MOLECULAR WATER MOTIONAL BEHAVIOUR IN VOLCANIC GLASSES FROM MAGMATIC AND PHREATOMAGMATIC EXPLOSIONS

A magma is permeable to the diffusion of volatile species which are in solution in the melt phase. Among volatile components in magmas, water is the most abundant. Decompression, cooling and mineral crystallization cause water exsolution out of the melt, and in supersaturation conditions the pore spaces filled by water molecules may become the sites for the formation of hydration bubbles. Such bubbles may expand through the progressive drainage of water from the surrounding melt by diffusion. In the condition of non-equilibrium degassing, as in highly viscous magma or during a rapid ascent, continuous bubble nucleation occurs and the magma becomes increasingly fragmented by pore steam explosions, thus having the conditions for an explosive burst. Explosive hydrovolcanic eruptions may also occur as a consequence of the interaction of magma with external water, at the proper water/magma ratio and depending on the P,T conditions. During hydration, the reactions of aqueous solutions that enters the melt may allow ion-exchanges among cations and proton.

In the present study, volcanic glasses from deposits related to magmatic and phreatomagmatic explosions of the Agnano-Monte Spina (AMS) eruption, in the Campi Flegrei caldera (CFc), have been investigated. The AMS eruption has been dated at about 4100 years before present and occurred during the third epoch of volcanism in the CFc, by vents located in the North-eastern sector of the Neapolitan Yellow Tuff caldera, likely by the intrusion of a dyke along a normal fault in a sector under a tensional stress regime. The AMS is the highest magnitude eruption occurred during the third epoch of activity within the CFc, and was accompanied by a volcano tectonic collapse partially responsible for the morphology of the present Agnano plain. The scenario of this eruption, characterized by alternate magmatic and phreatomagmatic explosive phases, represents the one expected in case of renewal of volcanic activity.

All the glasses from the different members of the AMS eruptive sequence have alkali-trachytic composition. The surface BS-SEM images show that pumice glasses represent the products of the rupture of a vesiculated, disordered foam, with subspherical and, in some cases, strained vesicles, partly coalesced (Fig. 1).
Several bubble generations are also observed in some of the glasses (Fig. 2), with smaller bubbles which nucleated among larger vesicles, indicating inhomogeneous gas exsolution inside a magma column.
Deformation textures in response to shear during decompression are sometimes preserved, suggesting the sudden increase of the melt structural relaxation time associated to high cooling rates while bubbles were still deforming.

These observations suggest that non-equilibrium degassing probably occurred. The glass shards from the highly fragmented explosive phases are characterized by both angular clasts of unaltered glass, with both spherical vesicles including inter-bubble expansions and elongated vesicles with almost circular sections attributable to the melt flowing, and clasts with sub-rounded shape, showing evidence of glass alteration ascribed to the interaction with reacting solutions.

The $^1$H MAS NMR spectra show that all samples are characterized by a large spinning sideband pattern with peaks spaced at integer multiples of the spinning speed, with an overlapping central contribution, more intense in the shard glasses with respect to pumices. The spectra are best simulated by the contribution of three different types of proton nuclei with correspondingly different $^1$H-$^1$H dipolar couplings of 45 kHz, 22 kHz and 11 kHz.

![Diagram](image)

**Fig. 3 -** Hydrogen vs. Sr isotopic composition diagram. Open circles: pumice glasses; filled circles: shards.

The former contribution represents the inhomogeneous dipolar coupling of an isolated two-spin system such as $^1$H-$^1$H in rigidly bound water molecules. This species is interpreted as the solute form of water in the melt structure prior to the gas partitioning into a separate phase. The latter two contributions are due to water subject to anisotropic motions, possibly attributable to molecules or clusters rather mobile and slowly diffusing in the glass structure in response to decreasing gas solubility, during magma decompression and cooling. In these melts most of the water was not allowed to flow into a totally free state before melt permeability decreased, as a consequence of high decompression rates, a condition for the triggering of magmatic explosions. Shard glasses show a further narrow resonance with a dipolar coupling of about 200 Hz, which is accounted for by assuming water molecules which move in a freely rotating state. This contribution is attributable to micropore liquid water or clusters of mobile water molecules linked by hydrogen bonds into the glass structure. The observed different structural and motional features of water in the glasses are likely to reflect the different features of the
eruptive mechanism; in particular, the increasing amount of free water component would imply higher compressed gas energy and melt disruption during fragmentation.

Some of the glass shards have the same Sr isotopic composition of the corresponding pumices, suggesting that the hydrous component was probably of magmatic origin. Other glass shards are characterized by a significantly higher $^{87}\text{Sr} / ^{86}\text{Sr}$ ratio compared with pumices. Since the strontium of the solute in groundwater or surface water encountered by the rising magma during a phreatomagmatic explosion is likely to be isotopically distinct from that of the melt, the observed isotopic variability in the latter glasses supports the hypothesis that during this blast the magma interacted with external fluids (Fig. 3).