

## Isotopic analysis of ice core carbon dioxide inclusions by means of quantum cascade laser cavity enhanced absorption spectroscopy

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In the context of a globally warming climate it is crucial to study the climate variability in the past in order to understand which natural feedbacks can be expected on the atmospheric CO<sub>2</sub> concentration in a future warmer world. The composition of gas from bubbles in polar ice presents a paleo-climate archive that provides a powerful means to study the mechanisms involved in the ~40% increase in atmospheric CO<sub>2</sub> between glacial and interglacial climates. The source of the CO<sub>2</sub> released into the atmosphere during previous deglaciations can be constrained from isotopic measurements. Unfortunately, such studies have been seriously hampered by the experimental difficulty of extracting the CO<sub>2</sub> without contamination or fractionation, and measuring the isotope signal off-line on an isotope ratio mass spectrometer (IRMS).

Here we present an alternative method that leverages the extreme sensitivity afforded by Optical Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS) in the Mid-Infrared. This region of the spectrum is accessed by a custom-developed Quantum Cascade Laser operating near 4.35 μm. The feedback to the laser of light that has been spectrally filtered by a high-finesse enhancement cavity has the effect of spectrally narrowing the laser emission and to auto-lock the laser frequency to one of the cavity's longitudinal modes, with clear advantages in terms of acquisition time and signal-to-noise ratio of the measurement. The line strengths in this region are about 5 orders of magnitude higher than in the more easily accessible NIR region near 1.6 μm. A small cavity volume of ~20 mL, this enables the analysis of nmol-sized samples with high precision (< 0.05‰) in a fraction of the time required by the conventional IRMS-based technique. We will show an instrument characterization and preliminary results.

## Redox characterization of Fe-bearing clay minerals using electrochemical and spectroscopic techniques

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Fe-bearing clay minerals serve as important redox buffers in natural and engineered environments, where they readily undergo electron transfer reactions with bacteria, nutrients, and contaminants. Despite much interest, modeling the extent and kinetics of these interfacial redox reactions has proven to be challenging due to the inability to describe clay mineral redox properties in terms of reduction potential ( $E_H$ ) values. Such values have been difficult to obtain experimentally because of sluggish electron transfer rates and redox equilibration between clay minerals and electrodes.

Recently, we demonstrated that this challenge can be overcome using mediated electrochemical analyses, in which soluble redox mediator compounds facilitate rapid mineral-electrode electron transfer and redox equilibration [1]. In this approach, the oxidation state of the structural Fe is measured across a series of applied  $E_H$  values. In the current study, we applied this technique to four natural Fe-bearing smectites having varied structural Fe-contents, layer charges, elemental compositions, and redox histories to determine how clay mineral redox properties deviate as a function of these variables. X-ray absorption spectroscopy complimented these experiments to determine how structural molecular-scale variations influenced macroscopic redox properties.

All four smectites displayed complex redox behavior; high Fe-content smectites exhibited metastable states during redox cycling and all the smectites were redox-active over a wide range of  $E_H$  values spanning an array of redox regimes, ranging from methanogenesis to aerobic respiration. These results indicate that smectites likely play important roles in determining the fate of contaminants and biological nutrients under a variety of redox conditions.

- [1] Gorski, Aeschbacher, Soltermann, Bayens, Marques, Hofstetter, and Sander, (2012), *Environ. Sci. Technol.* **46**, 9360-9368.