

Foliar transfer of TiO₂ and Ag nanoparticles in lettuce

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Introduction: The possible transfer of engineered nanoparticles (ENPs) into plants should be evaluated in the perspective of human exposure through ingestion of crops. The mechanisms of ENPs transfer and on their fate inside plants are poorly understood, particularly for the foliar pathway [1]. The fate of TiO₂ and Ag⁰ ENPs in lettuce leaves was studied after foliar exposure by wet deposition. The localization of ENPs and the speciation of Ti and Ag were studied by SEM- and TEM-EDX, micro X-ray fluorescence (μ XRF) and micro X-ray absorption spectroscopy (μ XAS) based on synchrotron radiation.

Results and Conclusion: TiO₂ exposure did not induce any visible toxicity symptoms, whereas Ag (both ionic and nano) induced some necroses on leaves. Imaging techniques show the presence of large agglomerates of Ti or Ag both on the surface of the epidermis and inside leaves (Figure 1). No sign of TiO₂ dissolution was observed by μ XAS whereas Ag ENPs are partially dissolved with the formation of secondary Ag species (Ag⁺ bound to organic ligands). These results suggest that crops exposed to atmospheric deposition of ENPs may undergo contamination due to foliar transfer of ENPs.

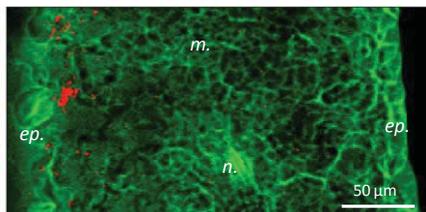


Figure 1: Ti (red) and K (green) distribution in lettuce leaves after foliar exposure. *ep.* epidermis, *m.* mesophyll, *n.* nerve.

[1] Fernandez & Eichert (2009) *Crit. Rev Plant Sci.* **28**, 36-68.

Chemistry of H-Li-Na-K-Cl-H₂O brines up to high concentrations (< 40 molal) and temperatures (0 - 250°C)

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Introduction

Lithium interest for industrial production has been increasing during the last few years. This alkali metal is of primary importance in the battery production for electricity storage, in vehicles and electronic devices. Because of very high solubility of lithium in water, the chemical behaviour of lithium minerals – brines systems is highly non-ideal and very complex. Its characterization requires specific approaches. The ion-specific interactions model developed by Pitzer [1] is particularly well suited for dealing with ionic strengths ranging from low up to very high salinities, i.e. above several tens of moles per kg of water [2].

Description of the work

In this work, we studied the H-Li-Na-K-Cl-H₂O chemical system, and determined new relevant Pitzer interaction parameters using the recent procedure developed by André et al. [3]. In the binary LiCl-H₂O system, this set of parameters, together with the aqueous complexation constant of the LiCl⁰ aqueous species, allows the description of the phase diagram for temperatures ranging from 0 to 250°C and for salinities up to saturation, i.e. up to 40 mol/kgw. The presence of the LiCl⁰ aqueous species has been investigated by NMR (Nuclear Magnetic Resonance) as described in a companion communication [4]. Using this parametrization (which includes the LiCl⁰ aqueous species) in the ternary LiCl-KCl-H₂O, LiCl-NaCl-H₂O, and LiCl-HCl-H₂O systems, phase diagrams can be satisfactorily described up to 30 mol/kgw, and 150°C.

The set of new interaction parameters determined in this study should allow the description of the chemical behaviour of the quinary LiCl-KCl-NaCl-HCl-H₂O system over a wide range of salinities (0.001 to 40 molal) and temperatures (0 to 250°C). The model presented here is a continuation of the previously established model for lithium hydroxide systems [5], and is consistent with the related set of specific interaction parameters. This extension is of great importance to better characterize the chemical behaviour of complex systems like natural Li-bearing brines found in hydrothermal systems (e.g., Soultz-Sous-Forêt, Salton Sea, etc.).

[1] Pitzer (1991) *Activity coefficients in electrolyte solutions*, 2nd ed., CRC Press

[2] Lassin et al. (2009) *19th Goldschmidt Conf.*

[3] André et al. (2009) *19th Goldschmidt Conf.*

[4] Montouillout et al. (2012) *22nd Goldschmidt Conf.*

[5] Lassin et al. (2011) *21st Goldschmidt Conf.*