt.% – Part 3

	HK14-05-1		HK14-05-3			HK14-05-8		HK14-05-9			HK14-26-1		HK14-26-3	HK14-26-7	HK14-44-1	
	CpxI	CpxII	CpxI	Pl	Sp	CpxI	Sp	CpxI	CpxII	Sp	CpxI	Sp	CpxI	CpxI	CpxI	CpxII
SiO₂	40.59	27.19	44.09	53.16	11.01	42.67	0.67	40.23	24.55	0.00	40.79	0.14	40.58	41.30	41.53	23.78
TiO₂	2.17	5.53	3.07	0.14	2.51	2.00	1.77	1.61	3.66	2.84	6.63	0.00	2.98	2.80	3.05	10.05
Al₂O₃	13.31	18.48	7.26	29.55	4.20	11.04	12.44	12.33	16.12	9.90	13.22	0.32	13.54	15.07	11.65	19.04
FeO*	10.72	24.94	11.99	1.19	68.35	10.57	68.06	11.51	27.86	74.22	7.48	69.41	9.71	9.77	12.94	21.83
MnO	0.00	0.10	0.19	0.01	0.55	0.19	0.29	0.08	0.20	0.20	0.10	0.04	0.12	0.17	0.10	0.09
MgO	9.52	10.26	10.64	0.13	8.82	10.63	10.15	10.05	10.79	5.44	9.89	0.07	9.85	7.76	10.19	12.20
CaO	22.24	10.28	21.52	12.21	0.59	21.79	0.13	22.01	11.40	0.36	21.39	0.00	21.09	20.64	16.31	11.33
Na₂O	0.25	1.16	0.75	4.15	0.21	0.47	0.00	0.50	0.94	0.04	0.73	0.00	0.52	0.89	1.57	1.09
K₂O	0.02	0.46	0.07	0.25	0.19	0.01	0.00	0.03	0.13	0.00	0.21	0.01	0.00	0.51	0.25	0.03
P₂O₅	0.53	0.25	0.52	0.12	0.09	0.41	0.09	0.46	0.20	0.00	0.55	0.00	0.49	0.39	0.39	0.18
Cr₂O₃	0.10	0.00	0.00	0.03	0.00	0.05	0.82	0.05	0.00	0.00	0.13	0.38	0.06	0.11	0.12	0.10
NiO	0.03	0.00	0.00	0.00	0.02	0.07	0.00	0.00	0.03	0.21	0.00	10.71	0.03	0.06	0.35	0.11
Total	99.49	98.65	100.14	100.94	96.56	99.91	94.41	98.91	95.89	93.21	101.21	81.08	99.02	99.49	102.72	99.83

Table 5: Silicate melt inclusion daughter minerals major element compositions. Concentration in wt.%.

Comment	HK14-05-1	HK14-05-3	HK14-05-8	HK14-05-9	HK14-26-1	HK14-26-3	HK14-26-7	HK14-44-1	HJ14-31-1	HJ14-31-3	HJ14-31-5	HJ14-31-6	LH4a-5	LH4a-6	LH4a-8
Cpx + Sp corrected compositions															
SiO ₂	54.27	51.01	54.44	49.20	53.18	45.59	47.15	45.60	46.54	58.23	57.15	57.98	69.31	64.92	66.80
TiO ₂	1.41	0.53	1.15	0.87	3.40	1.64	1.25	3.92	0.04	1.62	1.36	1.55	0.36	0.53	0.38
Al ₂ O ₃	21.87	22.58	17.87	21.41	17.74	15.97	17.53	18.78	33.09	20.37	21.30	20.39	14.13	15.10	14.92
FeO _{tot}	5.26	3.61	7.10	7.82	5.68	10.84	4.57	9.98	1.33	1.95	3.10	2.86	1.82	2.77	2.22
FeO	3.42	2.89	4.97	5.87	3.69	7.59	2.97	7.48	1.07	1.27	2.02	1.86	0.91	1.38	1.11
Fe ₂ O ₃	2.04	0.80	2.37	2.17	2.21	3.61	1.78	2.77	0.30	0.76	1.21	1.11	1.01	1.54	1.23
MnO	0.05	0.04	0.10	0.08	0.04	0.08	0.08	0.07	0.00	0.17	0.13	0.05	0.02	0.05	0.05
MgO	2.40	0.99	3.52	3.01	4.86	5.02	3.20	5.82	0.07	0.45	0.66	0.78	0.21	0.52	0.31
CaO	7.43	9.35	7.53	11.10	6.92	11.89	9.11	7.61	16.29	6.34	7.29	6.89	0.93	1.58	1.29
Na ₂ O	4.27	3.92	4.01	3.63	4.19	3.57	3.75	5.06	1.97	5.13	5.02	5.21	3.94	4.72	4.50
K ₂ O	1.58	0.87	1.72	0.96	2.14	1.43	3.03	1.19	0.05	2.54	2.27	2.58	4.73	3.91	4.22
P ₂ O ₅	0.41	0.22	0.36	0.28	0.66	0.48	0.35	0.99	0.20	0.45	0.37	0.62	0.03	0.12	0.06
SO ₂	0.14	0.03	0.10	0.05	0.01	0.08	0.05	0.00	0.00	0.05	0.06	0.06	0.01	0.02	0.01
Cl	0.06	0.03	0.06	0.03	0.01	0.03	0.03	0.03	0.00	0.09	0.07	0.09	0.10	0.09	0.11
H ₂ O	1.06	0.53	1.81	0.99	1.40	1.80	1.10	0.69	0.43	0.43	0.50	0.52	4.32	4.52	4.65
CO ₂	230	137	188	133	103	779	48	103	132	115	142	144	95	95	306
[Fe ³⁺ /Fetot]	0,35	0,20	0,30	0,25	0,35	0,30	0,35	0,25	0,20	0,35	0,35	0,35	0,50	0,50	0,50
Crystallization rates															
X Fo	0.000	0.026	0.000	0.020	0.000	0.065	0.000	0.000	0.018	0.012	0.025	0.018	-	-	-
KD	0.324	0.298	0.322	0.297	0.447	0.301	0.349	0.475	0.298	0.297	0.300	0.303	-	-	-
Ol corrected compositions															
SiO ₂	54.27	50.68	54.44	48.96	53.18	45.17	47.15	45.60	46.39	58.00	56.70	57.61	-	-	-
TiO ₂	1.41	0.52	1.15	0.85	3.40	1.53	1.25	3.92	0.04	1.60	1.32	1.52	-	-	-
Al ₂ O ₃	21.87	21.99	17.87	20.98	17.74	14.93	17.53	18.78	32.49	20.13	20.77	20.03	-	-	-
FeO tot	5.26	4.04	7.10	8.06	5.68	11.07	4.57	9.98	1.70	2.16	3.48	3.14	-	-	-
FeO recal.	3.42	3.34	4.97	6.15	3.69	8.03	2.97	7.48	1.44	1.49	2.42	2.15	-	-	-
MnO	0.05	0.04	0.10	0.08	0.04	0.08	0.08	0.07	0.00	0.17	0.12	0.05	-	-	-
MgO	2.40	2.06	3.52	3.76	4.86	7.63	3.20	5.82	0.78	0.94	1.69	1.52	-	-	-
CaO	7.43	9.11	7.53	10.88	6.92	11.13	9.11	7.61	15.99	6.27	7.12	6.77	-	-	-
Na ₂ O	4.27	3.82	4.01	3.56	4.19	3.34	3.75	5.06	1.93	5.07	4.90	5.12	-	-	-
K ₂ O	1.58	0.85	1.72	0.94	2.14	1.34	3.03	1.19	0.05	2.51	2.21	2.53	-	-	-
P ₂ O ₅	0.41	0.21	0.36	0.27	0.66	0.45	0.35	0.99	0.20	0.44	0.36	0.61	-	-	-
S	0.14	0.03	0.10	0.05	0.01	0.08	0.05	0.00	0.00	0.05	0.06	0.06	-	-	-
Cl	0.06	0.02	0.06	0.03	0.01	0.03	0.03	0.03	0.00	0.09	0.07	0.09	-	-	-
H ₂ O	1.06	0.52	1.81	0.97	1.40	1.69	1.10	0.69	0.43	0.43	0.49	0.51	-	-	-
CO ₂	230	133	188	130	103	729	48	103	129	114	139	141	-	-	-
Volatiles corrected from bubble															
H ₂ O	1.12	0.54	2.00	1.02	1.53	1.83	1.23	0.75	-	-	-	-	-	-	-

CO ₂	4006	4570	3887	2451	1968	6260	1579	2351	-	-	-	-	-	-	-
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Table 6: Silicate melt inclusion corrected compositions; compositions are corrected from post-entrapment crystallization processes and shrinkage bubble formation. Concentration in wt.% except for CO₂ in ppm.

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	P° fluid saturation (Kbars)		Density
	Melt	Melt+Bubble	Bubble
HJ14-31-1	0.549	-	-
HJ14-31-3	0.285	-	-
HJ14-31-5	0.343	-	-
HJ14-31-6	0.340	-	-
HK14-05-1	0.611	8.4	0.181
HK14-05-3	0.395	17.1	0.130
HK14-05-8	0.697	6.7	0.191
HK14-05-9	0.405	6.1	0.128
LH4a-5	1.403	-	-
LH4a-6	1.554	-	-
LH4a-8	1.937	-	-
HK14-26-1	0.413	3.3	0.111
HK14-26-3	1.243	8.0	0.328
HK14-26-7	0.259	3.0	0.068
HK14-44-1	0.231	3.2	0.072

Table 7: Determined fluid densities for silicate melt inclusions

Comment	HK14-05-1	HK14-05-3	HK14-05-8	HK14-05-9	HK14-26-1	HK14-26-3	HK14-26-7	HK14-44-1
H ₂ O	12,6	5,2	33,8	18,1	40,9	19,8	45,5	19,6
CO ₂	87,4	94,8	66,2	81,9	59,1	80,2	54,5	80,4

Table 8: Determined fluid compositions into bubble obtained with Rhyolite-MELTS program
(Gualda et al., 2012; Ghiorso and Gualda, 2015)

	Bubble Volume (Vol. %, Measured)	Bubble Volume (Vol. %, Calculated)
HK14-05-1	5,9	1,8
HK14-05-3	7,3	1,5
HK14-05_8	7,2	2,7
HK14-05_9	5,9	2,6
HK14-26-1	8,7	2,7
HK14-26-3	5,2	4,0
HK14-26-7	9,5	2,5
HK14-44-1	10,2	3,0

Table 9: Calculated bubble volume following the method described in Moore et al., (2015) and measured bubble volume determined by X-ray microtomography.

Highlights:

- Silicate melt inclusions (SMI) can present post-entrapment processes (crystallization and/or shrinkage bubble)
- SMI modified by post-entrapment processes (PEP) are often avoid or corrected by high temperature (HT) homogenization
- SMI modified by PEP generally difficult to interpret and general preference is given to select the SMI that experienced minimal PEP
- New method to correct post-entrapment processes developed: the mathematical initial composition determination
- The method is an innovating coupling of: X-ray microtomography, geochemistry and thermodynamical modeling

Figure 1

Figure 2