Surface chemical heterogeneity of bacteriogenic iron oxides from a subterranean environment

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Bacteriogenic iron oxides play a significant role in the control of metal partitioning in pristine and contaminated environments.

This study quantifies the surface chemical heterogeneity of bacteriogenic iron oxides (BIOS) and its end-members (2-line ferrihydrite and intermixed intact and fragmented bacteria). On a dry weight basis, BIOS consisted of 64.5 ± 1.8 % ferrihydrite, and 34.5 ± 1.8 % organic matter. Enrichment of Al, Cu, Cr, Mn, Sr and Zn was shown in the solid versus the aqueous phase ($1.9 < \log_{10} K_d < 4.2$). Within the solid phase Al (69.5 %), Cu (78.7 %) and Zn (77.9 %) were associated with the bacteria, whereas Cr (59.8 %), Mn (99.8 %) and Sr (79.4 %) preferred ferrihydrite. Acid-base titration data from the BIOS and bacteria were fitted using FOCUS pK_a spectroscopy. The bacteria spectrum, with pKa's of 4.18±0.37, 4.80±0.54, 6.98±0.45 and 9.75±0.68, was similar to discrete and continuous spectra for intact and fragmented bacteria. The BIOS spectrum recorded pKa's of 4.27±0.51, 6.61±0.51, 7.89±1.10 and 9.65±0.66 and was deconvoluted to remove overlapping binding site contributions from the bacteria. The resulting residual iron oxide spectrum coincided with discrete MUSIC spectra for goethite and lepidocrocite with pKa values of 4.10±0.43, 6.53±0.45, 7.81±0.76 and 9.51±0.68**.** Surface site density analysis showed that acidic sites ($pK_a < 6$) were contributed by the bacteria (37%), whereas neutral sites ($6 < pK_a < 8$), were characteristic of the iron oxide fraction (35%). Basic sites ($8 < pK_a$) were higher in the bacteria (57%), than in the BIOS (44%) or iron oxide fractions (47%). This analysis suggested a high degree of bacterial group masking and a similarity between the BIOS and goethite and lepidocrocite surface reactivity. An understanding of the BIOS surface chemical heterogeneity and inherent proton and metal binding capacity was obtained through the use of FOCUS pKa spectroscopy.

The xenon record of the evolution of Mars

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SNC meteorites (Chassigny, ALH84001, Nakhlites Nakhla and NWA817 and shergottites NWA480, NWA856, NWA1068) contain xenon produced by the decay of ^{129}I ($T_{1/2}$ = 16 Ma), the fission of the extinct radionuclide ^{244}Pu ($T_{1/2}$ = 82 Ma) and solar-like xenon presumably of Martian mantle origin.

The SNC source ratio (^{129}Xe/^{136}Xe)*, where ^{129}Xe* is decay product of extinct is systematically lower than expected from decay in a closed Martian mantle. The inferred low I/Pu ratio requires early degassing of volatile iodine with respect to refractory plutonium ≤ 50 Ma after start of solar system formation, which may represent the time of mantle-atmosphere differentiation through, e.g., large-scale magmatism.

Because the decay of ^{244}Pu exceeds reasonable time interval for planetary formation and Pu is a refractory element, plutogenic xenon is a tracer of mantle degassing rather than of planetary formation ones. Both fissiogenic and trapped Xe isotopes are much more abundant that Xe isotopes in Earth's mantle-derived rocks, even after correction for degassing loss, outlining that the Martian mantle is less degassed and therefore less dynamic than the terrestrial mantle. Modelling of Pu-Xe suggests Martian mantle degassing could have continued for a few hundreds of Ma, but the major phases of magmatism ceased probably within the first Ga.

Petrological studies of nakhlite NWA817, which contains the largest amount of fissiogenic ^{136}Xe*, suggest fast cooling (Mikouchi and Miyamoto, 2001; Sautter et al., 2001), possibly due to magma crystallisation very close to the surface (less than 10 m, Mikouchi and Miyamoto, 2001), If this was the case, then volatile elements including xenon were degassed efficiently from the magma at the time of crystallisation. The quantitative occurrence of fissiogenic ^{136}Xe* in this meteorite suggests that magmatism having settled the composition of SNCs took place when ^{244}Pu was still present, and that its chronometric age of 1.3 Ga is not related to a magmatic episode.