The fate and effect of trace metals during the oxidative transformation of sulphate green rust

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Nanoparticulate sulphate green rust (GR, $Fe(II)_4Fe(III)_2(OH)_{12}$-$SO_4 \cdot xH_2O$) has a layered double hydroxide structure consisting of positively charged Fe(II)-Fe(III) hydroxide sheets and interlayers of sulphate ions and water molecules. Due to its very reactive redox properties - provided by the Fe(II) - and layered structure, GR can reduce or immobilize toxic metal cations and significantly lower their solubility and bioavailability. Although it is stable in suboxic environments, in the presence of air the Fe(II) in the structure oxidizes, and GR rapidly transforms to various ferric (oxyhydr)oxide phases. Neither the fate nor the effects of metals during such oxidative transformations have been thoroughly investigated, even though these processes may influence the potential use of GR in permeable reactive barriers for the remediation of contaminated groundwater.

In this study we used synchrotron-based X-ray Absorption Spectroscopy (XAS) to determine the bonding environment and valence states of Zn, Se and Rb co-precipitated with GR during its oxidative transformation. These results were complemented by experiments where the effect of these metals on the kinetics and mechanism of GR transformation were investigated by *in situ* and time resolved Energy Dispersive X-ray Diffraction (EDXRD).

At neutral pH both in the pure and metal systems GR transformed to lepidocrocite (LP) and/or goethite (GT) via dissolution-reprecipitation. All data showed that the mechanism of the phase conversion from GR to LP/GT was not influenced by the metals. In the presence of Zn (Zn/Fe = 0.01) fine grain LP was formed from GR, but the kinetics of the transfromation reaction was not influenced. XAS data revealed that Zn became incorporated into the $Fe_6(OH)_{18}$ layer of the GR. Selenium accelerated the transformation by about 50% (Se/Fe = 0.01) and a mixture of LP/GT was formed. The redox sensitive selenate became reduced to selenite and elemental selenium by GR, and only a part of it was reoxidized to selenate during the oxidative transformation. An initial Fe(II)/Rb ratio of 0.1 is resulted in ~75% reduction of the reaction rate and Rb-GR transformed to fine grain GT. XAS data showed that Rb was outer sphere sorbed to the GR. X-ray Diffraction confirmed a shift in d-spacing towards a higher value, suggesting the possibility of incorporation of Rb into the interlayer.

Quantifying global subseafloor microbial abundance: Method and implications

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The marine subseafloor biosphere is estimated to be up to 1/3 of all life on Earth or 50-80% of the Earth's microbial biomass. These estimates are based on theoretical calculations and cell counts from ODP sites located in areas of high primary productivity and cell abundances from $10^8 - 10^{10}$ cells-cm^{-3} at the surface and 10^6 cells-cm^{-3} at 10 to 100 m depth. In contrast, recent cell counts from the low primary productivity region of the South Pacific Gyre and the Central Equatorial Pacific are up to four orders of magnitude lower and decrease more strongly with depth. To obtain a more accurate measure of subseafloor biomass, we combined well-correlated cell counts and depth relationships with the global distribution of sea-surface chlorophyll, organic carbon burial rates, and distance to land.

Using our new and published data, we performed linear regressions of cell counts as a function of depth plotted in log-log space. For all sites with an $R^2 > 0.5$, the cell count at 1 m depth and the log-rate of cell count decrease with depth were then compared to each of the three global parameters at corresponding geographic locations. The relationship between each global parameter and the cell counts were then used to create a global grid of predicted cell abundance at 1 m and decrease with depth, followed by integration of corresponding sediment thickness (maximum sediment thickness of 4 km) to obtain an estimate of global cell counts. The resulting total cell counts are surprisingly similar for each of the global parameters (e.g., 4.2×10^{29} for sea-surface chlorophyll, 5.9×10^{29} for organic carbon burial rates, and 3.8×10^{29} for distance from land) and suggest cell counts that are 10-20% of the previous estimate of 3.5×10^{30}. These results imply a significantly smaller marine subseafloor biosphere that only comprises 1/20th of all life on Earth or 5-15% of the Earth's microbial biomass.