

New spectroscopy developments to study water in basaltic melts

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Micro-Raman spectroscopy is a powerful technique to assess the water content and diffusion profiles in silicate glasses, at micrometer scale. The potential of Raman spectroscopy to quantify water has been recently demonstrated for hydrous, silicic glasses [e.g., 1-2]. However, Raman analysis of hydrous, basaltic glasses is more delicate. We examine here the effects of laser beam (heating and oxidation) on these glasses and the dependence of Raman calibrations on iron redox state and compositions of glasses. We studied 28 dry natural glasses having a large range of polymerization degree (NBO/T: 0 to 1.17), 2 sets of basaltic glasses with variable Fe³⁺/ΣFe ratios and 4 sets of synthetic hydrous mafic glasses (H₂O: 0.4 to 5.3 wt%). In order to prevent analytical condition bias, Raman calibration for water (internal calibration) has been based on the ratio of the H₂O total stretching band (3500 cm⁻¹) relative to spectral features (LF: 490 cm⁻¹ and HF: 960 cm⁻¹) of the glass network. Internal calibration is glass composition dependent. Our results on dry glasses demonstrate that the ratios between LF and HF spectral bands correlate with the sum of structural modifiers (SM). It thus allows us to predict the composition dependency of Raman internal calibrations. Moreover, the iron oxidation state of basaltic glasses does not influence the Raman calibrations. We demonstrate that internal calibration of water is reliable, using the HF and LF bands, respectively, for depolymerised and polymerised glasses.

References

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Growth of calcium carbonates in gels in the presence of organic and inorganic additives

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Biomimetalisation provides a great variety of crystal morphologies. For example the brachiopod *Mergelia Truncata* [1] forms extremely tortuous strands of calcite crystals. In order to understand the biologically induced crystal morphologies, the growth of crystals in gels is an excellent method to study the influences of additives on the morphology of the growing crystals. Different striking effects on the morphology of calcite crystals have been shown for inorganic [2] as well as organic additives [3] using this method. Additionally, biomimetalisation often results in crystals with incorporated cations (e.g. Mg²⁺ in calcite [1]). The focus of this work, therefore, is the investigation of the combined influences of organic and inorganic additives on the crystal morphologies and polymorph formation of calcium carbonate. We used acrylamide as well as sodium silicate hydro-gels with MgCl₂, SrCl₂, aspartic acid, and succinic acid as additives. The crystals were investigated using XRD, micro-Raman spectroscopy, and SEM. We obtained vaterite, aragonite, and calcite polymorphs. The crystal morphologies range from spheres (Fig. 1) and morphologies known from inorganically grown crystals (rhombohedra, aragonite twins) to crystals with strongly distorted morphologies such as dumbbell-shaped crystals. The experiments show that the combined influences of inorganic and organic additives are able to change the growth behavior of calcium carbonate, generating a variety of crystal morphologies.



Figure 1: Calcite sphere grown in an acrylamide cryogel (gelation at -20°C).

References

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