

## Sulfate adsorption at buried mineral/solution interfaces probed via vibrational surface spectroscopy

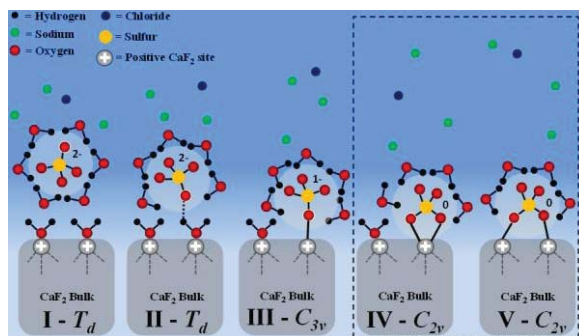
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### Introduction

Understanding the structure and energetics of adsorbed ions at the buried mineral/solution interface has great importance to the geochemical and atmospheric chemistry communities. Vibrational spectroscopy is a powerful tool for the study of mineral/solution interfaces as these techniques can be applied *in situ*, are sensitive to surface structures, and are generally non-destructive. Sulfate ( $\text{SO}_4^{2-}$ ) adsorption at buried mineral (fluorite, silica, hematite)/sulfate-solution interfaces was studied using either vibrational sum frequency generation spectroscopy (VSFG), which is inherently interface specific, or total internal reflection (TIR) Raman spectroscopy. Sulfate is a simple, inorganic anion whose behavior is important to understand as it is ubiquitous in the environment being the third most prevalent ionic species in seawater by weight [1].



**Figure 1:** Idealized possible sulfate adsorption complexes at fluorite surface.

### Results and Conclusions

The use of VSFG and TIR-Raman allows for the spectral resolution of anion adsorption complex structure, i.e. inner-sphere versus outer-sphere adsorption, Figure 1, at the mineral surface. Utilizing VSFG the sulfate anion is observed to adsorb with a bidentate inner-sphere structure at the fluorite surface with a surface free energy of adsorption of  $-33 \pm 2$  kJ/mole for pH 7 solutions at 298 K. The use of TIR-Raman spectroscopy to examine sulfate behavior at silica and hematite surfaces, which feature differing surface charges at pH 7, allows for the direct observation of anion adsorption behavior as a function of the model oxide mineral surface charge.

[1] Kester *et al.* (1967) *Limnol Oceanogr.* **12**(1), 176-180.

## Use of *in vivo* and *in vitro* assays for refining human health exposure assessment for As-contaminated soil

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### Introduction

When quantifying exposure to arsenic (As) for human health risk assessment calculations, As bioavailability is assumed to be 100% which presumes that all of the As has been solubilised in the gastrointestinal tract and absorption into systemic circulation has occurred. In reality, a fraction of the soil-borne As may only be bioavailable and as such this assumption may overestimate the chemical daily intake thereby influencing risk assessment [1]. In order to refine risk calculations by adjusting the default bioavailability value, reliable assays are required that can quantitatively measure site specific bioavailability.

In this study, As bioaccessibility and As relative bioavailability was assessed in contaminated soils using a variety of *in vitro* and *in vivo* assays. *In vitro* results were compared to *in vivo* relative As bioavailability data (swine assay) to determine which methodologies have the potential to act as surrogates for *in vivo* assays.

### Materials and Methods

Contaminated soils used in this study were collected from regional areas where the soil type, source of As and As-soil residence time varied. Arsenic bioaccessibility was determined using SBRC [2], IVG [3], PBET [1], DIN [4] and UBM [5] assays while *in vivo* As relative bioavailability was determined using a swine model according to Rees *et al.* [6].

### Results and Conclusions

Comparison of *in vitro* and *in vivo* results demonstrated that the *in vitro* assay encompassing the SBRC gastric phase provided the best prediction of *in vivo* relative As bioavailability ( $r^2 = 0.75$ , Pearson correlation = 0.87). However, As relative bioavailability could also be predicted using gastric or intestinal phases of IVG, PBET, DIN and UBM assays but with varying degrees of confidence ( $r^2 = 0.53-0.67$ , Pearson correlation = 0.73-0.82).

[1] Ruby *et al.* (1996) *Environ. Sci. Technol.* **30**, 422-430. [2] Kelley *et al.* (2002) *Assessing Oral Bioavailability of Metals in Soil*. Battelle Press, Ohio. [3] Rodriguez *et al.* (1999) *Environ. Sci. Technol.* **33**, 642-649. [4] DIN (2000) *Soil Quality - Absorption availability of organic and inorganic pollutants from contaminated soil material*. DIN E 19738. [5] Wragg *et al.* (2011) *Sci. Total Environ.* **409**, 4016-4030. [6] Rees *et al.* (2009) *Environ. Geochem. Health* **31**, 167-177.