

## Characterization of reactive ferrous iron in titanomagnetite ( $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ) nanoparticles for contaminant reduction

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Sediments at the Hanford nuclear processing site, WA, USA contain significant amounts of reactive ferrous iron, which can occur as magnetite containing structural impurities, including a substantial proportion of titanium. Titanomagnetites ( $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$ ) have electron equivalents available for reduction of key polyvalent metal contaminants, e.g. pertechnetate. Compositionally controlled  $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$  bulk powders and nanoparticle suspensions were synthesized to provide pristine materials for development of a molecular-level understanding of rate controlling factors, e.g. surface passivation and Fe (II) resupply, in the heterogeneous reduction of Tc (VII). A solid solution of bulk powders from magnetite ( $x=0$ ) to ulvöspinel ( $x=1$ ) were synthesized at 900°C.  $\text{Fe}_{3-x}\text{Ti}_x\text{O}_4$  nanoparticles, synthesized under ambient conditions, were found to accept structural Ti (IV) into the octahedral sublattice with concomitant increase in lattice Fe (II) up to  $x=0.35$ ; higher  $x$  yielded discrete amorphous Fe (II)/Ti (IV) phases on the surface. Characterization using *in situ* XRD, Mössbauer spectroscopy, XANES/EXAFS, and *ex situ* TEM and XMCD enabled analysis of Fe (II)/Fe (III) ratios in the bulk and at the surface. Bond lengths and charge and spin distributions calculated from first principles were used for interpretation. Information on local coordination, bond distances and magnetic ordering allowed discrimination of different reactive pools of ferrous iron, including Fe (II) in octahedral and tetrahedral sublattices and sorbed Fe (II). For nanoparticles with compositions of  $x \leq 0.35$ , fast initial Fe (II) release kinetics at pH 8 were followed by slower reabsorption of Fe (II) into the lattice. This suggests a highly interactive surface phase with a more stable core, the relative proportions of which are related to the structural disorder caused by substitution of tetravalent Ti into the metal sublattice. Contaminant reduction kinetics strongly depend on the relative proportions of these different Fe (II) pools.

## Microbial community diversity under extreme euxinia: Mahoney Lake, Canada

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Mahoney Lake, British Columbia, Canada, is shallow (15 m), with a stable hypolimnion containing  $> 400 \text{ mM SO}_4^{2-}$  and  $> 30 \text{ mM S}^{2-}$ , far more euxinic than the Black Sea. The densest plate of phototrophic bacteria ever detected ( $10^9$  cells/mL,  $\sim 10 \text{ cm}$  thick) is found at the boundary with the oxic mixolimnion. This layer is reported to contain predominantly the *Chromatiaceae* (purple sulfur bacteria), *Amoebobacter purpureus* (98%) and *Thiocapsa roseopersicina* (2%) [1, 2]. To date, little information has been reported on other members of the Mahoney lake microbial ecosystem, and there is no information about the microbial community residing in the aphotic hypolimnion or in the lake sediments. Suggestions that the deep lake is not active are based on the absence of gradients in  $\text{SO}_4^{2-}$  and  $\text{S}^{2-}$  profiles and on a general abundance of fragmented, rather than intact, DNA in sediments [3]. In support of this argument, much of the sulfide appears to be supplied by sulfate reduction from within the phototrophic plate, rather than from the deeper lake [1,4].

A better understanding of Mahoney Lake could help reveal if or what types of microbes are found in extreme euxinia. Here we profiled distributions of 16S rRNA genes using PhyloChip, a high-density microarray able to detect  $> 10,000$  different prokaryotic OTUs [5]. Our results yield a semi-quantitative picture of the Mahoney Lake mixolimnion (5 m), chemocline (7 m), hypolimnion (8 m), and sediments. For comparative purposes, traditional clone libraries (150-200 clones/sample) also were sequenced. Both approaches suggest that microbial diversity is greatest in the hypolimnion and sediments. Diversity is lowest in the photosynthetic plate. Comparison of PhyloChip data with clone libraries reveals the limitations and strengths of each approach, but both are consistent with active sulfate reduction persisting below the photosynthetic plate, despite the overwhelming sulfide concentration.

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