Ligand effects on Hg^{II} reduction by magnetite

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Abiotic redox transformations of Hg are important in understanding the fate and mobility of Hg in reducing environments. The presence of complexing ligands significantly modifies the reduction potential of Hg^{II}, influencing its abiotic reduction. We tested the ability of magnetite, a biogenic mineral commonly found in subsurface environments, to reduce Hg^{II} complexed with carboxyl, chloride, and sulfhydryl ligands. These ligands are important constituents of subsurface geomedia. Since the binding constants of Hg -chloro complexes fall between -carboxyl and -sulfhydryl complexes, we further investigated the reduction of the Hg-chloride complex by magnetite containing varying Fe^{2+} stoichiometry (the bulk Fe^{2+}/Fe^{3+} ratio, x).

Hg^{II} adsorbed to *Bacillus subtilis* at high and low Hg:biomass ratios (corresponding to Hg complexation predominantly with carboxyl and sulfhydryl groups, respectively) was reacted with magnetite under anoxic conditions, and the solid phase was examined by Hg L_{III} edge XAS. When Hg^{II} was bound predominantly to carboxyl groups, reduction of Hg^{II} to Hg^0 occured within 2 h and 2 d at pH 6.5 and 5.0, respectively. When Hg^{II} was bound to sulfhydryl groups, it was not reduced by magnetite after 2 months of reaction at pH 6.5 or 5.0. In the presence of chloride, Hg^{II} was rapidly reduced to Hg^0 by stoichiometric (x=0.48) magnetite. The reduction of the Hg^{II}-chloride complex by more oxidized forms of magnetite (x=0.38 and 0.28) was kinetically hindered due to the formation of calomel ($Hg^{I}_2Cl_2$) as a stable intermediate reaction product. However, reaction kinetics slowly progressed towards reduced Hg^0 after 4 months of reaction.

These results suggest that the complexation of Hg^{II} with carboxyl, chloride, and sulfhydryl exhibits a progressively increased inhibition of the reduction of Hg^{II} to Hg^0 by magnetite. Since Hg is typically present in aquatic and terrestrial systems at low concentrations, binding of Hg^{II} to high affinity sulfhydryl sites on bacteria could have important implications for the potential reduction of Hg^{II} to Hg^0 and the overall mobility of Hg under Fe-reducing conditions.

[1] Mishra (2011) *ES&T* **45**, 9597-9603.

Multidisciplinary study of an enclave swarm in the Évora granitoid

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The enclave swarm of Pomarinho is located in the SW edge of Évora granitoid [1], in the SW sector of the Ossa-Morena Zone (Iberian Variscides). The swarm, with a privileged 3D exposure, was sampled for geophysical, petrographic and geochemical studies in order to better understand the chemical and mechanical processes involved in the genesis of that structure.

The enclaves have tonalitic and granodioritic compositions, whereas the host correspond to a very homogeneous light-coloured granodiorite. Major and trace elements as well Sr and Nd isotopic data suggest a derivation of the enclaves and the host granodiorite from a common primitive melt through magmatic differentiation. The parental melt is related to a mantle source, with no or only small contribution of metasedimentary crustal materials [2].

The tonalitic enclaves have Mg-hornblende [$Mg/(Mg+Fe^{2+})$= 0.56-0.68] and biotite [$Mg/(Mg+Fe^{2+})$=0.50-0.53], whereas in granodioritic enclaves the biotite [$Mg/(Mg+Fe^{2+})$=0.47-0.50] is the main mafic phase. Plagioclase of tonalitic enclaves have compositions of An_{23-42} with normal zoning whereas plagioclase of granodiorite is more evolved with An_{13-44}. One granodioritic enclave testifies for a more complex mechanisms once it preserves plagioclases with a widest compositional range (from An_{18} to An_{69}) in agreement with the role of a more primitive parental melt.

In order to infer the petrofabric, two types of magnetic fabrics were evaluated: anisotropy of magnetic susceptibility (AMS) and anisotropy of anhysteretic remanent magnetization (AARM). AMS results from granite and swarm enclave samples collected along two profiles show very similar results, defining an overall mean tensor with K1 = 179.1°/33.4°, K2 = 315.4°/47.6° and K3 = 73.0°/22.9° for 71 samples from granite and 25 of the enclave. AARM measurements from granite define an ellipsoid with principal axes that share the same orientation of the AMS ellipsoid. In what concerns the enclaves, AARM ellipsoid shows a distinct orientation, with principal axes defined by R1 = 248.7°/31.0°, R2 = 89.0°/57.3° and R3 = 344.4°/9.2°.

The absence of agreement between the orientations of AMS and AARM ellipsoids for samples of the enclave could be related with the presence of single domain magnetite (giving rise to an inverse magnetic fabric) or with the existence of distinct alignments of the paramagnetic and ferromagnetic fractions due to changes of the stress field during their recrystallization.

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[1] Carvalhosa (1983) *Comun. Serv. Geol. Portugal*, **69 (2)**, 201–208.
[2] Moita, et al., (2011) *Abstract, Hutton Symposium.*, pp: 99-100.