GEOCHEMICAL STUDY OF THE SOLCHIARO (PROCIDA ISLAND, CAMPI FLEGREI) ERUPTIVE PRODUCTS BY MICROTHERMOMETRY AND MICROANALYSIS OF FLUID AND MELT INCLUSIONS

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ABSTRACT

For the following study, 107 selected melt inclusions (MI), 77 open glasses, (from four representative samples from the Solchiaro eruption) were analyzed for major and trace elements and volatiles. Two groups of MI were recognized based on major element composition: 1) K_2O-rich MI that has the same composition as bulk rock from the Phlegrean Volcanic District (PVD), as reported in the literature and 2) K_2O-poor MI that has never been reported in the literature on the PVD. The MI are 95% K_2O-rich and originated mostly in within-plate setting. The remaining 5% of the MI shows anomalous composition. H_2O-CO_2 concentrations dissolved in glass suggest that magma was saturated in volatiles at a minimum depth of 12.5 km. Volatile concentrations show that CO_2 and S started to exsolve from the melt at early stages of the Solchiaro eruption and that Cl and F were retained into the melt until later stages of the eruption.

INTRODUCTION

This study includes the work done during the four years of the PhD program that was part of the internationalization program of the Italian research system approved by Ministero della Ricerca e dell'Università (MIUR) between Università degli Studi di Napoli "Federico II", (Dipartimento di Scienze della Terra) and Virginia Polytechnic Institute and State University (Department of Geosciences). This project is an extension of the results obtained by Dr. Claudia Cannatelli in the previous international doctorate program (see Cannatelli *et al.*, 2007).

The Phlegrean Volcanic District (PVD), Italy, (also known simply as Campi Flegrei) comprises three volcanic fields: the Campi Flegrei (CF) caldera and the islands of Ischia and Procida. The PVD contains many volcanic centers (cinder cones, tuff rings, calderas) and has experienced intermittent volcanic activity for at least 50 ka with the most recent eruption being the Monte Nuovo eruption in 1538 AD. Some of these eruptions have been highly explosive, but a wide range in eruptive styles is suggested by the volcanic deposits. Because of its location near Naples and the towns surrounding Pozzuoli Bay (1.5 million inhabitants), it is imperative to develop a better understanding of the history of the PVD system.

Melt inclusions are small samples of silicate melt which, during magma crystallization processes, are entrapped in precipitating minerals. In the last decades, analyzing MI has been used as a valid tool to establish the magmatic evolution (Kent, 2008, and references therein). MI are the best tool to detect volatile concentrations before an eruption (Métrich & Wallace, 2008, and references therein) assuming they have not been compromised following entrapment. Thus, MI is the best source of information concerning minimum depths at which the magmas were generated or evolved, and if magmas were saturated in volatiles prior to an eruption. Some studies have noted that MI record temporal changes in volatile composition in a single volcanic system (Anderson *et al.*, 2000; Saito *et al.*, 2001).

GEOLOGICAL OUTLINES

The PVD is located near the margin of the Campanian Plain and is part of a more widespread Plio-Quaternary volcanic event that occurred in the circum-Tyrrhenian area (Peccerillo, 1999). Of the three volcanic fields that make up the PVD, this project studies the island of Procida. At Procida, volcanic activity began as early as 50 ka ago, with the emplacement of the Vivara tuff (De Astis *et al.*, 2004), and terminated with the Solchiaro eruption at about 17.3 ka (Lirer *et al.*, 1991). The last stratigraphic study on Procida volcanites was conducted by De Astis *et al.* (2004). Five volcanic vents have been recognized on the island: Vivara, Terra Murata, Pozzo Vecchio, Fiumicello and Solchiaro (from the oldest to the youngest). The recognized volcanoes are considered to be monogenetic (De Astis *et al.*, 2004). The Solchiaro eruption is the most primitive (along with Vivara eruption) in composition of all of the eruptions in the PVD. The style of this eruption varied through time. Early products are of phreatomagmatic origin while late products are more characteristic of magmatic origin (De Astis *et al.*, 2004).

SAMPLING

Although during the doctoral study (2005-2009), 15 volcanic units from the PVD were sampled, the focus was on the volcanic unit of Solchiaro. Other samples (Neapolitan yellow tuff, Bacoli, Agnano Monte Spina, Solfatara, Astroni and Fossa Lupara) are not sufficiently studied to be included here and only preliminary results have been obtained thus far. Four representative samples (RESC2, RESC3, RESC4, RESC5) of the Solchiaro eruption were collected to test for geochemical variations as a function of stratigraphic height. RESC2, RESC3 and RESC4 consist of ~ 20 cm of base surge deposits of the Solchiaro eruption. The three samples consist mainly of gray ash, dark brown lapilli and phenocrysts of olivine and clinopyroxene always rimmed by glass. The samples also contain xenocrysts (?) of sanidine (from 0.5 mm to 1 mm) showing euhedral morphology. RESC2 is the earliest erupted sample while RESC4 is the latest. RESC5 is representative of the yellow tuff facies, characteristic of lower and proximal products of the Solchiaro eruption (Di Girolamo *et al.*, 1984; De Astis *et al.*, 2004). The lithification processes obliterated the stratigrafic elements and complicated the chronostratigraphic correlation between the RESC5 sample and the others.

ANALYTICAL METHODS

The selection of MI was based mainly on size (> 20 μm) due to the minimum spot size suggested for Secondary Ion Mass Spectroscopy (SIMS) analyses. Phenocrysts were mounted in an indium probe mount in order to prevent H_2O and CO_2 epoxy contamination at high vacuum of the SIMS (Shimizu, personal communication). Phenocrysts were first gold coated and examined on the scanning electron microscope (SEM; at Virginia Tech Department of Geosciences, Blacksburg VA, USA) to test for homogeneity of the glass in the MI, to look for evidence of crystallization on the inclusion walls, and to investigate for zoning of the host phase. Next, the MI, glass rim, and adjacent olivine were analyzed using an electron microprobe to determine the major element chemistry. A first set of MI, glass embayment and olivines were analyzed by a Jeol 8900 electron microprobe (EMP) for major elements at the USGS (Reston VA, USA;). Then, the same set of MI and glass were analyzed by a SIMS Cameca IMS 1280 for volatiles at the Woods Hole Oceanographic Institution (Woods Hole, MA, USA). A second set of phenocrysts, rim glasses, embayments, and MI were analyzed by EMP and SIMS at Virginia Tech. For EMP analysis, precision is < 5% one-sigma when the oxide concentration is > 1 wt.%. When the concentration of an oxide was between 1 and 0.1 wt.% one-sigma is < 10%. Relative precision for volatiles by SIMS is < 10% relative for all the volatile considered (Shimizu, personal information) based on repeated analyses of the same standards. In addition, all MI and some olivine were analyzed by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA ICP-MS) at the Department of Geosciences, Virginia Tech. Precision is estimated at < 10% on the analyzed elements based on repeated analysis of NIST612 (SRM) analyzed as unknown. For each sample, 500 g were treated for analysis with X-ray fluorescence spectrometry.

RESULTS

Olivine compositions from all four samples of Solchiaro eruption range from Fo_{79} to Fo_{90} with Fo mol.%. All of the studied MI are naturally homogenized glass. Some contain one or more bubbles and others contain no bubbles. MI size ranges from 1 to 400 μm in diameter. Shape is variable ranging from elliptical and spherical through faceted (negative shape of olivine) to irregular. In some crystals, MI show constant V_{melt}/V_{bubble} ratio whereas in others the same ratio is highly variable. MI from all the Solchiaro samples are often associated with chromite solid inclusions. The $V_{melt}/V_{chromite}$ ratio ranges from 1 to close to 0, indicating that chromite is not a daughter crystal.

Every glass in contact with olivine but not included into it, was categorized as open glass. Within this category are embayments (connected through one or more narrow necks to the outside), glass reentrants, glass rims, and highly vesciculated glasses. Generally, bubble size increases with increasing distance from the olivine rims. Microphenocrysts of plagioclase, diopside, olivine, and chromite were observed in open glass.

MI composition may show strong chemical disequilibria with the adjacent host phase. In fact, MI composition could have been modified by post entrapment crystallization (PEC) (Kent, 2008, and references therein). Thus, chemical compositions of MI were corrected for possible PEC. Compositions were recalculated using PETROLOG software Danyushevsky (2001). Using the TAS diagram by Le Bas *et al.* (1986), corrected MI and glass composition plot on the fields from basalt through trachy-basalt to basaltic trachy-andesite with few points on the phono-tephrite. MI composition spans a wide range in major and trace elements and volatiles relative to both bulk rock and open glass. Mg# decrease with decreasing CaO/Al_2O_3 ratio. This suggests that along with olivine diopsidic clinopyroxene is also crystallizing. The major element in corrected MI with the greatest range in concentration is K_2O (from 0.5 to 6 wt.%). This is a variation that is also found for whole rock analyses from the Solchiaro eruption (De Astis *et al.*, 2004). Based on the K_2O contents MI were subdivided into two groups: K_2O-poor MI with K_2O < 2 wt.%, and K_2O-rich MI with > 2 wt.%.

Trace element contents from K_2O-poor MI are significantly different relative to K_2O-rich MI. In particular, the former group compositions show positive Sr and Eu anomalies typical of a plagioclase melt. REE of K_2O-poor MI show gradually flatter distribution with decreasing K_2O content.

K_2O-poor MI show the lowest contents for CO_2, S, Cl, and F. The highest content of CO_2 is in sample RESC2, the earliest volcanic product that was sampled. In addition to CO_2, S shows the same correlation with stratigraphic height. The lowest F and Cl contents are characteristic of the earliest erupted sample (RESC2). H_2O-CO_2 concentrations of all glasses approximate a degassing path calculated using VolatileCalc software (Newman & Lowenstern; 2002) (Fig. 1). Maximum pressures of formation are around 3.5 kbar. If samples are considered separately, maximum depths recorded by glass compositions are greater in sample RESC2 followed by RESC5, RESC3, and RESC4. Therefore, there is a relationship between stratigraphic heights and volatile concentrations.

DISCUSSION

The overlapping of corrected MI compositions with the bulk rock compositions (from both this study and the literature) suggests that corrected MI compositions are representative of the Solchiaro magma, the Procida Island magmatism, and the whole PVD. One of the concerns in studying MI is to establish if its dissolved volatile content represents the dissolved volatile content at the moment of

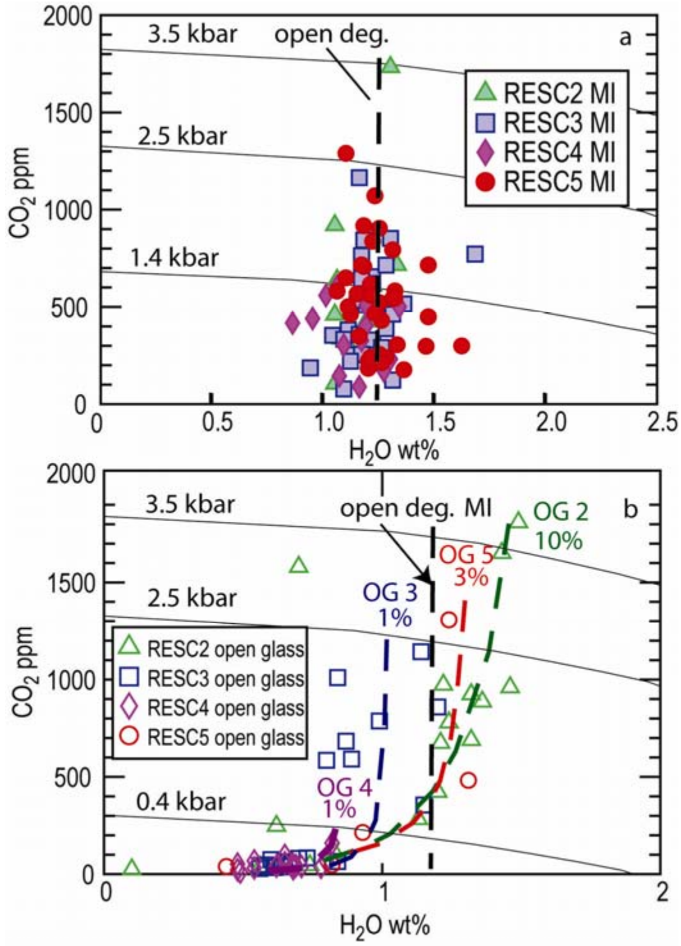

Fig. 1 - CO_2 *vs.* H_2O plot. Isobars (grey lines) are calculated using VolatileCalc by Newman & Lowenstern (2002) considering SiO_2 = 49 wt.% and 1200ºC. a) Degassing path of MI for all samples (black dashed line) assuming open system degassing. b) Degassing path (dashed colored line) assuming closed system degassing. Open glass of sample RESC2 (OG 2) is interpreted to represent closed system degassing (green dashed line) with 10% initial gas phase. Open glass of sample RESC5 (OG 5) is interpreted to represent closed system degassing (red dashed line) with 3% initial gas phase. Open glass of sample RESC3 (OG 3) is interpreted to represent closed system degassing (blue dashed line) with 1% initial gas phase. Open glass of sample RESC4 (OG 4) is interpreted to represent closed system degassing (purple dashed line) with 1% initial gas phase.

entrapment, especially for MI containing bubbles. In addition to PEC, part of the volatile content may be transferred to the "vapor" phase (bubble included into the MI). Since CO_2 is the least soluble among volatiles, one should expect a CO_2-rich fluid coexisting with the glass. Although CO_2 fluid was detected in the bubble by Raman spectroscopy in some of the selected MI, bubble-free MI and bubble bearing MI with similar CaO/Al_2O_3 ratio have comparable CO_2 concentration. This suggests that CO_2 dissolved into the glass closely represents the original concentration. Diffusion of volatiles through the host phase is also a possible source of underestimation or overestimation of volatile concentrations from MI. However, volatile concentrations of both the open glass and the MI overlap, indicating that volatile diffusion does not significantly affect the original volatile concentrations.

Open glass H_2O-CO_2 compositions fit closed degassing paths while MI compositions fit open degassing paths (Fig. 1). In this study, glasses show reverse correlation between calculated maximum pressure (~ maximum CO_2) and stratigraphic height. S from open glass also shows maximum content in the sample RESC2 (bottom of the stratigraphic column). F and Cl increase with increasing stratigraphic height. Saito *et al.* (2001) describe a similar volatile evolution for the Satsuma-Iwojima volcano in Japan. From earlier to later products, calculated pressures decrease from earlier maximum pressure of *ca.* 1.7 kbar to later maximum pressure of *ca.* 0.75 kbar. This is interpreted to represent the magma ascending the crust with time. Volatiles associated to the Solchiaro magmas may be evolved as described for the Satsuma-Iwojima volcano in Japan. Glasses from a single sample record large range of depths from 3.5 kbar down to almost atmospheric pressure (RESC2). Similar large ranges have been reported from several studies based on MI (Métrich & Wallace, 2008, and references therein). MI compositions record different pressure because they can be entrapped at different time and thus at different depth while the magma is ascending the crust or they represent degassing under narrow range of pressure due to magma convection in a conduit (Kazahaya *et al.*, 1994). No studies have been reported volatile contents from open glass as much as 1800 ppm of CO_2. The first possible explanation for the observed data is that open glasses were quenched also at great depth because of the high explosive eruption. The second possible solution is that at the moment of the eruption open glasses were under super-saturation condition due to magma recharging from deeper level that triggered eruptive explosion.

Sample RESC5 fit in all diagrams between samples RESC2 and RESC3 suggesting that RESC5 was erupted later than RESC2 and before RESC3. If the hypothesis of systematic correlation between stratigraphic height and volatile contents is correct, then analysis of glasses is a useful tool to asses relative ages for Solchiaro outcrops otherwise of difficult interpretation.

The greatest pressure recorded by glasses of Solchiaro is 3.5 kbar that assuming 280 bar/km gradient results in depth of 12.5 km. This is in agreement with maximum pressures estimated by Belkin *et al.* (1985) based on fluid inclusions from ejected nodules Somma-Vesuvius volcanic system. In addition, Guidarelli *et al.* (2006) recognized a low velocity zone under both the PVD and the Somma-Vesuvius system at around 10 km depth. Orsi *et al.* (1999) argued the presence beneath the Island of Procida of gabbroic bodies from 2 to 10 km possibly representing ancient cooled magmatic chamber related to the basic magmatism of this volcanic field in agreement with depth of MI entrapment calculated in this study.

The lowest K_2O content detected in this work is 0.51 wt.% that is much lower than the lowest K_2O from the literature (1.56 wt.%. from D'Antonio *et al.*, 1999). MI hosted in Fo-rich olivine (87-90 mol.%) plus Cr content as much as 240 ppm suggest that some of the MI are primitive in character. All glass compositions show MgO > 4 wt.% and are suitable for understanding the origin of this magma. Zr-Ti-Y discriminant diagrams indicate that most of the glass compositions show within plate basalt affinity.

However, 4 MI of the K_2O-poor group plot differently relative to all the other glass compositions showing volcanic arc signature. Also spider diagrams suggest two different kinds of magma. However, the hypothesis of two different kind of parental magma is hazardous due to the not extremely primitive character of most of phenocrysts and glasses. Further investigations are certainly needed on this issue.

CONCLUSION

Analysis of volatiles from Solchiaro glasses show that CO_2 is the less soluble volatile followed by S. These two volatile contents, dissolved into the melt, decrease from earlier to later volcanic product. Cl and F are instead retained in glass from the earlier to the later erupted products. Greatest depth obtained from H_2O-CO_2 in MI is consistent with recent geophysical data (Guidarelli *et al.*, 2006) and fluid inclusion data (Belkin *et al.*, 1985) in the region. K_2O-poor MI show anomalous composition never reported in the literature for the PVD.

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