

## Water loss from melt inclusions in pyroclasts of differing sizes

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Our understanding of the pre-eruptive H<sub>2</sub>O contents of parental magmas has come to rely on the measurement of olivine-hosted melt inclusions, and yet there is increasing recognition of the potential short-comings of olivine as a perfect container of undegassed melt. Several laboratory experiments have now demonstrated how melt inclusions can lose or gain H<sub>2</sub>O through host olivine on short timescales (hours to days), relevant to eruptive processes. Here we have designed an experiment using natural tephra samples that cooled at different rates: ash ( $\leq 1$  mm diam.), lapilli (2 cm), and bomb (6-7 cm) samples that were deposited on the same day (10/17/74) of the sub-plinian eruption of Volcán de Fuego in Guatemala. Ionprobe, laser ablation-ICPMS and electron probe analyses of olivine-hosted melt inclusions yield a similar range in major element (50-59% SiO<sub>2</sub>), trace element (Ba/Zr = 4-6) and olivine compositions (Fo#72-79) in the different clast populations, that also match the range in the host bulk tephra and groundmass. Melt inclusions from the ash and lapilli samples record the highest H<sub>2</sub>O contents, up to 4.4 wt%. On the other hand, melt inclusions in the bomb samples indicate up to 30% lower H<sub>2</sub>O contents (loss of ~1 wt% H<sub>2</sub>O), despite similar S, CO<sub>2</sub> and K<sub>2</sub>O concentrations, consistent with the longer time available for re-equilibration with degassing magma through the olivine. Inclusions from bombs also record up to 10% post-entrapment crystallization of olivine, while those from the ash samples record none. Thus, taken at face value, melt inclusions from small bombs may lose H<sub>2</sub>O and crystallize olivine within the 10 minutes maximum that it takes for a 3-4 cm radius bomb core to cool conductively. This could only occur if the fast redox exchange mechanism for H diffusion in olivine were operating ( $D \sim 10^{-9}$  to  $10^{-10}$  m<sup>2</sup>/s). On the other hand, several lines of evidence point to some of this water loss also occurring pre-eruptively, during magma ascent and degassing in the conduit. Some of the smallest melt inclusions (< 50 micron diameter) within ash and lapilli appear to have lost up to 10% water, and yet sufficient time is not available during post-eruptive cooling to allow this even given the fastest known H diffusivities. Moreover, inclusions selectively sampled from the outer cm of bomb clasts record greater water loss than those in 1 cm radius lapilli, consistent with a longer timescale for H<sub>2</sub>O loss for all the bomb magma, and not just the slowly cooled bomb interiors. Thus, our results point to both slower post-eruptive cooling and slower magma ascent affecting bomb melt inclusions, leading to H<sub>2</sub>O loss over the timescale of 10 minutes to hours. The important implication of this study is that a significant portion of the published data on H<sub>2</sub>O concentrations in olivine-hosted melt inclusions may record some H<sub>2</sub>O loss and not primary water, particularly for samples taken from lavas or bombs, or small inclusions (< 40 microns diameter) in general. Future sampling and analysis should bear these considerations in mind.

## Characterisation of the Cr isotopic signature of marine sediments deposited in the S1 Mediterranean sapropel

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The record of past changes in the dissolved oxygen concentration of seawater is crucial for understanding past climate changes, and for predicting future climate scenarios. Initial measurements of chromium (Cr) stable-isotope fractionation showed the potential of Cr as a tracer of dissolved oxygen concentrations in groundwaters (Ellis et al., 2002). More recently, analyses of ancient marine carbonates and banded iron formations have revealed large variations in  $\delta^{53}\text{Cr}$  values, from -0.28 to 5.00‰, (Bonnand et al., 2011; Frei et al., 2009, 2011), which are distinct from the continental crust and terrestrial mantle (~-0.12 ‰; Schoenberg et al., 2008) and are interpreted to reflect past variations in seawater oxygenation.

In order to fully assess the validity of this new proxy, the effects of post-depositional diagenesis on Cr and Cr isotopes need to be quantified. To this end, we will present the results of analyses of Cr isotopes in sediment cores that record the deposition of the most recent eastern Mediterranean sapropel (S1) between 7 and 10 <sup>14</sup>C kyrs BP. The sapropel has experienced heavy diagenetic alteration which is revealed by the presence of maxima in the concentration of many redox-sensitive elements outside of the sapropel layer (Thomson et al., 1995). The Cr data will be compared with these other redox-sensitive elements, and measurements of the Cr isotopic composition of seawater samples that have different levels of dissolved oxygen. These new data will allow us to assess the mobility of Cr during diagenesis and the robustness of Cr isotopes as a redox-proxy.

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