

## Role of weak complexing agents in metal uptake by phytoplankton

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The presence of weak ligands enhances the bioavailability of metals bound to strong chelating agents. For example, addition of cysteine (Cys) to EDTA-buffered media increases the rate of uptake of zinc (Zn) by model phytoplankton. Such enhancement of uptake may result from 1) specific uptake of the Zn-Cys complexes, 2) alleviation of diffusion limitation by dissociation of the complexes in the boundary layer of the cells, or 3) exchange of Zn with uptake ligands, X, via formation of a ternary complex X-Zn-Cys. Mechanism 1 is ruled out by the facts that L- and D- isomers of Cys are equally effective at enhancing the Zn uptake rate and that weak ligand addition increases rather than decreases uptake in the absence of EDTA. Mechanism 2 does not explain the effect of weak ligands, for this effect is seen when diffusion does not limit uptake of the free metal. The enhancement of Zn uptake kinetics by weak ligands under various conditions is consistent with mechanism 3: i) enhancement of uptake is particularly effective in Zn-deplete cells whose high affinity transport molecules should be most able to exchange Zn with external ligands; ii) a variety of weak ligands have similar effects on uptake, showing that the mechanism is relatively non-specific; and iii) ligands that bind Zn in complexes that make the formation of a ternary complex difficult do not increase Zn uptake. When essential metals are bound to strong chelating agents in natural waters, binding to weak complexing agents may increase their bioavailability to ambient microorganisms.

## The amphoteric behaviour of water in silicate melts: Raman observations and physico-chemical description

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Water plays a fundamental role in the dynamics and evolution of magmas in the deep interior and during volcano eruption. However, water speciation in silicate melts is not fully understood, despite Infrared, Raman and NMR spectroscopy had provided some valuable information about the H<sub>2</sub>O/OH speciation and its variations as a function of temperature, pressure, and water contents of melts. Some issues still remain unsolved about OH and H<sub>2</sub>O linkages to the silicate network and we lack a general physico-chemical description of acid-base exchanges of water in melts. This includes the amphoteric behavior displayed by the water component into depolymerized glasses and melts.

By adopting a Raman-spectroscopy calibration of water dissolved in aluminosilicate melts [1], we studied the Raman OH-stretching bands of hydrous glasses. OH-stretching Raman band records the vibrations of OH groups in molecular water or differently linked to the glass structure or metal cations. To constrain more in detail the evolution of such bands, we performed a set of in situ experiments on rhyolite, basalt and albite glasses using a micro-furnace at ambient atmosphere. We observed new high-temperature Raman features near 3650-3700 cm<sup>-1</sup>, and also changes of water speciation that occurred below glass transition while quenching to room temperature. Our results will be used to constrain the acid-base exchanges occurring in melts and give insights into the relations between water and silicate network in melts.

[1] Le Losq, C., Neuville, D. R., Moretti, R., Roux, J., 2012. Determination of Water Content in Silicate Glasses using Raman Spectrometry: implications for the study of explosive volcanism. *American Mineralogist*, in press.