Stability of Cu adsorbed onto clay surfaces: An experimental and computational study

MÁRIO A. GONÇALVES[1], DAVID MARTINS[1] AND STEPHEN C. PARKER[2]

[1]Departamento de Geologia and CREMINER/LA-ISR, Faculdade de Ciências U. Lisboa, Lisboa, Portugal (mgoncalves@fc.ul.pt, dmmartins@fc.ul.pt)
[2]Department of Chemistry, University of Bath, Bath BA2 7AY, United Kingdom (s.c.parker@bath.ac.uk)

The stability of adsorbed metals onto mineral surfaces is an essential property in controlling their ultimate fate in the environment. This study addresses this problem with the analysis of batch and flow-through (kinetic) experiments using Cu and illite, complemented with ab-initio and molecular dynamics studies. Experiments were performed at pH 4.5 to 6.5, and 10^{-4}M – 10^{-3}M ionic strength.

Batch and kinetic experiments gave consistent results on total adsorbed Cu per gram of adsorbent: 6.4 – 9.1 × 10^{-5} mol/g for pH 4.5, and 9.0 – 13.0 × 10^{-5} mol/g for pH 5.5. Results follow a Langmuir-type adsorption isotherm, but at pH 6.5 surface Cu precipitation occurs.

Desoprtion rates were measured with the results from flow-through experiments, and ranged between 1.0 – 2.4 × 10^{-10} mol/m^2/min. The amount of desorbed Cu ranged between 6 and 54% of the total adsorbed Cu. These results indicate that Cu surface stability is favoured for high pH/low ionic strength solutions, also lending support on the Eigen-Wilkins-Werner mechanism [1]. Metal adsorption on edge surface sites of clays is shown by spectroscopic studies [2].

We are also investigating the edge surface sites further by calculating the different modes of adsorption of Cu complexes at edge sites and comparing them to adsorption on (001) surface using atomistic simulation techniques. Initially, the static simulation code METADISE [3] was used to explore the structure and the stability of the different surface cuts for the (010), (100), and (-110) edge surfaces of an idealised pyrophyllite structure. Inner and outer-sphere Cu complexes are currently being optimised using DFT within the VASP code [4] to aid in the interpretation of the experimental results.

Contribution of Project KADRWaste PTDC/CTE-GEX/82678/2006 funded by FCT (Portugal).

[1] Sposito, G. (2004), *The Surface Chemistry of Natural Particles*, OUP. [2] Morton *et al*. (2001), GCA **65**, 2709-2722. [3] Watson *et al*. (1996), *J. Chem. Soc. Farad. Trans*,. **92**, 433-438. [4] Kresse & Furthmuller (1996), *Phys. Rev. B*, **54**, 11169-11186.

Redox state of lithospheric mantle in central Siberian craton: A Mössbauer study of peridotite xenoliths from the Udachnaya kimberlite

A.G. GONCHAROV[1,2]*, D.A. IONOV[2], L.-S. DOUCET[2] AND I.V. ASHCHEPKOV[3]

[1]IPGG RAS, Saint-Petersburg, Russia (*correspondence: ag.goncharov@ipgg.ru)
[2]Université J. Monnet, Saint-Etienne 42023, France
[3]Inst. Geology & Mineralogy, Novosibirsk 630090, Russia

Redox state in a vertical profile of lithospheric mantle in central Siberian craton (Russia) was determined based on peridotite xenoliths from the 360 My old Udachnaya kimberlite. Equilibration temperatures (*T*) and pressures (*P*) for garnet peridotites are 860-1340°C [1]; P values for spinel peridotites were estimated from *T* (760-965°C) projections to a conductive geotherm defined by the gar peridotites. Mössbauer spectroscopy was used to obtain $Fe^{3+}/\Sigma Fe$ ratios in garnet from 15 samples (9–23%) and spinel from 7 samples (6-22%). Oxygen fugacity (f_{O2}) was calculated using oxygen thermobarometry. The f_{O2} decreases with pressure, hence depth. Low-T samples (750-1000°C; P = 2.6-5.3 GPa) yield f_{O2} (ΔFMQ) = (0.0) to (-1.8) log units whereas high-T (1200-1350°C; 5.4-6.8 GPa) samples have f_{O2} (ΔFMQ) = (-2.4) to (-3.1) log units. The low-T peridotites overlap the graphite and carbonate stability fields; the high-T gar peridotites plot in the diamond stability field. Speciation of hypothetical C-O-H fluids coexisting with the rocks was assessed from the T, P and f_{O2} data. Fluids for the high-T, hence the deepest, samples mainly consist of methane and water indicating that these "craton roots" are not likely to contain partial melts because of high T's of peridotite solidus in the presence of reduced C-H compounds.

[1] Ionov *et al.* (2010) *J. Petrology* **51**: 2177-2210