

## Monitoring dynamics of species and adsorption reactions at the corundum-oxalate-solution interface by *in situ* ATR-FTIR spectroscopy

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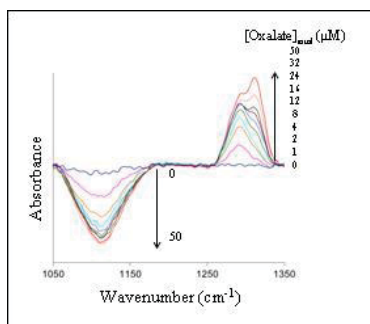
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### Introduction

We addressed the molecular level description of the interactions occurring at low pH between oxalate ions and the surface of corundum colloids, for oxalate in the low concentration range relevant to freshwater (1-50 μM). We monitored the dynamics of species at the corundum- solution interface during the oxalate sorption process by using a highly sensitive technique, namely Attenuated Total Reflectance – FTIR spectroscopy, joint to a method of layer deposition of corundum particles on the ATR crystal [1-3].

### Results and conclusion

Examining changes in IR spectra during the oxalate sorption process, for frequency regions characteristics of oxalate, surface hydroxyls and ClO<sub>4</sub><sup>-</sup> electrolyte ions, has revealed the existence of two types of sorption mechanisms dependent on the oxalate concentration.



**Figure 1:** In situ ATR-FTIR monitoring of the corundum-solution interface during gradual increase of [Ox]<sub>T</sub> at pH 4.7, 0.01M NaClO<sub>4</sub>.

In the trace level concentration range, the uptake of oxalate is accompanied by removal of ionisable surface hydroxyls and weakly adsorbed ClO<sub>4</sub><sup>-</sup>. This is direct spectroscopic evidence that a reaction of surface ligand exchange controls the oxalate sorption. The other sorption reaction involves no surface hydroxyls or counter-ions and it exists in a wider range of oxalate concentration, indicating weak sorption of hydrated oxalate via H-bonds. Our study suggests that the sorption of oxalate at the trace level influences surface reactivity and charge of oxides in soils, as well as colloid aggregation and mobility.

[1] Del Nero *et al.* (2010) *J. Colloid Interf. Sci.* **342**, 437-444. [2] Galindo *et al.* (2010) *J. Colloid Interf. Sci.* **347**, 282-289. [3] Halter *et al.* (2010) *Applied Surf. Sci.* **256**, 6144-6152.

## Laser spectrometry for tracing evaporation in a Mediterranean wetland (Rhône delta, France)

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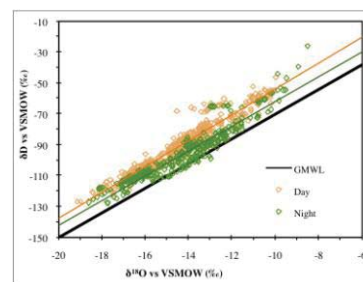
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### Context

Evaporation from wetlands may contribute significantly to local atmospheric moisture, and may thus provide an additional water source to regional precipitation. In the context of global change, the distribution of wetlands is expected to vary, making necessary to better understand the influence of wetlands on climate. Isotopic tracing ( $\delta^{18}\text{O}$ ,  $\delta\text{D}$ ) is an efficient tool for detecting the contribution of local vapor to the atmospheric component of the water cycle, because the fractionation that occurs during evaporation induces a modification of the deuterium excess [1].

### Results and conclusions

We performed continuous measurements of the isotopic composition of the atmospheric vapor during summer 2011, near a lagoon located in the Rhône delta, using wavelength-scanned cavity ring-down spectrometer (WS-CRDS). Calibrations were regularly performed with 3 different water compositions, and for mixing ratio varying between 4 to 33 g/kg. Linear calibration results were obtained, except for mixing ratio higher than 25 g/kg. Laser spectrometer measurements were compared to atmospheric vapor samples collected by cryogenic trapping (65 samples). The difference between results from the two methods was acceptable for  $\delta^{18}\text{O}$  ( $\pm 0.36\text{‰}$  on average), while the laser spectrometer slightly overestimated  $\delta\text{D}$ , by 4.3‰ on average. Based on hourly-averaged time series, we evidenced a clear difference in deuterium excess between day-time and night-time data (Figure 1), resulting from the influence of local evaporation. Further work is under way to elucidate the shift in deuterium measurements. Preliminary attempts for a quantitative interpretation of deuterium excess variations in terms of evaporation fluxes [2] will be discussed at the meeting.



**Figure 1:** Isotopic composition of atmospheric water vapour between 2011/07/19 and 2011/08/13. Data are hourly averaged. Solid lines represent linear regressions (orange:  $\delta^2\text{H}=8.3\times\delta^{18}\text{O}+30.1$  ; green:  $\delta^2\text{H}=8.0\times\delta^{18}\text{O}+18.5$ ), with the Global Meteoric Water line in black.

[1] Gat & Airey (2006) *Global and planetary change* **51**, 25-33. [2] Lai & Ehleringer (2011) *Oecologia* **165**, 213–223.