

Vanadate complexation to ferrihydrite: X-ray absorption spectroscopy and CD-MUSIC modeling

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Sorption of vanadate(V) to iron (hydr)oxides is one of the most important processes affecting vanadium bioavailability and transport in soils. We characterised vanadate(V) adsorption to 2-line ferrihydrite by means of batch experiments, EXAFS spectroscopy, and surface complexation modeling using the CD-MUSIC model for ferrihydrite [1, 2].

Vanadate(V) sorption was strongest at low pH, and it decreased in the presence of *o*-phosphate, as expected. Results from EXAFS spectroscopy showed that vanadate(V) is sorbed primarily as an edge-sharing bidentate complex with a single V···Fe distance of ~2.87 Å. Our conclusion differs from earlier work on vanadate(V)-sorbed goethite, for which a corner-sharing bidentate complex with V···Fe distances of ~3.25 Å was identified [3].

The CD-MUSIC model could describe vanadate(V) sorption well when two surface complexes were considered. One of them was a bidentate $\equiv\text{FeO}_2\text{VO}_2^{1.5-}$ complex (in line with the EXAFS results), which dominated vanadate(V) sorption under most conditions. The best modeling results were obtained when one of the surface oxygens of this complex was assumed to be singly coordinated to iron, whereas the second one was doubly coordinated. At low pH and at low Fe:V ratios the modeling exercise suggested the additional presence of another complex, which may be an outer-sphere surface complex involving H_2VO_4^- and a diprotonated $\equiv\text{FeOH}_2^{2+}$ surface group. The implications of these results are that vanadate(V) may be strongly sorbed to iron (hydr)oxides in acid to neutral environments; however, the sorption affinity is related strongly to, e.g. competition with *o*-phosphate.

[1] Hiemstra & Riemsdijk (1996) *J. Colloid Interface Sci.* **179**, 488-508. [2] Gustafsson *et al.* (2009) *Appl. Geochem.* **24**, 454-462. [3] Peacock and Sherman (2004) *Geochim. Cosmochim. Acta* **68**, 1723-1733.

The location of microorganisms in petroleum reservoirs

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Summary

Geochemical and geological inferences have suggested, based on analysis of chemical gradients in biodegraded oil reservoirs that the site of microbial activity must be largely focussed at the oil-water-transition zone (OWTZ) at the base of the oil column[1]. Using a combined geochemical, geological and microbiological analysis of an actively biodegrading Canadian heavy oil reservoir shows that petroleum degrading microorganisms are indeed focussed in a zone of high water saturation at the base of the oil column in the OWTZ but that surprisingly, it is much thicker than expected, occupying a zone of active biological activity exceeding 10 meters. Through the oil column, gradients in biodegradation related oil physical and chemical properties are driven from this OWTZ with chemical gradients in, for example, concentrations of alkylaromatic hydrocarbons and aromatic heterocompounds significantly steepening in this “biological burn out zone”. 16S rRNA gene qPCR data suggest on the order of 10^6 to 10^7 cells/gm of sediment are present in the burn out zone, numbers that are consistent with an active biological system and around 10^4 to 10^5 cells/gm outside the burnout zone. The bacterial abundances in the OWTZ are in line with the trend of bacterial abundance with depth that has emerged from extensive analysis of microbial cells in deep subsurface sediments [2], implying that in terms of the deep biosphere, oil reservoirs are nothing special! The bacterial abundance is about 2 orders of magnitude higher within the burnout zone than within the oil leg, consistent with the notion that microbial activity and abundance in the deep subsurface is elevated at geochemical interfaces[3]. This broad result appears to support the original hypothesis that microbial activity must be largely focussed at the oil-water-transition zone (OWTZ) at the base of the oil column. We discuss the impact of these results on both the uniformity of processes in the deep biosphere and the substantial challenges this imposes on engineering accelerated microbial conversion of liquid petroleum to methane or hydrogen on production timescales.

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[2] Parkes R.J., Cragg B.A., Bale S.J., Getliff J.M., Goodman K., Rochelle P.A., Fry J.C., Weightman A.J. and Harvey, S.M. (1994). Deep bacterial biosphere in Pacific- Ocean sediments. *Nature* 371, 410-413. (1994).

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