

## Water speciation in sodium silicate melts: Constraints from high temperature IR spectroscopy

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Knowledge of the water speciation in silicate melts is of importance for understanding the mechanisms of incorporation and transport of water in magmas. Recent advances in high temperature infrared (IR) spectroscopic techniques made it possible to tightly constrain the water speciation in silicate melts, but previously published studies focus on rhyolitic melts and do not cover basic, depolymerized compositions. Here we present results from high temperature IR spectroscopy of hydrous sodium tetrasilicate melts to understand the effect of melt composition on the water speciation.

Near-IR absorption peaks due to SiOH groups (4500 cm<sup>-1</sup>) and molecular H<sub>2</sub>O (5200 cm<sup>-1</sup>) were investigated in sodium tetrasilicate glasses (1.0-5.1 wt% total water) as a function of temperature between ~25 and 325 degree C and at ambient pressure, using a heating stage fitted to an IR microscope. The concentrations of SiOH groups and molecular H<sub>2</sub>O were determined from the absorption peak heights. The molar absorption coefficients were calibrated at each temperature, assuming that SiOH groups and molecular H<sub>2</sub>O are the only hydrogen-bearing species in the glasses and that the concentrations of these species are scaled by the heights of the two peaks. This assumption appears to be valid because the total water contents in the glasses are reproduced by our calibrated IR technique with better than ±0.1 wt% of accuracy, over the temperature range investigated.

The results can be modeled adequately on the basis of the speciation reaction molecular H<sub>2</sub>O + bridging O = 2OH and ideal mixing of these three quasi-oxygen species. The speciation equilibrium remains unchanged regardless of temperature in the glass state, but is shifted to the right-hand side with increasing temperature above the glass transition. The temperature dependence of the speciation equilibrium in the melts is expressed by  $\ln K = -3770/T + 5.19$  (i.e., 31.4 kJ/mol of the standard enthalpy and 43.2 J/mol per K of the standard entropy) and is insensitive to total water content. The equilibrium constant K obtained in this study is approximately two order magnitudes greater than those obtained by previous authors in rhyolitic melts, at similar temperature. Such a large composition dependence of the water speciation is a probable cause for a greater solubility for water in a melt having more depolymerized silicate composition.

## Is amino acid-containing dissolved organic matter molecularly different between surface and deep seawaters?

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Dissolved organic matter (DOM) in the ocean is one of the largest reduced carbon pools in the global carbon cycle. Dynamics of DOM, in terms of production and degradation processes/mechanisms are least known, however, since the tangential flow type ultrafiltration technique was introduced, high molecular mass (HMM)-DOM have been well documented. <sup>15</sup>N NMR spectroscopy demonstrated organic nitrogen was in the form of amide and protein molecules were also found in HMM-DOM. However other chemical forms except proteins in HMM-DOM were less understood.

Total hydrolyzable amino acids (THAA) and fluorescent properties in the bulk and four molecular mass fractions (GF/F-0.1µm, 0.1µm-10kDa, 10kDa-5kDa, 5kDa>) of DOM were determined in the surface (10m) and deep (1000m) waters at the Sagami Bay, Japan. Levels of THAA and protein-like fluorescent intensities in the bulk DOM were highest in the surface layer and decreased with increasing depth. It is well known that protein-like fluorophores were observed in the marine DOM, however, materials responsible for the fluorophores were not understood. We found that tyrosine- and tryptophan-like fluorescent intensities were significantly correlated with actual concentrations of tyrosine and tryptophan, respectively, in the bulk DOM, indicating that protein-like fluorophores were derived from aromatic amino acids in seawater.

Molecular mass fractionation demonstrated that THAA was dominant in the fraction of 5kDa>, accounting for 86.6% and 88.7 % of the total in surface and deep waters, respectively. Although proportion of THAA in the fraction of >5kDa were similar between surface and deep waters, quite different fluorescent properties were found between the surface and deep waters. Tryptophan-like fluorophore was dominant in the surface water, in contrast, tyrosine-like fluorophore was dominant in the deep water. These differences indicated that chemical forms of amino acid-containing HMM-DOM were different between the surface and deep waters.

In conclusion, amino acid-containing DOM in the high molecular mass fractions was comprised of polypeptides or least-degraded protein molecules in surface water, but in deep water, other forms of amino acids were dominant even though sharing the same HMM fractions.