GEO-CARS: 3-D, chemically selective imaging of fluid inclusions with multimodal nonlinear optical microscopy

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3-D images and spectra of methane-rich fluid inclusions have been recorded for the first time with coherent anti-Stokes Raman scattering (CARS) and associated nonlinear optical methods (second harmonic generation, SHG, and two-photon excitation fluorescence, TPEF). Laser scanning confocal microscopy (LSCM) with CARS was developed for biomedical imaging of lipids [1] (based on C-H stretching vibration) suggesting that we could image CH_4 in fluid inclusions. The CARS microscope uses a single ultrafast laser source that simultaneously generates additional nonlinear imaging modes (SHG and TPEF) [1]. All three signals are generated in the same focal volume and collected on separate detectors, creating high-resolution 3-D images with complimentary information such as evidence of aromatic hydrocarbons (TPEF) and sub-micrometer crystallographic disorder and internal surfaces in host minerals (SHG), in addition to the chemically-specific Raman spectral information from CARS at 2100 to 4500 cm^{-1}.

CARS images and spectra of CH_4-rich inclusions in sedimentary, igneous, and metamorphic rocks provide new information on methane in the crust. 3-D images of CH_4 and water clearly identify aqueous inclusions with CH_4-rich vapour bubbles that coexist with one-phase CH_4-rich inclusions. In crude oil inclusions, CARS spectra of CH_4 are clearly separated from fluorescence emission of the oil, allowing us to record, for the first time, the pressure sensitive peak position of CH_4 [2] in oil inclusions for input to PVT models of oil migration. Healed microfractures are visible in SHG allowing identification of distinct generations of CH_4-rich inclusions associated with specific fracture orientations. Some CH_4-rich inclusions in metamorphic and igneous rocks show TPEF signals that indicate the presence of aromatic hydrocarbons associated with CH_4. We believe this work demonstrates the broad potential of multimodal nonlinear optical microscopy and spectroscopy to provide new insight to the geochemistry of carbon in the crust and upper mantle.

[1] Pegoraro *et al*. (2010) *App. Phys.* **49**, F10-F17. [2] Lu, *et al*. (2007) *GCA* **71**, 3969-3978.

The role of microbial sulfidogenesis in shaping iron-sulfur-arsenic interactions within floodplain soils

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Introduction and objectives

Dissimilatory SO_4^{2-}-reducing bacteria play a key role in shaping the biogeochemical behaviour of Fe and As in floodplain wetland soils. These bacteria gain metabolic energy by coupling the anaerobic oxidation of organic C or H_2 with the reduction of SO_4^{2-}. This results in the generation of sulfide, which can interact via a series of often competing and complex reactions with both Fe and As. Here we discuss our recent research aimed at unraveling the role of microbial sulfidogenesis in shaping Fe-S-As interactions within flooded soils. More specifically, we examine how the onset of sulfate-reduction in floodplain soils can drive transformations in Fe mineralogy and cause associated changes in As mobility.

Methodological approach

To address this issue, we have employed a multi-scale approach spanning (1) field-scale investigations that include an essential integration of hydrological, geomorphological and geochemical observations, (2) a series of controlled advective-flow experiments with a pure culture of a sulfate-reducing bacteria (*Desulfovibrio vulgaris*) and (3) relatively simple batch-type incubations with a natural assemblage of anaerobic microorganisms.

Results and discussion

Aqueous sulfide is a powerful and facile reductant of Fe(III) that can drive the rapid reductive dissolution of poorly ordered ferric (hydr)oxides, such as ferrihydrite and schwertmannite. In the case of these poorly-ordered phases, the resulting production of Fe(II) can drive rapid formation of goethite – an Fe mineralogical transformation that appears to significantly retard As mobility. Under strongly sulfidogenic conditions, magnetite formation occurs preferentially along with the accumulation of Fe sulfide minerals.

Whilst sulfidogenesis initially causes pH-dependent release of Fe(II), sulfidogenesis can eventually sequester Fe via the the precipitation of Fe sulfide minerals. These minerals include mackinawite, greigite and pyrite – which appear to exhibit vastly contrasting affinities for As. Hence, the effect that Fe sulfide accumulation has on As mobility within floodplain soils is heavily dependent on Fe sulfide mineralisation rates.