Resolving Problems of EPMA-derived Water Contents of Melt Inclusions

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Melt inclusions (MIs) are pockets of melt trapped inside crystals which grow from magmas. MIs typically quench to a glass upon eruption, providing a unique insight into the magma composition pre-eruption, especially the volatile content (e.g., H₂O and CO₂). MIs are small, ~1 – 100 μm in diameter, and therefore require micro-analytical techniques for their characterisation. EPMA is commonly used to measure the composition of MIs due to its wide accessibility and ability to measure a wide range of elements (natural silicate glasses contain ten or more oxide components). In hydrous glasses, although H cannot be measured directly using EPMA, Water By Difference (WBD) can be used to estimate the water content by measuring all the elements in the glass, except H₂O, and iteratively calculating the complete glass composition (including H₂O) to generate a total of 100 wt% [1].

Unfortunately, WBD consistently overestimates water content of silicate glasses (Figure 1a). Hydrous glasses are difficult to analyse as they are unstable under the electron beam [2], hence element migration (e.g., Na, K) can cause low analytical totals, but this can be corrected for using Time-Dependent Intensity measurements [3]. Peak positions can be structure dependent [4], therefore care must be taken to peak-up on appropriate standards to avoid analysing off-peak and underestimating the concentration. Also, oxygen is rarely measured and is instead calculated using stoichiometry, hence the oxidation state of multivalent elements (e.g., Fe and S) must be known independently for accurate WBD. The H₂O must also be included in the matrix correction to account for absorption by this oxygen [5]. We analysed a set of hydrous glasses with known H₂O and CO₂ using SIMS/FTIR, Fe oxidation state using wet chemistry and S oxidation state using EPMA [6]. We found that the overestimation of WBD is still observed even when there is no element migration, H₂O is included in the matrix correction, Fe oxidation state is constrained and appropriate standards are used (Figure 1b).

Instead, we suggest the sub-surface charging distorts the φρz curve causing the low analytical totals observed. As silicate glasses are insulators, they trap electrons during electron beam irradiation, generating a region of sub-surface negative charge, even when a conductive coat is used [7]. The effects of this are commonly observed, resulting in phenomena such as alkali-loss, commonly observed during silicate glass analyses [8]. This sub-surface charging also causes changes in X-ray generation and absorption, due to the deceleration of incoming electrons, which has been shown to occur both experimentally [9] and by modelling [10]. We modelled the effects of sub-surface charging in hydrous silicate glasses using Win X-ray [11]. Our results imply that a maximum electric field strength on the order of 0.01-0.1 V·nm⁻¹ reproduces the observed overestimation of WBD (Fig. 1b), which is similar to values that have been experimentally measured in glasses previously [12].

The effects of sub-surface charging cannot currently be included in matrix corrections, as this would require measuring the magnitude of sub-surface charging during analysis which is very difficult. Standards which experience the same magnitude of charging could be used for all elements analysed but as it is not possible to know the amount of charging the sample and unknown have experienced, picking appropriate standards would be impossible. Also, the error on any individual element is small therefore it is only the WBD itself that needs correcting. Therefore, we would recommend calibrating WBD on a set of well-characterised hydrous glass standards, which allows accurate H₂O analyses from EPMA to ±0.4 wt% H₂O [13].
Figure 2a) Water By Difference (WBD) against independently constrained water contents from the literature for basalts to rhyolites, where colour indicates SiO$_2$ (red = basaltic, blue = rhyolites) and open/closed indicates unknown/known Fe oxidation state. Black solid line is the 1-to-1 and dashed line is the best fit to the data. b) WBD against SIMS H$_2$O collected for this study with WBD contours (solid lines) generated using Win X-ray for different maximum electric field strengths.